Superconductors as giant atoms predicted by the theory of hole superconductivity

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The theory of hole superconductivity proposes that superconductivity originates in the fundamental electron-hole asymmetry of condensed matter and that it is an 'undressing' transition. Here we propose that a natural consequence of this theory is that superconductors behave as giant atoms. The model predicts that the charge distribution in superconductors is inhomogeneous, with higher concentration of negative charge near the surface. Some of this negative charge will spill out, giving rise to a negative electron layer right outside the surface of the superconductor, which should be experimentally detectable. Also superconductors should have a tendency to easily lose negative charge and become positively charged. Macroscopic spin currents are predicted to exist in superconducting bodies, giving rise to electric fields near the surface of multiply connected superconductors that should be experimentally detectable.

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I. MOTIVATION

The presence of the discrete ionic potential in a metal causes the nature of the charge carriers in electronic energy bands to change from electron-like to hole-like as the Fermi level rises from the bottom to the top of the band. The theory of hole superconductivity proposes that superconductivity originates in a fundamental asymmetry between electron and hole carriers in metals; holes are always more dressed than electrons in a band, and this asymmetry is especially large for materials that are high temperature superconductors, for materials reasons discussed elsewhere. Superconductivity is an 'undressing' transition, whereby dressed hole carriers in the normal state undress upon pairing and become more free and more electron-like in the superconducting state.

In (ideal) superconductors, electrons behave as if they were totally free. The conductivity is infinite and they exhibit a perfect Meissner effect. As pointed out by London, such properties would be expected from a big atom (‘ein grosses diamagnetisches Atom’). Furthermore, experiments that measure the London moment and the gyromagnetic effect show that the superfluid carriers have the electronic charge (negative sign) and the free electron mass.

In this paper we carry the principles suggested in the two paragraphs above to their logical ultimate consequence. The reason that holes exist in the first place is due to the interaction of the electron with the discrete ionic lattice potential, and the holes are dressed because of electron-electron interactions in the presence of the ionic potential. In other words, the effective mass of carriers in the normal state of metals is different from the free electron mass both because of electron-ion and electron-electron interactions. In order for carriers to become completely free in the superconducting state, as indicated by the above mentioned experiments, they need to 'undress' from both of those interactions. We assume that is what happens to the antibonding electrons at the top of the Fermi distribution when a metal goes superconducting. This leads to a description of superconductors as giant atoms, and to some unusual and interesting consequences. A preliminary discussion of the implications of charge imbalance in the theory of hole superconductivity leading to a 'giant atom' picture was given in Ref. 9.

II. THE MODEL

The BCS theory of hole superconductivity is not very different from conventional BCS theory. In BCS theory the Fermi distribution in a range of roughly $2\Delta$ around the Fermi energy gets modified by the development of pairing correlations. The same is true in the BCS theory of hole superconductivity, except that in addition to pairing those carriers lower their effective mass and their kinetic energy as well as increase their quasiparticle weight, i.e. they 'undress'. We assume that as a consequence of this a fraction of roughly $2\Delta/\epsilon_F$ of the carriers become totally undressed from interactions with the discrete ionic charge distribution. Here $\epsilon_F$ is the Fermi energy measured from the bottom of the electronic energy band, and

$$N_u \sim \frac{2\Delta}{\epsilon_F}N_c$$

is the number of undressed electrons, with $N_c$ the total number of electrons in the band.

We consider a superconductor of spherical shape and assume that the undressed electrons see a continuous positive charge distribution of macroscopic dimensions, a macroscopic Thomson atom of radius $R$, of total charge $Ze$ uniformly distributed over the sphere. The value of $Z$ will be discussed later. The electric field at position $\mathbf{r}$ from the center seen by the undressed electrons
is
\[ E(r) = \begin{cases} \frac{Ze^2}{R^3} & r < R \\ \frac{Ze^2}{r^2} & r > R \end{cases} \] (2)

and the electronic potential energy is, with \( U_0 = -3Ze^2/2R \)
\[ U(r) = \begin{cases} U_0 + \frac{1}{2} \frac{Ze^2}{R^3} r^2 & r < R \\ -\frac{Ze^2}{r} & r > R \end{cases} \] (3)
defined so that \( U(r = \infty) = 0 \). Thus we have a harmonic oscillator potential inside the sphere and the ordinary Coulomb potential outside.

III. BOHR ORBITS

We follow the treatment of the Bohr atom for the model Eq. (2). Assume the electron moves in a circular orbit of radius \( r \), with energy
\[ E(r) = \frac{1}{2}mv^2 + U(r) \] (4)
For the motion to be stable the centripetal acceleration equals the electrostatic attraction
\[ \frac{mv^2}{r} = \frac{Ze^2 r}{R^3} \] (5)
so that
\[ v(r) = \omega r \] (6a)
\[ \omega = \left( \frac{Ze^2}{mR^3} \right)^{1/2} \] (6b)
Note that this is a ‘rigid rotation’ with angular velocity \( \omega \).

As in the Bohr atom, the orbital angular momentum will be quantized
\[ L = mv = nh \] (7)
which leads to a quantization of the orbits
\[ r_n = r_0 \sqrt{n} \] (8a)
\[ r_0 = \left( \frac{R^3 a_0}{Z} \right)^{1/4} \] (8b)
with \( a_0 = h^2/me^2 \) the ordinary Bohr radius. The radius of the orbit increases much more slowly than in the Bohr atom. The energy of an electron in the \( n \)-th orbit is
\[ \epsilon_n = \hbar \omega n + U_0 \] (9)

FIG. 1: Single electron Bohr orbits for a giant atom that can accommodate 6 orbits in its interior. The surface is denoted by the dotted line. The orbits outside (dashed lines) are ordinary Bohr orbits.

When \( r_n \) exceeds the radius \( R \), Eq. (8) are replaced by the ones of the ordinary Bohr atom, \( r_n = r_0Bn^2 \), \( r_0B = a_0/Z \). Figure 1 shows a picture for a body that can accommodate 6 orbits in its interior.

To determine the number of electrons that can fit in each orbit we resort to the solution of the three-dimensional quantum harmonic oscillator[13]. The eigenenergies are given by Eq. (9), and the degeneracy of the \( n \)-th energy level (per spin) is
\[ C_n = \frac{(n+1)(n+2)}{2} \] (10)
so that approximately (for large \( n \)) the number of electrons of both spins in the \( n \)-th orbit is simply
\[ g_n = n^2 \] (11)
which is one-half of that in the ordinary Bohr atom.

Because of the large degeneracy Eq. (11) and the fact that the radius of the orbit increases slowly with \( n \) (Eq. (8)), the undressed electrons will pile up in the orbits with large \( n \). We can estimate the dependence of the undressed electron density with \( r \). The spacing between two neighboring orbits is
\[ r_{n+1} - r_n \sim \frac{r_0}{2 \sqrt{n}} = \frac{r_0^2}{2r_n} \] (12)
hence the density of undressed electrons at \( r \) is
\[ n_u(r) \sim \frac{n^2}{4\pi r^2 (r_{n+1} - r_n)} = \frac{r^3}{2\pi r_0^6} \] (13)
and it increases rapidly with \( r \). We conclude that the superfluid undressed electrons are pushed out of the bulk of the superconductor towards the surface, as discussed
in Ref. [9]. The enhanced charge density near the surface can also be understood from the fact that a harmonic oscillator spends most of the time near the region of maximum elongation.

In this simple one-electron picture, the quantum number of the orbit at the surface \( n_{\text{max}} \), corresponding to \( r_{\text{max}} = R \) is given by

\[
n_{\text{max}} = \left( \frac{Z R}{a_0} \right)^{1/2}.
\] (14)

The number of electrons that fit in all orbits up to \( n_{\text{max}} \) is

\[
N_f = \sum_{n=0}^{n_{\text{max}}} 2C_n \sim \frac{n_{\text{max}}^3}{3} = \frac{1}{3} \left( \frac{Z R}{a_0} \right)^{3/2} \] (15)

It is interesting to note that (for fixed \( Z \)) \( N_f \) increases as \( R^{3/2} \). On the other hand, we expect that the number \( N_u \) of electrons that undress Eq. (1) is proportional to the volume, i.e. \( R^3 \). This suggests that some of the undressed electrons will 'spill over' the surface and occupy orbits outside the superconducting body. To obtain an estimate of this effect we need to take into account the effect of screening.

IV. SCREENING AND SPILL-OVER

According to Eq. (15), the number of electrons that fit inside the sphere is much larger than \( Z \). If \( Z = N_u \), the number of undressed electrons, this would indicate that the undressed electrons do not reach the surface. This is however incorrect, because as the inner orbits become filled the effective charge seen by the electrons in the outer orbits becomes much smaller than the bare \( Z \) due to screening by the electrons in the inner orbits.

As a simple approximation we modify Eq. (8) to read

\[
r_n = r_0 \sqrt{n} \tag{16a}
\]

\[
r_0 = \left( \frac{R^3 a_0}{Zn} \right)^{1/4} \tag{16b}
\]

and take as the effective charge \( Z_n \) the bare charge \( Z \) minus the charge of the electrons in orbits smaller than \( n \), i.e.

\[
Z_n \sim Z - \frac{n^3}{3} \tag{17}
\]

Calling again \( n_{\text{max}} \) the quantum number for the orbit corresponding to \( r_{\text{max}} = R \), it satisfies

\[
n_{\text{max}} = \left( \frac{R}{a_0} \left( Z - \frac{n_{\text{max}}^3}{3} \right) \right)^{1/2} \tag{18}
\]

and

\[
N_{\text{spill}} = Z_{n_{\text{max}}} \tag{19}
\]

This is the number of electrons that 'spill over' the surface. If \( N_{\text{spill}} \ll Z \) (as confirmed below) we have approximately \( n_{\text{max}} = (3Z)^{1/3} \) and Eq. (18) yields

\[
N_{\text{spill}} \sim \frac{2a_0}{R^2} Z^{2/3} \tag{20}
\]

as the number of electrons that are expelled from the superconductor. Since \( Z = N_u \propto R^3 \), \( N_{\text{spill}} \) increases linearly with \( R \). For a superconductor of 1 cm radius, \( N_{\text{spill}} \) could be of order \( 10^8 \) electrons.

Once outside the superconductor the electrons will occupy the lowest Bohr orbit available to them near the surface, which certainly has enough degeneracy to accommodate all \( N_{\text{spill}} \). Because they are outside the superconductor these electrons should be easily removed by contact or friction. Consequently it should be much easier for a metal to lose electrons by contact with other bodies if it is in the superconducting state, and superconductors should quite generally be at the top of the triboelectric series\[14\]. A qualitative picture of superconductors as it emerges from the physics discussed here is shown in Fig. 2.

Furthermore, the electronic layer outside the surface is likely to affect the friction properties of the superconductor, by providing a 'lubricating layer' on top of which another material would slide. As a matter of fact, an abrupt drop in sliding friction between a lead surface and solid nitrogen has been observed when \( Pb \) enters the superconducting state.\[17\] We infer that this effect is due to the physics of the electron layer outside the surface discussed here, and hence that a friction drop should be observed for all superconductors.

We predict that this electronic layer outside the surface should exist for all simply connected superconductors. It may be possible to confirm this by direct observation through sensitive optical detection techniques. The sur-
face will become more 'fuzzy' when the metal enters the superconducting state.

V. SPIN CURRENTS

In a giant atom there will be a large spin-orbit coupling. It is then not surprising that the picture discussed here will give rise to macroscopic spin currents flowing in the superconductor. The qualitative picture is shown in Figure 3. The orbits depicted have lower energy than the corresponding ones obtained reversing either the velocity direction or the magnetic moment direction. In this state, parity is broken but time-reversal invariance is preserved.

First we give a heuristic argument for why spin currents will develop when a material goes superconducting. As discussed in the previous sections, negative charge, i.e., electrons, are expelled from the interior towards the surface. Electrons carry spin and an associated magnetic moment \( \vec{m} \). As discussed in Ref. [17], a magnetic moment moving with velocity \( \vec{v} \) generates an electric dipole in the laboratory frame

\[
\vec{p} = \gamma \frac{\vec{v}}{c} \times \vec{m}
\]  

A force will be exerted on this dipole due to the positive background, which will deflect it in direction \(-\vec{p}\), as shown schematically in Fig. 4. This physics was discussed in Ref. [17] in connection with the anomalous Hall effect in ferromagnetic metals. When electrons move towards the surface, up and down spin electrons are deflected in opposite directions perpendicular to \( \vec{m} \) and to the radial velocity, building up the spin current.

We can discuss this effect using the same analysis as for atoms. In the rest frame of the orbiting electron, the electric field gives rise to a magnetic field that couples to the magnetic moment of the electron and gives rise to the spin-orbit interaction energy. Including the correction for Thomas precession, \[18\]

\[
U_{so} = \frac{e^2}{2mc^2} \vec{S}(\vec{v} \times \vec{E})
\]  

with \( \vec{S} \) the electron spin. This yields for our model

\[
U_{so} = \frac{\omega^2}{2mc^2} \vec{L} \cdot \vec{S}
\]  

so that the energy is minimized when \( \vec{L} \) is antiparallel to \( \vec{S} \), or \( \vec{L} \) is parallel to \( \vec{M} \), as shown in Fig. 3. The magnitude of the spin-orbit coupling increases as the orbit approaches the surface.

A spin current flowing in a solid will give rise to an electric polarization and an associated electric field originating in the elementary electric dipoles Eq. (21). In this way electric fields can arise in and around a solid in the absence of electric charges, charge currents and magnetic fields. This unusual physical effect has been discussed in the past in connection with a proposed symmetry-broken state of the metal Cr that would sustain a spin current \[19, 20\], and in connection with a possible state of aromatic molecules that may exhibit a spin current \[21\]. Recently the equations governing electric fields from spin currents and the resulting electric field patterns have been analyzed in connection with possible spintronics applications \[22\].

The electric field generated by a spin current in a simple slab geometry is \[20\]

\[
\vec{E} = \frac{4\pi}{c} \mu_B \vec{j}_{spin}
\]  

\[
\vec{j}_{spin} = n_\uparrow v_\uparrow - n_\downarrow v_\downarrow
\]

with \( n_\sigma \) the density of electrons of spin \( \sigma \) and \( v_\sigma \) their velocity, and \( \mu_B \) the Bohr magneton. From Eq. (6) with
FIG. 5: Pattern of electric field (curved lines) expected to arise from a superconducting disk with a cavity. The vertical arrows denote the direction of the magnetic moment of the superelectrons and the horizontal arrows the direction of their motion. No magnetic field nor charge current is present.

$$R = 1\, \text{cm}$$ and $$Z = 1 \times 10^3$$ we obtain a velocity at the surface $$v \sim 16,000 \text{cm/s}$$. For $$\Delta/\epsilon_F \sim 10^{-3}$$ and assuming $$n_\sigma \sim 10^{23}/\text{cm}^3$$, we obtain as an estimate for the electric field near the surface

$$E \sim 20\, \text{mV/mm}$$ \hspace{1cm} (25)

This is a large field, easily measurable. We emphasize however that this estimate is very rough. Figure 5 shows an example of a superconducting ring with spin currents and the associated electric field pattern. An electric field would not appear for a simply connected superconductor. Far from the superconductor the electric field decays rapidly as the fourth power of the distance since it is quadrupolar in nature.

Detection of such electric fields originating in spin currents in superconductors by direct measurement should be experimentally possible, although care must be taken to avoid extraneous contributions from stray charges. Another manifestation of these electric fields is that a force should exist between two superconducting rings, in the absence of magnetic fields and currents, as shown in Figure 6: depending on their relative orientation the force can be repulsive (a) or attractive (b). The force should exist in the absence of charge currents and magnetic fields.

VI. SOME QUALITATIVE CONSIDERATIONS

As discussed by London, a ‘giant atom’ of dimensions larger than the London penetration depth will exhibit a Meissner effect. Thus the model discussed here in a sense justifies the London equation. It is also interesting to note that the present picture allows for an understanding of the Meissner effect from the point of view of a ‘perfect conductor’. Recall that in the usual understanding a perfect conductor would not expel magnetic flux if the magnetic field preexists before the perfectly conducting state is attained. However, if charge is expelled from the interior when the system goes superconducting as described here, the Lorenz force on the radially moving charge will deflect it so as to set up circulating currents that will screen the magnetic field in the superconductor.

Furthermore the present picture allows for an intuitive understanding of the ‘London moment’, the observation that magnetic fields exist in the interior of rotating superconductors. The conventional description is that when a superconductor is set into rotation the superfluid electrons ‘lag behind’ near the surface due to inertia and zero viscosity, thus creating a current and a magnetic field in the interior. However such description does not make sense when the system is rotating in the normal state and is subsequently cooled to become superconducting. In the description here the lagging supercurrent at the surface will naturally arise because the superfluid that is expelled from the interior will experience a Coriolis force when moving radially outwards.

Also one may ask the question whether a magnetic field would be observed if the superconductor is at rest and the observer is rotating. In the usual understanding no magnetic field is expected. In the present description however a magnetic field would be observed due to...
the existing spin currents: the spins moving in direction opposite to the observer will be Lorenz-contracted relative to the opposite spin, giving rise to a magnetic field. This then extends the principle of relativity to rotating superconductors.

Finally we note that the existence of spin currents in superconductors predicted here is naturally expected in a BCS description. Namely, a Cooper pair \( c_{k\uparrow}^\dagger c_{-k\downarrow} \) carries a spin current (i.e. spin up moves in the \( k \), spin down in the \(-k\) direction). It is only because in the ordinary BCS treatment \( k \) and \(-k\) are equally occupied by Cooper pairs that no spin currents were found before. The description of the physics discussed in this paper in a BCS framework will be the subject of future work.

**VII. DISCUSSION**

Many different theories of superconductivity exist and it is difficult to ascertain which describes reality, since they often propose competing but seemingly plausible explanations for known experimental facts. For that reason it is useful to spell out predictions of theoretical frameworks before experiments to test these predictions are performed. We summarize here the predictions of the theory of hole superconductivity in connection with the physics discussed in this paper. Except for the ones noted, none of these predictions has yet been experimentally tested, and to our knowledge no other theory has made similar predictions thus far.

1) The superfluid carriers in all superconductors are bare electrons. Unfortunately this particular one is a 'postdiction', verified in many superconductors long ago. \( \text{[6, 7]} \).

2) Superconductors have a tendency to expel negative charge from their interior. As a consequence, the charge distribution inside simply connected superconductors is inhomogeneous, with more positive charge deep in the interior and more negative charge close to the surface.

3) A layer of negative charge should exist just outside the surface of any simply connected superconductor. Hopefully this should be verifiable by direct observation. This should lead to an anomalous drop in sliding friction between the surface of a superconductor and a non-superconductor, and an even larger drop in friction between the surfaces of two superconductors, as the superconducting state sets in. This friction drop has so far been observed in a single superconductor (Pb) with another non-superconducting body. \( \text{[17]} \). It is not known experimentally whether the effect will exist for other superconductors nor for friction between two superconductors.

4) A superconductor should easily lose electrons by contact or friction with a non-superconducting body.

5) Consequences of charge expulsion physics in the mixed state and for the properties of grain boundaries were discussed in ref. \( \text{[5]} \).

6) Macroscopic spin currents should exist in all superconductors. They should lead to observable consequences, in particular electric fields should arise near the surface of superconducting rings (or any topology that can sustain persistent currents) in the absence of electric charges, magnetic fields and electric currents.

7) The existence of these electric fields should give rise to attractive or repulsive forces between two superconducting rings depending on their relative orientation, in the absence of magnetic fields and charge currents.

8) Differences in cross sections in scattering experiments that are sensitive to the parity broken ground state of superconductors such as spin polarized neutron scattering or photoelectron spectroscopy with circularly polarized light should be observed, resulting from the presence of spin currents.

9) An observer rotating on top of a superconductor with angular velocity \( \vec{\omega} \) will measure a magnetic field that corresponds to a magnetic field in the interior of the superconductor

\[
\vec{B} = \frac{2mc}{e} \vec{\omega},
\]

the same that is measured if the observer is at rest and the superconductor is rotating with angular velocity \(-\vec{\omega}\). This magnetic field would not be observed in the absence of spin currents in the superconductor.

In connection with the existence of forces between superconductors (point 7) above) the possibility of Van der Waals forces also comes to mind, which should be especially important in the case of spherical superconductors. Such forces may play a role in the remarkable experiments of Tao et al. \( \text{[24]} \).

The physics discussed in this paper reflects the fundamental asymmetry of positive and negative charge that is the foundation of the theory of hole superconductivity. To the extent that all superconductors exhibit this charge asymmetry the physics proposed by the theory of hole superconductivity is validated. If a single superconductor were not to show this physics it would disprove the fundamental principle on which the theory is based.

In the normal state of a metal there is no experiment that can determine the sign of the elementary charge carriers without extracting the electron from the metal. \( \text{[27]} \). In the superconducting state instead there are experiments that show that the superfluid carriers inside the superconductor have negative charge. \( \text{[8]} \). Moreover, the results in this paper predict that superconductors make the fundamental charge asymmetry of matter extraordinarily apparent by pushing the negative electrons outside the surface of the superconducting body.

There exist many classes of materials that become superconducting and exhibit a variety of different properties in the normal state, and different theories have been proposed to explain each of them. It is common to emphasize that the more important problem is to explain the normal state properties. Instead, the theory of hole superconductivity focuses on what is common to
all superconductors which it predicts to show up crystal-clearly in the superconducting state as discussed in this paper. If the theory of hole superconductivity is correct, cuprates are not d-wave superconductors, heavy fermion materials are not d-wave nor p-wave superconductors, $\text{Sr}_2\text{RuO}_4$ is not a p-wave superconductor, organic superconductors are not unconventional, and conventional superconductors and $\text{MgB}_2$ are not electron-phonon-driven. Instead, superconductivity is a manifestation of the fundamental charge asymmetry of matter, namely that positive protons are 2000 times heavier than negative electrons. All superconductors exhibit the same essential physics and are driven superconducting by the same physical principle, hole undressing, which converts dressed holes into undressed electrons. Confirmation of these predictions and usage of the criteria derived from the theory of hole superconductivity that favor higher $T_c$’s should pave the way for finding new and better superconducting materials.

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