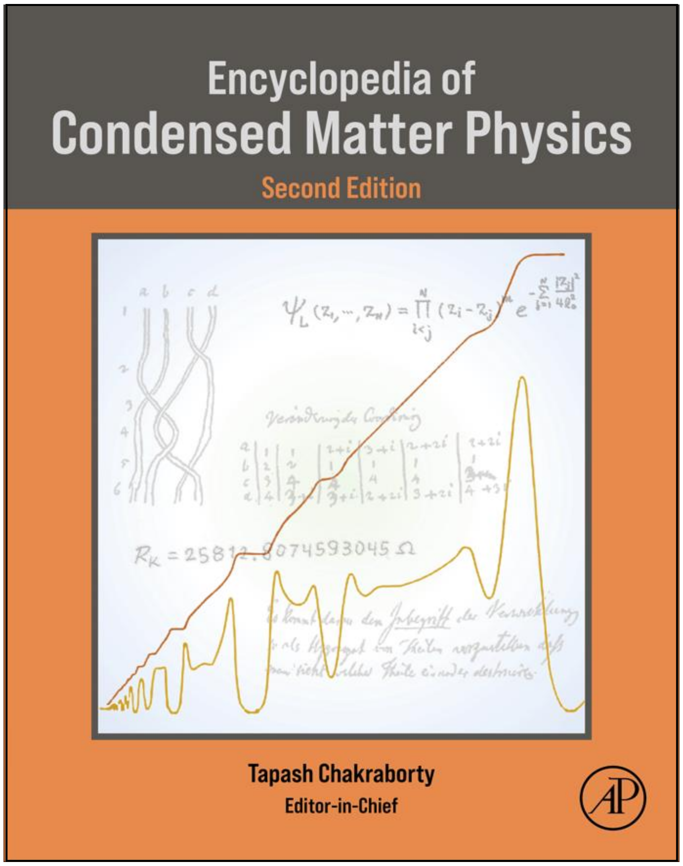

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Unconventional superconductivity

Igor I Mazin, Department of Physics & Astronomy, George Mason University, Fairfax, VA, United States

Abstract

The division of the broad field of superconductivity into *conventional* and *unconventional* is conditional, just as any binary division based on a subjective notion of "conventionality". It is often in the eye of the beholder. Still, it is often a useful, even if fuzzy, line between superconductivity that follows, with modifications, the traditional framework established by Bardeen, Cooper, Schrieffer, and Eliashberg, and that which deviates from that path.

Key points

- Defining unconventional superconductivity
- Higher angular momenta
- Examples of unconventional superconductors
- Odd-frequency order parameter
- Conditions conducive for unconventional superconductivity
- Some useful theorems
- Multigap superconductors
- Further reading

Unconventional superconductivity is an umbrella term that has been used by different researchers with different meaning. Common definitions refer to conventionality in three separate aspects: pairing mechanism, pairing symmetry, and transition temperature. In addition, occasionally conventional in their mechanism superconductors are considered unconventional because of their specific unusual properties. Examples of that include, for instance, Ising superconductors and topological superconductivity.

The most restrictive definition of conventional superconductors (CSC) stipulates that CSC are (a) mostly mediated by adiabatic (*e.g.*, respecting the Migdal theorem) harmonic phonons, (b) have isotropic or nearly-isotropic s-wave order parameter and (c) have critical temperature below 20–30 K. Such a limiting definition is rarely called for. Recently discovered superconducting superhydrates are believed to be phonon-mediated and isotropic s-wave, despite having critical temperatures approaching the room temperature and possibly nonadiabatic and anharmonic phonons, yet they are usually classified as CSC. In fact, these criteria are not independent. Indeed, a purely attractive interaction, such as phonon-mediated, cannot generate a superconducting state with a sign-changing order parameter, and, conversely, a pure repulsive (in the momentum space) interaction cannot generate a state that has an order parameter of the same sign everywhere.

Most scientists agree that a pairing state that involves an order parameter of lower point group symmetry than the hosting crystal (p-wave, d-wave etc.) should be classified as unconventional, regardless of the transition temperature. Obviously, such states cannot originate from pure phonon attraction, so pairing interaction is by definition unconventional in that sense. On the other hand, repulsive interactions, such as those of magnetic origin, may result in a sign-changing order parameter of the s-wave angular symmetry. Such states are often called $s_{\pm}$, and also usually classified as unconventional.

At the dawn of superconductivity it was believed that unconventional superconductors are but a theoretical Kunststück that is not supposed to occur in real materials, for the reason that nonmagnetic impurities are pair-breaking for such a state, and—as it was thought—would kill such superconductivity dead except in exceptionally clean samples.

It turned out that reality is not that bleak, and, in particular, that unconventional superconductors tend to have short coherence lengths, and therefore less prone to pair breaking (which is controlled by the ratio of the coherence length and the mean free path). In the moment, a number of well-studied superconductors have been convincingly demonstrated to have unconventional pairing symmetries. This includes high-T_c cuprates (d-wave), Fe-based superconductors ($s_{\pm}$); a number of heavy fermion systems, where the exact symmetry of the order parameter has not been established above reasonable doubt, are generally believed to host unconventional, possibly triplet, superconductivity. Same can be said about many organic (quasi-1D) superconductors. An interesting case is Sr_2RuO_4: For at least 20 years it was believed it was a triplet p-wave superconductors, but recent experiments convincingly point toward a singlet state. Yet, there is little doubt that superconductivity there, while still unresolved, is unconventional.

A separate, even more exotic case is the so-called odd-frequency superconductivity, whereby the frequency-dependent order parameter is assumed to change sign not (or not only) in the momentum space, but when the frequency argument changes its sign. No realistic candidates among real materials have been identified, albeit there were some proposals of this character, but there is some experimental evidence that such states can be generated by proximity effects near superconductor-ferromagnet interfaces.

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The number of unconventional superconductivity candidates identified in the last decades is considerable, and suggests several empirical rules that are conducive for UCSC. These tend to be low-dimensional (quasi-1D or quasi- 2D), and tend to have a phase diagram where superconductivity emerges near magnetic (usually antiferromagnetic) states. This is not unexpected, given that UCSC is likely to be mediated by some kind of spin fluctuations, and both proximity to magnetism and low dimensionality favor spin fluctuations.

Let us now discuss in more details the principal classes of UCSC.

High-T_c cuprates emerge in the vicinity of the Mott-Hubbard metal insulator transition. The Cu^{2+} ions have one hole in the rather localized *d*-shell, which is therefore subject to strong local Coulomb repulsion, $U \gg t$, where t is the one-electron hopping parameters for *d*-electrons. This generates a nearest neighbor antiferromagnetic superexchange, proportional to t^2/U. In parent compounds this results in a checkerboard antiferromagnetic ordering with the wave vector $\mathbf{Q} = (1,1,0)\ \pi/a$. Upon doping the magnetic order melts and the insulating state is being transformed into a strongly correlated metal. Instead of the static order, Cu spins now fluctuate with the same wave vector **Q**.

The one-electron band structure of these cuprates is formed by a single x^2–y^2 orbital, so the corresponding Fermi surface is close to a circular cylinder. It is easy to see that if one postulates the *d*-wave order parameter with the same symmetry, x^2–y^2, spin fluctuations with the wave vector **Q** will be spanning two parts of the Fermi surface with the opposite signs of the order parameter and therefore be pairing. This simple argument has led to the view, shared by a majority of researchers, that superconductivity in cuprates is driven by spin-fluctuations.

Similarly, in Fe-based superconductors, the magnetic order in the parent antiferromagnets corresponds to $\mathbf{Q} = (1,0,0)\pi/a$ in the single-Fe unit cell, and the Fermi surface, in most cases, consists of two groups, one centered around $\mathbf{q} = (0,0,0)\pi/a$ and the other around $\mathbf{q} = (1,0,0)\pi/a$; so assigning different signs to the order parameters in the two sets assures that spin-fluctuations are pairing. Thus, a plurality, and may be even majority of scientists believe these materials, as well, to be fluctuations-driven.

These two example are, arguably, the best studied UCSC. Yet, there is a solid body of evidence in favor of unconventional pairing in numerous other materials, including, but not limited to organic metals, heavy fermions, or twisted bilayer graphene.

Some useful theorems regarding unconventional pairing symmetries are: (1) A fully local (*i.e.*, contact) Coulomb repulsion, such as the Hubbard interaction, cancels out if the order parameter integrates to zero over the entire Fermi surface (regardless of the nature of the pairing interaction). This can be also reformulated by applying the Fourier transform and considering the structure of a Cooper pair in coordinate space. In this case, the component of the pair are localized on different lattice sites. In case of cuprates (*d*-wave) these are nearest neighbors in the square lattice, and in case of Fe-based superconductors ($s_\pm$) on the second neighbors. (2) While the order parameters itself may follow a lower-symmetry representation than the full crystal symmetry (A_{1g}), its amplitude, *i.e.*, the excitation gap, usually does follow the full symmetry (some exceptions to this rule, often called "nematic" superconductivity, have been proposed theoretically). (3) Even if the order parameter does not obey the point group, it is, including the phase, subject to the Bloch theorem, so that $\Delta(\mathbf{k}) = \Delta\ (\mathbf{k} + \mathbf{G})$, where **G** is a reciprocal lattice vector. It is a powerful theorem because it forces order parameter nodes at some special high-symmetry points.

Finally, it is worth bringing up yet another class of materials, multigap superconductors, where the magnitude of the order parameter changes exceptionally strongly over the Fermi surface or between different Fermi surface pockets. These are not usually called UCSC now, but they were not appreciated (albeit theoretically discussed already in the late 50s) until the discovery of a two-gap superconductivity in MgB_2 in 2001—at that time MgB_2 was routinely referred to as an unconventional, but phonon-driven superconductor.

Further reading: (Sigrist and Ueda, 1991; Zhou et al., 2021; Norman, 2011; Moriya and Ueda, 2003) (general), (Mazin and Antropov, 2003) (MgB_2), (Lee et al., 2006) (cuprates), (Hirschfeld et al., 2011; Hosono and Kuroki, 2015) (Fe-based).

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