The fundamental role of charge asymmetry in superconductivity

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Neither BCS theory nor London theory contain any charge asymmetry. However it is an experimental fact that a rotating superconductor always exhibits a magnetic field parallel, never antiparallel, to its angular velocity. This and several other experimental observations point to a special role of charge asymmetry in superconductivity, which is the foundation of the theory of hole superconductivity. The theory describes heavy dressed positive hole carriers in the normal state that undress by pairing and become light undressed negative electron carriers in the superconducting state. Superconductivity is driven by kinetic energy lowering rather than by electron-phonon coupling as in BCS. In quantum mechanics, kinetic energy lowering is associated with expansion of the electronic wave function, and hence we predict: (1) Superconductors expel negative charge from their interior which consequently becomes positively charged; (2) Macroscopic electrostatic fields exist in the interior of superconductors always, and in certain cases also outside near the surface; (3) Macroscopic spin currents exist in the superconducting state; (4) Superconductors are ‘rigid’ with respect to their response to applied longitudinal electric fields. These predictions apply to all superconductors and are testable but are as yet untested. The theory predicts highest $T_c$’s for materials for which normal state transport occurs through (positive) holes in negatively charged anions.

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I. CHARGE ASYMMETRY MANIFESTATIONS

The fundamental charge asymmetry of matter manifests itself in the fact that the negative electron is 2000 times lighter than the positive proton. However normal metals do not clearly display this charge asymmetry, since their transport properties can be sometimes understood as originating from mobile negative carriers (electrons) and sometimes from mobile positive carriers (holes).

The observation that superconductivity occurs predominantly in materials where the carriers in the normal state are holes rather than electrons was made long ago. It has been further reinforced by the finding that both in high $T_c$ cuprates and in $MgB_2$ the carriers that drive superconductivity appear to be hole-like (this also appears to be the case in the electron-doped cuprates). Other manifestations of charge asymmetry in superconductors are the sign reversal of the Hall coefficient right below $T_c$ (it goes from positive in the normal state to negative in the superconducting state) and the voltage asymmetry in NIS tunneling in high $T_c$ cuprates (higher conductance for negatively biased sample).

Furthermore it has been known theoretically since 1933 and experimentally since 1964 that rotating superconductors possess a magnetic field in their interior that gives rise to a magnetic moment that points always in the same direction as their angular velocity, as depicted in Fig. 1. Qualitatively this can be understood as resulting from the fact that the negative superfluid lags behind when the positive ions are rotating, and hence indicates that the superfluid carriers are always negatively charged. The importance of this observation has not yet been widely recognized.

The theory discussed here implies, in agreement with these observations, that in the transition to the superconducting state hole-like normal state carriers become electron-like superconducting carriers. Our theory has in common with BCS theory that superconductivity occurs through pairing of time-reversed carriers, and with London theory that the Meissner effect originates in macroscopic quantum coherence. There are however significant differences with the conventional theories.
II. HOLES AND ANTIBONDING ELECTRONS

If the concept of holes had never been invented\[10\], understanding of superconductivity would perhaps have come much easier. In a metal where transport is said to occur through holes, the carriers at the Fermi energy are in fact antibonding electrons. It is the antibonding electrons at the Fermi energy that are the key to superconductivity in our theory.

Electrons in energy bands have increasingly higher energy as more electrons are added to the band, due to the Pauli exclusion principle. Bose-condensed particles attain the lowest possible energy state. It is only natural to conclude that superconductivity becomes more favorable when the electrons at the Fermi level are farthest away from the bottom of the band, because it is then that electrons at the Fermi energy gain the most by Bose-condensing. Because only bosons can Bose-condense, antibonding electrons have to go from half-integer spin to integer-spin particles, hence they have to pair.

When the Fermi level is close to the top of the band, carriers at the Fermi energy are undressed electrons. Their spectral weight is all in the quasiparticle $\delta$--function, and when an external force $F$ is applied they respond with a change in velocity $\Delta v$ in the same direction as the applied force. Instead when the Fermi level is close to the top of the band quasiparticles at the Fermi energy are dressed: they respond with a change in velocity opposite to the applied external force, and their spectral weight is mostly in the high frequency incoherent part of the spectral function $A(k, \omega)$.

Upon pairing these quasiparticles undress and spectral weight is transferred from high to low frequencies. Doping of holes or pairing of holes lead to an increase in the hole concentration around a given hole and to undressing.

III. SUPERCONDUCTIVITY FROM 'UNDRESSING'

It is indeed seen experimentally that superconductivity is favored ($T_c$ is highest) when the carriers in the normal state are hole-like and heavily dressed and the electrical conductivity is small, and that 'undressing' occurs upon transition to the superconducting state. Photoemission experiments in high $T_c$ cuprates show a sharp increase in the quasiparticle weight as the system goes superconducting\[15\]. Optical experiments show lowering of kinetic energy as the system goes superconducting\[15\], and the sign of the Hall coefficient changes from positive to negative as the system goes superconducting\[3\]. Experiments also show that 'undressing' occurs upon doping of holes in the normal state: the quasiparticle weight increases\[14\], optical spectral weight is transferred from high to low frequencies\[18\], and the sign of the Hall coefficient changes from positive to negative\[15\]. When the hole concentration becomes large carriers in the normal state are already undressed so undressing through pairing can no longer occur and superconductivity dissapears. The situation is schematically depicted in Fig. 3. Dynamic Hubbard models naturally describe this 'undressing'. Using a Lang-Firsov transformation on the microscopic Hamiltonians, the relation between bare (original) operators $c_{i\sigma}$ and transformed (quasiparticle) operators $c_{i\sigma}^{\dagger}$ is, in a hole representation\[20\]

$$
\begin{equation}
    c_{i\sigma}^{\dagger} = \frac{1 + \gamma \hat{n}_{i\sigma}}{1 + \gamma} c_{i\sigma}
\end{equation}
$$
FIG. 3: $T_c$ versus hole concentration $n_h$. For $n_h = 0$ the band is full. When the local hole concentration around a hole increases either through doping or through pairing, holes undress. From its maximum, $T_c$ decreases to the left as the number of carriers goes to zero and to the right as the carriers become undressed in the normal state and no longer benefit from pairing.

with $\Upsilon > 0$ and $\tilde{n}_\sigma = \tilde{c}_\sigma^\dagger \tilde{c}_\sigma$. The 'undressing parameter' Upsilon ($\Upsilon > 0$) describes the undressing of holes with increasing local hole concentration and drives the transition to superconductivity through the enhancement of the hopping amplitude $\Delta t = \Upsilon t_h$, as well as the undressing upon hole doping in the normal state. High (low) $T_c$ materials are described by large (small) values of $\Upsilon$, and the dressing of quasiparticles in the normal state is an increasing function of $\Upsilon$.

However nature is bolder than what the model Hamiltonians proposed so far suggest. Experiments on rotating superconductors show that the magnetic field in their interior generated for rotation frequency $\tilde{\omega}$ is $|\tilde{B}| = \frac{2m_e c}{e} \tilde{\omega}$ (2)

with $m_e$ and $e$ the bare electron mass and charge. This indicates that superfluid electrons in superconductors, just as in atoms, behave as totally bare undressed electrons (except for the pairing correlations). Hence the dressed quasiparticles (holes) in the normal state become bare undressed electrons in the superconducting state [2].

IV. NEGATIVE CHARGE EXPULSION

In cuprates the NIS tunneling current is observed to be larger for a negatively biased sample, i.e. when electrons tunnel out of the superconductor. The theory of hole superconductivity predicts that this is so for all superconductors due to the finite slope of the BCS gap function $\Delta_k = \Delta(\epsilon_k)$, with $\epsilon_k$ the hole band energy. The gap function versus $\epsilon_k$ and the quasiparticle energy $E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2}$ are depicted in Fig. 4. The asymmetry in the magnitude of the tunneling current suggests that superconductors have a tendency to lose electrons and become positively charged.

The minimum quasiparticle excitation energy occurs at the quasiparticle chemical potential $\mu'$ rather than at the chemical potential of the condensate $\mu$. As a consequence superfluid electrons are expelled from the interior of the superconductor, tending to equalize the two chemical potentials. This can also be seen through the temperature dependence of quasiparticle weights for electron and hole creation below $T_c$. The expelled negative charge accumulates near the surface and the balance between Coulomb charging energy cost and condensation energy gain determines the amount of negative charge expelled. For samples of dimension much larger than the penetration depth, the density of negative charge near the surface $\rho_-$ is independent of sample size, while the concentration of positive charge in the interior, $\rho_0$, decreases with increasing sample size. A qualitative picture of the charge distribution in a spherical superconductor is shown in Fig. 5. As in metal clusters one may expect some negative charge to spill out beyond the surface of the superconductor.

V. MACROSCOPIC ELECTRODYNAMICS

The predictions of the microscopic theory have a remarkably simple macroscopic electrodynamic description. The existence of the pairing gap implies the validity of the conventional London equation

$\vec{J} = -\frac{e}{4\pi\lambda_L} \vec{A}$  (3a)
FIG. 5: Schematic picture of a spherical superconducting body. Negative charge is expelled from the bulk to the surface and an outward-pointing electric field exists in the interior. Some negative charge spills out beyond the surface of the superconductor.

with \( \vec{A} \) the magnetic vector potential and \( \lambda_L \) the London penetration depth. However unlike the conventional theory we assume that \( \vec{A} \) in Eq. (3a) obeys the Lorenz gauge

\[
\vec{\nabla} \cdot \vec{A} = -\frac{1}{c} \frac{\partial \phi}{\partial t} \tag{3b}
\]

with \( \phi \) the scalar potential, instead of the conventional London gauge. Eqs (3) give rise to a new description of the electrodynamics of superconductors\[25\]. The charge density and electrostatic potential are related by

\[
\rho - \rho_0 = -\frac{1}{4\pi \lambda_L^2} (\phi - \phi_0) \tag{4}
\]

and the electrostatic equations for the charge density and electric field are

\[
\nabla^2 (\rho - \rho_0) = \frac{1}{\lambda_L^2} (\rho - \rho_0) \tag{5a}
\]

\[
\nabla^2 (\vec{E} - \vec{E}_0) = \frac{1}{\lambda_L^2} (\vec{E} - \vec{E}_0) \tag{5b}
\]

with \( \phi_0 \) the electrostatic potential resulting from a uniform positive charge density \( \rho_0 \) throughout the volume of the superconductor, and \( \vec{E}_0 = -\vec{\nabla} \phi_0 \). Eq. (5) implies that the expelled negative charge resides within a London penetration depth of the surface of the superconductor.

The electrodynamics of a superconductor is described by the remarkably simple four-dimensional covariant equation

\[
\Box^2 (A - A_\theta) = \frac{1}{\lambda_L^2} (A - A_\theta) \tag{6}
\]

with

\[
\Box^2 = \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \tag{7a}
\]

\[
A = (\vec{A}(\vec{r}, t), i\phi(\vec{r}, t)) \tag{7b}
\]

\[
A_\theta = (0, i\phi_0(\vec{r})) \tag{7c}
\]

The form Eq. (7c) is only valid in the rest frame of the superconductor. Eq. (6) can be ‘derived’ by assuming rigidity of the wavefunction of the superfluid in Klein Gordon theory\[25\]. The frequency dependent dielectric constant describing the superfluid response has the remarkably simple form

\[
\epsilon_s(q, \omega) = \frac{\omega_p^2 + c^2 q^2 - \omega^2}{c^2 q^2 - \omega^2} \tag{8}
\]

with \( \omega_p = c/\lambda_L \).

There are several experimentally testable consequences of these equations. Applied longitudinal electric fields should penetrate inside superconductors a distance \( \lambda_L \) rather than the much shorter Thomas-Fermi length. To test this effect the temperature should be low enough that very few quasiparticles are excited. We estimate that for temperatures lower than \( T_c/20 \) a measurable change (increase) in the capacitance of a capacitor with superconducting plates should be seen upon application of a magnetic field large enough to destroy the superconductivity.

The charge distribution and electrostatic field can be calculated analytically for a spherical geometry and numerically in other cases. When the superconductor is not spherical an electric field exists outside the superconductor. Fig. 6 shows the electric field lines for a superconductor of ellipsoidal shape. This should be experimentally detectable in small samples\[26\].

The plasmon dispersion relation that results from Eq. (8)

\[
\omega_s(q, \omega) = \omega_p^2 + c^2 q^2 \tag{9}
\]
VI. SPIN CURRENTS

Another remarkable prediction of our theory is the existence of macroscopic spin currents in the superconducting state in the absence of applied electric and magnetic fields. In the early days of superconductivity superconductors were expected to have macroscopic charge currents in their ground state. This was proven impossible by a 'Bloch theorem', however that theorem does not apply to spin currents.

It is interesting to note that a Cooper pair \( c_{k\uparrow}^\dagger c_{-k\downarrow} \) carries a spin current and not a charge current. A spin current will result if Cooper pairs \( (k \uparrow, -k \downarrow) \) and \( (-k \uparrow, k \downarrow) \) have different amplitudes. Anderson pointed out that superconductors should be insensitive to scattering by nonmagnetic impurities because electrons in a Cooper pair are in time reversed states. By the same argument, because a spin current does not break time reversal invariance it will not be degraded by potential scattering and will persist as long as the system is in the superconducting state. There is no way to stop it by any external perturbation.

Because a macroscopic electric field is predicted to exist in the interior of superconductors in our theory, the existence of macroscopic spin currents necessarily follows. The spin-orbit interaction energy

\[
U_{so} = \frac{e}{2\hbar c} \mathbf{S} \cdot (\mathbf{r} \times \mathbf{E})
\]

will be lowered by electrons orbiting predominantly such that their orbital angular momentum is parallel to their magnetic moment, as shown schematically in Fig. 7. Remarkably, the microscopic theory also shows that the superconducting condensation energy increases in the presence of spin-orbit splitting when the pairing is driven by lowering of kinetic energy as in the model of hole superconductivity.

Experiments that may be able to verify the existence of macroscopic spin currents in superconductors are spin-polarized neutron scattering and angle resolved photoemission using circularly polarized light. Furthermore we expect that in the presence of an applied magnetic field, spin currents will induce a quadrupolar electric field around a superconductor that should be experimentally detectable.

VII. SUPERCONDUCTORS AS GIANT ATOMS

It is well established that superconductors exhibit quantum coherence at a macroscopic scale. That is, the phase of the wavefunction is well defined over the entire volume of the superconductor. As first envisaged by London, the London equation can be understood by regarding a superconductor as a 'giant atom'. The theory discussed here carries the analogy one step further: not only is a superconductor a giant atom as far as its diamagnetic response is concerned, but just as an atom it has more positive charge near its center and more negative charge near its boundaries. Pairing of time-reversed electrons and an energy gap are still part of the theory as in the conventional one, but charge asymmetry is its most fundamental ingredient. The various indications of charge asymmetry in superconductivity seen so far in experiment such as the asymmetry in NIS tunneling are dwarfed by a much more dramatic manifestation of the fundamental charge asymmetry of matter: the macroscopically inhomogeneous charge distribution of positive and negative charge, qualitatively mirroring the one at the atomic level, that we predict to exist in all superconductors.

Local charge neutrality in normal metals results from minimization of the mobile electron potential energy. However if quantum mechanics acts on a macroscopic scale in superconductors the wavefunction is determined by minimization of the potential plus kinetic energy. When the normal metal goes superconducting, expansion of the electronic wave function leads to kinetic energy lowering only partially compensated by an increase in potential energy, resulting in the inhomogeneous charge distribution depicted in Fig. 5.

The existence of a macroscopic electric field inside superconductors can be deduced from Eq. (2) without necessity to invoke the microscopic theory. According to
Larmor’s theorem, electrons in the rest frame of a rotating superconductor experience a Coriolis force that is compensated by the magnetic field Eq. (2). However, Larmor’s theorem is only valid when the rotation frequency $\omega$ is much smaller than the intrinsic frequency of motion of the electron. Thus one is led to conclude that electrons in the superconductor traverse macroscopic orbits with angular velocity much larger than any rotation frequency of the superconducting body in a laboratory experiment, from which the existence of an internal macroscopic electric field follows.

However, it is possible that even after experiments determine that the charge distribution in superconductors is as predicted here, it will still be maintained that pairing is driven by electron-phonon interaction rather than by undressing. Such a statement cannot be proven wrong by experiment because it is non-falsifiable, so one can only hope that it will become increasingly irrelevant and in time fade away. The theory discussed here predicts that favorable material conditions to superconductivity are hole conduction through negatively charged anions and that any correlation with electron-phonon parameters is a consequence of those conditions.

The theory discussed here has many testable predictions, as discussed here and elsewhere. In particular the electrostatic field distribution around superconductors can be calculated for any given shape of the superconducting body. The field line configuration is predicted with no adjustable parameters, thus providing a stringent test of the theory. In particular, as seen in the example of Fig. 6, electric field lines always go in regions of high curvature and go out in regions of small curvature.

The theory discussed here applies to all superconductors and provides answers to many puzzles. The Meissner effect can be understood to arise from the Lorentz force on the expelled radially outgoing electrons when the system is cooled from above to below $T_c$ in the presence of a magnetic field. Similarly the generation of spin currents can be understood from a spin Hall effect on the expelled electrons. Similarly the generation of the London field Eq. (2) when a rotating normal metal is cooled below $T_c$ can be understood from the Coriolis force acting on the expelled electrons. The essential physics of superconductivity is predicted to be the same for high $T_c$ cuprates, $MgB_2$, heavy fermion superconductors, organic superconductors, conventional superconductors, as well as for all other superconducting materials.

[1] I. Kikoin and B. Lasarew, Nature 129, 57 (1932); ZhETF 3, 44 (1933); Physik.Zeits.d.Sowjetunion 3, 351 (1933); A. Papapetrou, Z. f. Phys. 92, 513 (1934); M. Born and K.C. Cheng, Nature 161, 1017 (1948); R.P. Feynman 29, 205 (1957); I.M. Chapnik, Sov,Phys. Doklady 6, 988 (1962); Phys.Lett.A 72, 255 (1979).
[2] W. Jiang et al, Phys.Rev.Lett. 73, 1291 (1994).
[3] S.J. Hagen et al, Phys.Rev.B 41, 11630 (1990).
[4] F. Marsiglio and J. E. Hirsch, Physica C 159, 157 (1989).
[5] P. W. Anderson and N. P. Ong, cond-mat/0405158 (2004) and references therein.
[6] R. Becker, F. Sauter and C. Heller, Z. Physik 85, 772 (1933).
[7] A.F. Hildebrand , Phys.Rev.Lett. 8, 190 (1964); A.A. Verheijen et al, Physica B 165-166, 1181 (1990).
[8] J.E. Hirsch, Phys.Rev.B 68, 012510 (2003).
[9] See www.physics.ucsd.edu/~jorge/hole.html for a list of references.
[10] W. Heisenberg, Ann. Physik 5, 888 (1931).
[11] J.E. Hirsch, Phys. Rev. Lett. 87, 206402 (2001); Phys.Rev.B 65, 214510 (2002); 66, 064507 (2002); 67, 035103 (2003).
[12] F. Marsiglio, R. Teshima and J.E. Hirsch, Phys.Rev.B 68, 224507 (2003).
[13] J.E. Hirsch, Physica C 201, 347 (1992).
[14] J.E. Hirsch, Phys.Rev.B 65, 184502 (2002).
[15] H. Ding et al, Phys. Rev. Lett. 87, 227001 (2001).
[16] H. J. A. Molegraaf et al, Science 295, 2239 (2002); A.F. Santander-Syro et al, Europhys.Lett. 62, 508 (2003).
[17] Z. M. Yusof et al., Phys. Rev. Lett. 88, 167006 (2002).
[18] S.Uchida, T.Ido, H.Talagi, T. Arima, Y. Tokura and S. Tajima, Phys. Rev. B 43, 7942 (1991).
[19] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida and Y. Tokura, Phys.Rev.B 40, 2254 (1989).
[20] J.E. Hirsch, Phys.Rev.B 62, 14487 (2000); Phys.Rev.B 62, 14498 (2000).
[21] J.E. Hirsch and F. Marsiglio, Phys. Rev. B 39, 11515 (1989); F. Marsiglio and J.E. Hirsch, Phys. Rev. B41, 6435 (1990).
[22] J.E. Hirsch, Phys.Lett. A 281, 44 (2001).
[23] J.E. Hirsch, Phys.Rev.B 68, 184502 (2003).
[24] J.E. Hirsch, Phys.Lett. A 309, 457 (2003).
[25] J.E. Hirsch, Phys.Rev.B 69, 214515 (2004).
[26] J.E. Hirsch, Phys.Rev.Lett. 92, 016402 (2004).
[27] P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).
[28] J.E. Hirsch, cond-mat/0406489.
[29] W. Heisenberg, Z. f. Naturforschung 32, 65 (1948); M. Born and K.C. Cheng, Nature 161, 1017 (1948).
[30] D. Bohm, Phys. Rev. 75, 502 (1949).
[31] J.E. Hirsch, Phys. Rev. B 41, 6828 (1990).
[32] M.E. Simon and C.M. Varma, Phys. Rev. Lett. 89 , 247003 (2002).
[33] F. London and H. London, Proc.Roy.Soc. A 149, 71 (1935); Physica 2, 341 (1935).
[34] H. Goldstein, ”Classical Mechanics”, Addison-Wesley, New York, 1980, Chpt. 5.
[35] R. Alben, Phys.Lett. A 29, 477 (1969).
[36] J.E. Hirsch, Phys.Lett. A 315, 474 (2003).
[37] J.E. Hirsch, Phys.Rev. B60, 14787 (1999).
[38] S. Murakami, N. Nagaosa and S.C. Zhang, Science 301, 1348 (2003).
[39] J. Sinova, D. Culcer, Q. Niu, N.A. Sinitsyn, T. Jungwirth and A.H. MacDonald, Phys. Rev. Lett. 92 , 126603 (2004).
[40] F. London, ‘Superfluids’, Dover, New York, 1961, p. 82.