Unconventional superconductivity after the BCS paradigm and empirical rules for the exploration of high temperature superconductors

Hai-Hu Wen

Center for Superconducting Physics and Materials, National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China

Superconducting state is achieved through quantum condensation of Cooper pairs which are new types of charge carriers other than single electrons in normal metals. The theory established by Bardeen-Cooper-Schrieffer (BCS) in 1957 can successfully explain the phenomenon of superconductivity in many single-element and alloy superconductors. Within the BCS scheme, the Cooper pairs are formed by exchanging the virtual vibrations of lattice (phonons) between two electrons with opposite momentum near the Fermi surface. The BCS theory has dominated the field of superconductivity over 64 years. Many superconductors discovered in past four decades, such as the heavy Fermion superconductors, cuprates, iron pnictide/chalcogenide and nickelates seem, however, to strongly violate the BCS picture. The most important issue is that, perhaps the BCS picture based on electron-phonon coupling are the special case for superconductivity, there are a lot of other reasons or routes for the Cooper pairing and superconductivity. In this short overview paper, we will summarize part of these progresses and try to guide readers to some new possible schemes of superconductivity after the BCS paradigm. We also propose several empirical rules for the exploration of high-temperature unconventional superconductors.

*hhwen@nju.edu.cn
I. INTRODUCTION

Superconductivity is a very interesting quantum state which exhibits zero resistivity and expulsion of magnetic field (Meissner effect). It has been well understood that this fascinating phenomenon is induced by the condensation of electron pairs (termed as Cooper pairs) at a finite temperature. Up to date, the superconducting state can only be achieved with these electronic Cooper pairs although some other novel pictures concerning other type of charged bosons have been proposed. Since its first discovery in April 1911 by Kamerling Onnes et al., the field of superconductivity has experienced glorious developments and achievements in past 111 years. Owing to the deep and interesting physics involved by the phenomenon of superconductivity, and the potential of large scale applications, the field has been pushed forward step by step, most of time by the discovery of new superconductors. We can expect more interesting phenomena and materials, which will eventually lead to the revolution, both on the fundamental understanding of condensed matter physics and bring in the dreamful industrial applications of superconductors.

The development of the field of superconductivity is however not straightforward, it is always mixed with some excitement and frustrations. In Fig.1 we present the time dependence of the superconducting transition temperatures $T_c$ of some representative superconducting systems when they were discovered. One can see that, the value of $T_c$ ramps up with a small slope before October 1986. After the tremendous efforts in 75 years, the $T_c$ finally reached about 23.2 K in $Nb_2O_5$ system. Most superconductors discovered before this time were single element metals or alloys. The basic reason for superconductivity, called as the superconducting mechanism, was unraveled in 1957 by Bardeen, Cooper and Schrieffer and named as the BCS theory. In this short review, we omit the description about the BCS paradigm. A short review can be found in our earlier review paper.[2] Since the field is rapidly moving forward, the understanding on the so-called unconventional superconductivity have not come to the mature status yet. Thus this paper serves only as a brief introduction and may be taken as a supplementary to other beautiful reviews in this fascinating field. Nowadays, it is known that either in conventional or unconventional superconductors, we have an energy gap that protects the superconducting condensate from breaking Cooper pairs or exciting so-called quasiparticles. In the BCS theory, the gap is given by

$$\Delta_s = 2\hbar\omega_D \exp^{-1/N(0)V}. \quad (1)$$

Here $\hbar\omega_D = k_BT_D$ is the Debye energy; $N(0)$ is the density of states (DOS) near the Fermi energy; $V$ is the interaction between two electrons involved in the pair-scattering process. In the weak coupling case, it is predicted that $\Delta_s = 1.75k_BT_c$. Therefore the superconducting state can be achieved at a finite temperature. One can see from the above description that, one of the basic conditions in the establishment of the BCS scheme is that $\Delta_s << \hbar\omega_D << E_F$. Once we have a system with $\Delta_s$ comparable with the Fermi energy $E_F$, this basic requirement is thus lost and we run into a new scheme of superconductivity. For superconductors with conventional superconducting pairing mechanism, the one with the highest transition temperature at ambient pressure is $MgB_2$ which was discovered in 2001.[3] In some pressurized hydrides[4], it was reported that the superconducting transition temperature rises to about 200K or beyond, but the pairing mechanism can still be described by the phonon mediated BCS picture.

II. UNCONVENTIONAL SUPERCONDUCTIVITY IN CUPRATES AND IRON PNICTIDES/CHACOGENIDES

In past four decades, many new superconductors were discovered. These systems exhibit some features which are clearly at odds with the BCS theory. These superconductors include the heavy Fermion[5], organic[6], cuprates, iron based superconductors and nickelates. Among them, the cuprate is a typical one which was firstly discovered by K. A. Müller and J. G. Bednorz[7]. They found that the superconductivity occurred at about 35 K in a typical copper oxide $La_{2-x}Ba_xCuO_4$. This discovery ignited an explosion in the field of superconductivity. In later 7-8 years, many other new superconducting systems were discovered, for example the $YBa_2Cu_3O_7-\delta$ ($T_c \approx 90K$)[8, 9], the bismuth family $Bi_2Sr_2CaCu_2O_8$ ($T_c \approx 90K$) and $Bi_2Sr_2Ca_2Cu_3O_{10}$ ($T_c \approx 125K$)[10], the thallium family[11] and the mercury family[12] etc. So far the highest superconducting transition temperature in cuprates is $T_c = 164$ K, which was discovered in the $HgBa_2Cu_2O_8+\delta$ under a high pressure of 45 GPa.[13].

No sooner after the discovery by Müller and Bednorz, it was found that the major players for superconductivity in the cuprates are the $CuO_2$ planes in the middle of the pyramid constructed by the octahedra of Cu and oxygen atoms. This plane is sketched in Fig.2. If we have a look at the formulae of some parent phase of cuprate systems, such as $La_2CuO_4$, a natural counting on the ionic state would lead to $Cu^{2+}$ with $3d^9$, and $O^{2-}$ with $2p^6$ as the outermost shell of electron orbitals. Taking the structural parameters of the system into consideration, a simple density-functional-theory (DFT) calculation will find out that the material should be a metal with $Cu - 3d$ orbitals as the conduction
FIG. 1. Correlation between the superconducting transition temperatures and the year for them to be found. The three horizontal red dashed lines represent the boiling temperatures of liquid helium, hydrogen, and nitrogen. The circles, squares, diamonds, stars represent the conventional, cuprate, iron-based and nickelate superconductors, respectively.

FIG. 2. Sketch of the CuO$_2$ planes of the cuprate superconductors. The small filled circles with arrows represent the Cu ions with the 3d$^9$ as the outermost orbital of electrons. The large circles represent the oxygen ions with the 2p$^6$ outermost orbitals.

band, forming a large electron like Fermi surface surrounding the Γ point, while later experiments show that it is an insulator due to Mottness, thus it is called as a Mott insulator [14]. Many transport properties indicate that the resistivity close to the undoped case cannot be described by a band insulating picture, rather it is described by a law $\rho(T) \propto \log(1/T)$ which manifests itself some exotic reasons. Almost simultaneously, researchers found that the undoped phase, here called as the parent phase of the cuprate superconductors, has a long range anti-ferromagnetic order with an ordering temperature at around 300 K and the super-exchange energy $J \approx 150\text{meV}$. Clearly the insulating behavior of the parent phase is due to the strong correlation effect. A Hubbard model based picture, namely the Zhang-Rice singlet [15] model, was proposed to interpret the electric conduction in the doped cuprates. In the cuprate system, due to its crystalline field effect, the 3d$_{x^2-y^2}$ orbital is lifted to the highest energy and is half filled. However, because of the strong Hubbard U (6-8 eV), this half-filled band will be split further into lower and upper Hubbard bands with a large U between them. In this case, the oxygen 2p band will hybridize with the lower Hubbard band, thus the doped holes would accommodate in this Cu-3d and O-2p hybridized band. The Zhang-Rice singlet model postulates that each doped hole on the oxygen site will couple to the Cu$^{2+}$ cation and form a spin singlet state, it is this composed singlet that moves, leading to electric conduction. Meanwhile there are many other models to interpret this interplay of charge and spin in the doped cuprate, for example the t-J model incorporating a SU(2)
FIG. 3. A general electronic phase diagram of the cuprate superconductors. The central yellow region shows the parent phase with a long range ordered antiferromagnetic insulating phase. The two dome like highlighted by red color show the regions for superconductivity. In the electron doped side, the AF order may enter the superconducting dome, showing a coexistence of superconductivity and AF order. The pairing symmetry has been proved to be d-wave in the hole doped region, it may be non-monotonic d-wave or s-wave pairing in the electron doped region. The solid and dashed lines represent the pseudogap temperatures according to different definitions or experimental measurements.

symmetry[16], and the phase string model[17], etc. All these different models can also interpret the finite coherent DOS at the Fermi energy and a superconducting state with a diluted superfluid density arising from a strongly correlated background. A typical electronic phase diagram is shown in Fig.3. More interestingly, this insulating feature will leave the way to a strange metallic behavior if we dope it with holes (hole doping) or electrons (electron doping). Above a certain threshold of doping ($p \approx 0.05$ for example in $La_{2-x}Sr_xCuO_4$) the superconductivity emerges at a finite temperature. The $T_c$ versus doping normally exhibits a dome like shape with the optimal $T_c$ around a doping level of about $p = 0.16$ in the hole doped side. In the overdoped side the $T_c$ drops down again and superconductivity vanishes at about $p \approx 0.25 – 0.30$. Phase separation picture was proposed to explain the dropping down of the superfluid density and the superconducting transition temperature in the overdoped region[18]. Recently, mutual inductance measurements on the systematically doped thin films illustrate also a rough linear correlation between the superfluid density and $T_c$ in the overdoped region, manifesting also a non-BCS mechanism[19].

The normal state of the cuprate superconductors is also drastically deviating from the very base for building up the BCS paradigm, the Landau-Fermi liquid picture. One of the exotic features here is the appearance of the so-called pseudogap far above $T_c$, as shown in Fig.3 by the solid and dashed lines. According to the different definitions, the pseudogap temperature $T^*$ is also quite different. For example, the Knight shift in the NMR measurements shows a decrease at a quite high temperature. This has been regarded as the opening of a spin gap[21]. The pseudogap can also be detected in the temperature dependence of resistivity in many cuprate systems. Below the pseudogap temperature, the resistivity shows a linear behavior with a kink at the pseudogap temperature. Similar behavior occurs in the specific heat data which exhibits also a decrease of the electronic specific heat coefficient below the pseudogap temperature[22]. While the Nernst effect measurements reveal a strong signal which may correspond to the existence of the simultaneous vortex-antivortex excitations[23]. The more direct evidence for the pseudogap is coming from the angle resolved photoemission spectroscopy (ARPES)[24]. One appealing picture for the normal state is the gapped feature near the anti-nodal area due to the correlation effect, while the electrons near the nodal point have still finite life-time recovering a certain weight of quasiparticles. This leads to the so-called truncated “Fermi surface” or Fermi arc. Although to reckon on the number of the conduction electrons through the well known Luttinger theorem is very questionable, while the superconducting condensation in the cuprates seem to be achieved by building up a gap on the so-called Fermi arc near the nodal point. When temperature is increased above $T_c$, the gap on the Fermi arc vanishes and the “Fermi arc metal” is recovered as the normal state[16]. Connected with this pseudogap feature, there are many other “intertwined orders/phases” existing in this region, such as the charge density wave (CDW) order, pair-density wave (PDW) order, spin-glass, etc. A recent overview gives a nice summary about this complexity[25]. Thus we see many very exotic features of the normal state of the cuprate superconductors. These abnormal features in the normal state of cuprate superconductors are certainly shaking the very base for the BCS picture. It is still under a hot debate how these facts can be put together to reach a reconciled picture. Although some people suggest that the BCS picture may be still applicable to interpret the superconductivity in the cuprate system, while significant modifications have to be undertaken, especially the focus is about whether the retarded weak
coupling picture, as the case for phonon mediated pairing, is still applicable here.

The discovery of iron based superconductors\cite{26} seems to help unraveling the puzzle of unconventional superconductivity. Up to date, many FeAs or FeSe based superconductors have been synthesized, which enriches the families of the iron based superconducting systems\cite{22}. A common knowledge now about the iron based superconductors is that the major electric conduction and the superconductivity are fulfilled by the FeAs or FeSe based planes. Theoretical calculations indicate that the Fe has a cationic state of $Fe^{2+}$ with 6 electrons in the five 3d orbitals, namely $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. One can estimate the crystalline field splitting of these five 3d orbitals in the system, which gives a quite weak effect. Therefore in principle, all the five 3d orbitals cross the Fermi energy leading to several sets of Fermi surfaces, two hole-like cylindrical Fermi pockets and a small 3D like electron pocket in the Brillouin zone center ($\Gamma$ point), and two more electron Fermi pockets in the zone corner ($M$ point). For most FeAs based superconductors, the Fermi surface contains a set of hole pockets centering at $\Gamma$ and a set of electron pockets near $M$ point, as sketched in Fig.4(b). Early but swift theoretical calculations indicate that the phonon spectrum and the electron-phonon interaction does not support to give superconductivity above 1 K\cite{28}. Interestingly the parent phase, for example, RFeAsO (R= rare earth elements) and BaFe$_2$As$_2$ all show an antiferromagnetic order at temperatures between 100-200 K.

Recently, superconductivity up to 15 K was found in hole doped Nd$_{1-x}$Sr$_x$NiO$_2$\cite{33}. Interests arose immediately after this discovery since this infinite layer system may also have a $d^0$ orbital as the dominant one for the electric conduction. The discovery of superconductivity has also been extended to other compounds, for example Pr$_{1-x}$Sr$_x$NiO$_2$ and La$_{1-x}$Ca$_x$NiO$_2$. The calculations based on DFT reveal that for the parent phase $Nd(\text{La})NiO_2$, the major bands crossing Fermi energy are $Ni - 3d_{x^2-y^2}$, $Nd - 5d_{3z^2-r^2}$, and $Nd - 5d_{xy}$ with some hybridizations. Thus it is clear that the major contribution of superfluid density comes from the orbital of $Ni - 3d_{x^2-y^2}$, but the $Nd - 5d$ bands also contribute partially to the DOS at the Fermi level\cite{34,35}. A common understanding is that the $Ni - 3d_{x^2-y^2}$ band constructs a large hole pocket around $\Gamma(0,0,0)$ at the $k_z = 0$, which changes into an electron pocket at the $k_z = \pi$ due to the dispersion along $k_z$ direction. The hole pocket at $k_z = 0$ looks like that of underdoped cuprate; while on the cutting plane at $k_z = \pi$, the electron pocket shrinks and becomes similar to the Fermi pocket in overdoped cuprate. There are two more electron pockets, one is surrounding $\Gamma$ which is contributed by the hybridization of the $Nd - 5d_{3z^2-r^2}$ and $Ni - 3d_{3z^2-r^2}$, another one surrounding $\Lambda(\pi,\pi,\pi)$ is constructed by the hybridization of $Nd - 5d_{xy}$ and $Ni - 3d_{3z^2-r^2}$. A spin excitation spectrum has been measured in the undoped system $NdNiO_2$, which indicates a wide band spin excitations up to an energy of 200 meV\cite{34}. Based on the scheme of repulsive interactions\cite{32}, $d$-wave pairing as the dominant one has been predicted on the central hole pocket. By measuring scanning tunneling microscopy, two types of gaps are observed\cite{37}, one has a $d$-wave gap function with gap maximum about 3.9 meV, another one exhibits a full gap about 2.35 meV. Some time a mixture of the two types of gap features appears on one single spectrum, which indicates that the $Nd_{1-x}$Sr$_x$NiO$_2$ thin film is a multigap system and probably with a $d$-wave pairing tendency as the dominant one. Due to the difficulties of synthesizing good samples, more results are desired to unravel the mystery of superconductivity in the nickelate systems.

III. PRELIMINARY UNDERSTANDING OF THE UNCONVENTIONAL SUPERCONDUCTIVITY

If there exist strong Coulomb interactions $U$ among electrons, or the ratio between the repulsive coulomb interaction and the band width $t$, i.e., $U/t$ is large, the free electron gas or the so-called Landau-Fermi liquid picture immediately becomes questionable. In this case one cannot assume a negligible potential energy in the electronic Hamiltonian, the latter has been adopted in building up the BCS picture. With the presence of strong correlations, the Hamiltonian has been considered based on the $t - U$, or $t - J$ or $t - J - U$ models. Since tremendous number of electrons need to be considered in the system, this multibody problem is not solvable. However, this problem may be at least inspected by assuming a low energy approach. In this case, a microscopic Hubbard-type Hamiltonian with a four fermion interaction can still be written as\cite{38}

$$H = \sum_{k,\alpha} \varepsilon_k \psi_{k\alpha}^+ \psi_{k\alpha} + \sum_{k_1,\alpha_1} U_{k_1,k_2,k_3,k_4}^{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \psi_{k_1,\alpha_1}^+ \psi_{k_2,\alpha_2}^+ \psi_{k_3,\alpha_3} \psi_{k_4,\alpha_4},$$

(2)
FIG. 4. Cartoon picture for the pair-scattering process based on a retarded weak coupling in (a) cuprates and (b) iron based superconductors. The open arrows represent two electrons with opposite momenta and spins before the pair-scattering; the filled arrows show the final states after the pair-scattering. The dashed lines show the pairing channel in the pair-scattering process through a retarded interaction. If the interaction $V$ is positive, this kind of pairing will induce sign change of the superconducting gaps in the momentum space, for example d-wave in cuprates and $s^\pm$-wave in iron-based superconductors.

Here $U^\alpha_1,\alpha_2,\alpha_3,\alpha_4$ represents the four electron interactions, $\psi^+_{\alpha_i,k_i} (\psi_{\alpha_i,k_i})$ is the creation (annihilation) operator for electrons with the spin $\alpha_i$ and momentum $k_i$ ($i=1,2,3,4$). For a single band Hubbard model with local Coulomb interactions, we have

$$U^\alpha_1,\alpha_2,\alpha_3,\alpha_4 = U \delta_{k_1+k_2-k_3-k_4} (\delta_{\alpha_1\alpha_4}\delta_{\alpha_2\alpha_3} - \delta_{\alpha_1\alpha_3}\delta_{\alpha_2\alpha_4}). \tag{3}$$

If only the interactions in the low energy area are considered, the situation can be treated by using the so-called random phase approximation (RPA) method. For a system with very good Fermi surface nesting, the electronic system will be instable to some long range ordered state, such as the charge-density-wave (CDW) or the spin-density-wave (SDW) state. In the iron based systems, the perfect nesting between the hole and electron pockets may just satisfy this situation leading to the formation of a long range SDW order in the parent phase in the FeAs based families. There are some arguments that the AF order is induced by the local super-exchange effect. By chemical doping, or applying a pressure, the perfect nesting situation deteriorates, and the long range ordered SDW state will be replaced by the state with strong antiferromagnetic spin fluctuations (AF-SF). The elementary excitations of this state are the so-called paramagnons. When an itinerant electron is passing through a position, it will polarize the spin cloud around it, this polarized spin cloud will be sensed by the second itinerant electron passing by. This process will build up a pairing interaction between the two electrons with a pairing interaction as

$$\Gamma_s(k, k') = \frac{3}{2} U^2 \frac{\chi_0(q)}{1 - U \chi_0(q)}, \tag{4}$$

where $U$ is the repulsive energy, $\chi_0$ is the bare spin susceptibility in absence of interactions, the subscript $s$ here represents the singlet pairing channel. One can see that $\Gamma_s$ is also peaked at the wave vector $q$ but is positive. If we use this pairing interaction and follow the BCS approach, the gap function can be written as

$$\Delta_k = -\sum_{k'} \Gamma_s(k, k') \frac{\Delta'}{2E_k} \tanh \frac{E_k'}{2T}. \tag{5}$$

Here $E_k' = \pm \sqrt{\epsilon_k'^2 + \Delta_k'^2}$. In iron based superconductors, this interesting pairing picture was first proposed by Mazin et al., and later further formalized by several other groups using different theoretical approaches. More details about the pairing order parameter can be found in a recent review. The basic idea of weak coupling picture is illustrated in Fig. 4(a) and (b) for cuprates and iron based superconductors, respectively. It still remains unclear whether this weak coupling based picture applies to the cuprates, since the pairing is very strong and Fermi surface is incomplete (truncated). In iron based superconductors, especially in FeAs based superconductors, the two electrons on the electron (hole) FSs (marked with the thick arrows indicating opposite directions of spins) are scattered to the hole (electron) FSs by exchanging the antiferromagnetic spin fluctuations (AF-SFs). If the pairing is established.
energies versus the superconducting transition temperature $T_c$ in many iron based superconductors. The small sized filled symbols are data collected in the inelastic neutron scattering measurements, the two red bigger square and circle symbols are determined from the bosonic mode on the tunneling spectrum. This figure is made by quoting to the data in Ref.[52]

through exchanging the AF-SFs, according to above equations, the so-called $S^\pm$ pairing model is expected, i.e., the DOS on individual FS are fully gapped (although the gap magnitude has some momentum dependent variation), but the signs of the superconducting gaps on the electron and hole pockets should be opposite. This kind of $s$-wave gap has been supported by the scanning tunneling experiment already[46]. The recent experiment in observing the in-gap quasi-particle states by non-magnetic Cu impurities in $NaFe_{0.97-x}Co_{0.03}Cu_xAs$ may provide a more decisive evidence for the $S^\pm$ pairing.[47] Furthermore, this sign reversal of gaps on the electron and hole pockets in $FeTe_{1-x}Se_x$ has been well checked by the phase referenced quasiparticle interference technique.[48]. This RPA based picture may also be extended to the case of cuprates for understanding the well known d-wave pairing symmetry. As shown in Fig.1(a), since there is only one set of Fermi surface in the cuprate, the pair-scattering would lead to a sign change on the different segments of the Fermi surface, this naturally leads to a d-wave gap function.

One of the consequences of the electronic system with the pairing gap with opposite signs is the appearance of a resonance peak in the imaginary part of the spin susceptibility at the wave vector of the SDW. This resonance peak with a typical energy $\Omega \lesssim 2\Delta$, can be detected with inelastic neutron scattering experiment and has been observed in cuprates[49], heavy Fermion[50] and recently in the iron pnictide superconductors[51]. This resonance peak may be understood as due to the spin flipping scattering when exciting a quasiparticle from the $k$ to $k + q$ with the pairing gap with the opposite signs, since in this case the BCS coherence factor is given by[39, 45]

$$I_{res} \propto \frac{1}{2} \left| 1 - \frac{\Delta(k)\Delta(k + q)}{E(k)E(k + q)} \right|.$$  \hspace{1cm} (6)

Here $I_{res}$ gives the intensity of the resonance peak, $E(k)$ is the dispersion of the Bogoliubov quasiparticles in the superconducting state $E(k) = \pm \sqrt{\varepsilon_k^2 + \Delta^2(k)}$. One can see that, if the superconducting gap has a sign reversal at momenta connected by vector $q$, that will produce a peak at this particular vector. The RPA calculations tell that this peak should locate at a energy of $\Omega \lesssim 2\Delta$, depending on the correlation strength. Although the resonance peak is regarded as the consequence of the sign-reversal gaps, sometimes it is called as the “egg” of the superconducting pairing state, not the pairing glue for superconductivity, we must emphasize that this “egg” can be naturally traced back to the scenario of the magnetic pairing, namely the origin of pairing. Therefore, although the resonance peak may be due to the spin-1 exciton mode of the sign reversal gaps, we can conclude that it is only possible that the pairing is induced through the electronic origin, either through exchanging the AF-SFs, or the superexchange itself, but certainly not through some non-magnetic origins, like exchanging phonons. In Fig.3 we present a collection of many resonant energies versus the superconducting transition temperature $T_c$ in different iron based superconductors. Here the filled symbols are data collected in the inelastic neutron scattering measurements, the two open symbols are determined from
FIG. 6. Evolution of the pairing from weak coupling to strong coupling, depending on the ratio $U/t$. The left hand picture shows the case for $U/t << 1$, the BCS scheme works well. Here the four blue circles represent the distortion of the atoms due to the electron-phonon interaction. This distortion will be “seen” by the second electron passing by in a retarded duration. The right hand one represents the possible situation of strong correlation effect where the local super-exchange may dominate the pairing. In the middle, the $U/t \approx 1$ which may be applicable for the case of AF-SF mediated pairing.

FIG. 7. Schematic camp for superconductivity. The BCS theory with weak coupling occupies a small region in the left hand side. We need a general or global camp to cover all possibilities for superconductivity, from weak coupling to strong local pairing.

the bosonic mode on the tunneling spectrum. In some iron based superconductors, the scanning tunneling spectroscopy measurements reveal extra peaks (humps) outside the superconducting coherence peaks, which is explained as the coupling of the quasiparticles with the spin resonance mode. In Fig.6 a simple ratio $\Omega \approx (4.3 \pm 0.5)k_B T_c$ is shown. This strongly suggests that the neutron resonance is indeed closely related to superconductivity. Similar linear relation between $\Omega$ and $T_c$ was also found in cuprate superconductors. A study on the superconducting condensation energy measured through specific heat and the intensity of the resonance peak in the $Pr_{0.88}LaCe_{0.12}CuO_4$ finds that both quantities decay with the applied magnetic field in the same way, indicating a close relationship between the resonance mode energy and superconductivity.

In above discussion, we have shown that the low energy approach, or called as the picture of weak coupling limit can give a reasonably good understanding of the superconductivity in many unconventional superconducting systems. In the systems with moderate Coulomb repulsion energy $U$, this seems to work quite well. In some systems with extremely large ratio $U/t$, it is questioned whether this picture based on retarded scattering can still be valid. In this case, some people argue that the local super-exchange $J$ dominates the pairing process, leading to the simultaneous pairing with a very strong pairing strength. One of the extreme cases is the so-called resonance-valence-bond (RVB) spin liquid state for the $s = 1/2$ systems, for example in the cuprates. In this case, the spin singlet pairs are naturally formed yielding a highly fluctuating quantum RVB state. This is certainly a very interesting picture which may get an indirect support from the strong gap, very strong superconducting fluctuation, or residual Copper pairs in the normal state far above $T_c$. The convincing evidence for this RVB state is still lacking. In Fig.6 we present a schematic show for the superconducting pairing for the cases ranging from the weak coupling (e.g., phonon mediated) pairing to the extreme case of the simultaneous pairing through the local super-exchange. The situation evolves with the ratio of $t/U$: (1) $t/U \gg 1$, weak coupling induced pairing; (2) $t/U \approx 1$, intermediate correlation
induced pairing; (3) \( t/U \ll 1 \) strong correlation and local pairing could occur. This picture follows a similar thought as that when considering the subtle balance between the correlation effect and the effective Drude weight for optimized superconductivity in a variety of compounds\(^{57}\). In the middle of Fig. 6, we have a delicate balance between the two extreme cases: complete itinerant \((U/t \ll 1)\) and strong correlation \((U/t \gg 1)\). The middle case may apply to the iron based superconductors, which still needs the retarded interaction as the pairing origin, but through exchanging the paramagnon or AF-SFs, not phonons. At the moment or in the near future, debate will go on about whether we need to have a more exotic picture which assumes the pairing completely coming from the local strong superexchange. Based on this idea, in Fig. 7, we sketch a big camp for superconductivity. The BCS theory occupies only a small area in the weak coupling limit. It remains to know how the pairing can evolve smoothly from the weak coupling limit to the extremely strong coupling limit. It is expectable that the condensation process for superconductivity will also evolve from the BCS type to BEC type, the superconducting transition temperature is determined by the gap in the BCS case, but by the phase stiffness in the BEC case\(^{58, 59}\).

IV. SOME EMPIRICAL RULES FOR THE EXPLORATION OF HIGH TEMPERATURE SUPERCONDUCTORS

It is always enthusiastic to explore new high temperature superconductors. However, beside those of pressurized hydrides, no theory can really predict how to get success, thus it has been a quite frustrated task. Even so, some empirical rules may be summarized here. Here we would like to propose several key points which may be the necessary ingredients for exploring high temperature superconductivity at ambient pressure.

A. Subtle balance between Mottness and itinerancy of \( d \) orbital electrons

As illustrated by Qazilbash et al.\(^ {57}\), the unconventional superconductors should have a delicate balance between Mottness and itineracy which governs the effective DOS at the Fermi energy. Strong Mottness may manifest a large superexchange energy \( J \) for the local pairing, but the ground state of that may be an insulator. Thus we need to effectively separate the dual roles of the \( d \)-orbital electrons. The \( 3d \) orbital electrons possess by them-self a possibility to balance between these two factors. Thus it may give more chances in the compounds with the \( 3d \) transition metal elements, like Cr, Mn, Fe, Co, Ni, Cu. Some \( 4d \) elements may also be considered, such as Ru, Pd, Rh etc.

B. Bad metal in vicinity of an AF order

Recalling both the iron based and cuprate superconductors, it is known that the parent phases are either Mott insulators or bad metals with or near an AF order. Most importantly, this AF order can be easily suppressed by chemical doping or applying a pressure. To satisfy this condition, it is important to have ions with lower magnetic moments, for example below \( 2\mu_B \). The spin density wave order due to the Fermi surface instability would help. To avoid the large magnetic moments, one may request the low filling or even number filling states of the \( 3d \) or \( 4d \) orbitals, such as the Cu-\( 3d^9 \) or Fe-\( 3d^8 \) cationic states. This is actually the case in iron based superconductors. In BaFe\(_2\)As\(_2\), for example, the cationic state is Fe\(^{2+}\), which yields a magnetic moment generally smaller than \( 2\mu_B \). In the cuprate, for example, each Cu ion in La\(_2\)CuO\(_4\) has a magnetic moment of 0.5-1.0 \( \mu_B \). The strong quantum fluctuation of the gauge field near the quantum critical point (QCP) may also help. An odd filling number of 3, 5, 7 of the \( d \) orbital will induce a strong Hund’s coupling leading to strong magnetic moments and localization of electrons.

C. Shallow and flat band near the Fermi energy

Some shallow and flat bands, or saddle points near the Fermi energy will result in the von Hove singularity of DOS, this is certainly helpful for the pairing instability. In iron based superconductors, it is known that some bands are very shallow, which yields a high DOS. In addition, a shallow band possesses a small Fermi energy \( E_F \), which leads to the small ratio \( E_F/\Delta_s \). This quantity measures the Cooper pair numbers within a coherence length \( \xi \) or volume \( \xi^3 \). If this value is small, one may expect a BEC type superconducting transition. Therefore, to have both strong pairing and high superfluid density, we probably need a system with both shallow and wide bands and together with a strong interband scattering, the shallow band produces a strong local pairing, the wide band contributes a high superfluid density.
D. Anion mediated superexchange may help

In cuprates and iron based superconductors, there are anions to mediate the superexchange for the antiferromagnetic order or spin fluctuations. Thus in the dominant conductive planes, some atomic chains like T-A-T are necessary, where $T$ represents a transition metal with $d$ orbital electrons, $A$ is an anion. For example, in cuprates the pairing through $J_1$ superexchange is established by the Cu-O-Cu bonds. While in iron based superconductors, the pairing may be established by the $J_2$ superexchange which is generated by the Fe-As-Fe bonds. However, this requirement may not be that strict for high $T_c$ superconductivity. In many binary alloy compounds, unconventional superconductivity coexists with the magnetic excitations. Thus for unconventional superconductivity, the anion bridge may not be the necessary component, but may be helpful for stabilizing the structure.

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