Modeling the Unconventional Superconducting Properties of Expanded $A_3C_{60}$ Fullerides

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The trivalent alkali fullerides solids of generic composition $A_3C_{60}$, where $C_{60}$ is the fullerene molecule and $A = K$, Rb, and Cs, are a well established family of molecular superconductors. The superconductive electron pairing is of regular $s$-wave symmetry and is accounted for by conventional coupling of electrons to phonons, in particular by well understood Jahn Teller intramolecular $C_{60}$ vibrations. A source of renewed interest in these systems are alarming indications of strong electron-electron repulsion phenomena, which emerged especially in compounds where the $C_{60}$-$C_{60}$ distance is expanded, by either a large cation size or by other chemical or physical means. Several examples are now known where this kind of expansion, while leading to a high superconducting temperature at first, gradually or suddenly causes a decline of superconductivity and its eventual disappearance in favor of a Mott insulating state. This kind of insulating state is the hallmark of strong electron correlations in cuprate and organic superconductors, and its appearance suggests that fullerides might also be members at large of that family.

Our approach to the fullerides is theoretical, and based on the solution of a Hubbard type model, where electrons hop between molecular sites. We take advantage of the fact that, unlike models for the strongly correlated cuprates, still under debate, in a Hubbard model of fullerides all the important electron correlations occur within the molecular site, efficiently soluble in the Dynamical Mean Field Theory (DMFT) approximation. DMFT solutions confirm that superconductivity in this model fulleride, although of $s$-wave symmetry rather than $d$-wave, shares many of the properties that are characteristic of high $T_c$ cuprates. The calculations are heavy; and while our working model is several years old, the new results we present in this Colloquium pertain to the most interesting case of three electrons per $C_{60}$ molecule, appropriate to $A_3C_{60}$, and have only been possible recently thanks to a stronger computational effort.

We have calculated the zero temperature phase diagram as a function of the ratio of intra-molecular repulsion parameter $U$ over the electron bandwidth $W$, the increase of $U/W$ representing the main effect of lattice expansion. The phase diagram is close to that of actual materials, with a dome shaped superconducting order parameter region preceding the Mott transition for increasing cell volume. Unconventional properties of expanded fulleride superconductors predicted by this model include: (i) an energy pseudogap in the normal phase; (ii) a gain of electron kinetic energy and of conducting Drude weight at the onset of superconductivity, as in high $T_c$ cuprates; (iii) a spin susceptibility and a specific heat behavior that is not drastically different from a regular phonon superconductor, despite strong correlations; (iv) the emergence of more than one energy scale governing the renormalized single particle dispersion, electronic entropy and the specific heat jump. These predictions, which if confirmed should establish fullerides, especially the expanded ones, as members of the wider family of strongly correlated superconductors, are discussed in the light of existing and foreseeable experiments.

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I. INTRODUCTION

Discovered by Kamerlingh Onnes nearly a century ago (Onnes, 1911), and first explained microscopically back in 1957 by Bardeen, Cooper and Schrieffer (BCS) (Bardeen et al., 1957a,b), superconductivity is still surprisingly a la page. On one hand, superconductivity is being constantly discovered in an ever increasing variety of solid state compounds. On the other hand, it appears more and more difficult to use basically the same standard theory, essentially BCS and its extensions (e.g. Parks, 1969, chapters 10 and 11) to account for all of them. In this standard, conventional theory, superconductivity arises from the condensation of electron pairs, the two electrons usually bound in a pair state of s-wave symmetry and held together by exchange of lattice phonons. The Coulomb repulsion between the two electrons opposes pair formation, but it does not suppress superconductivity because screening makes it weak enough.

The surprisingly favorable effect of repulsive electron correlations on superconductivity found in some systems, particularly in high-$T_c$ superconducting cuprates, where electron-electron repulsion is dominant, remains a standing puzzle. An immense amount of experimental and theoretical work has accumulated over the last two decades in the attempt to understand these phenomena, see e.g. the review by Bennemann and Ketterson (2008). Actually, cuprates are but the most spectacular members of a wider class of strongly correlated superconductors including heavy fermion and organic molecular compounds (Bennemann and Ketterson, 2008), systems for which there is no really comprehensive theory either. Among other factors, theoretical efforts have been hampered by the general inter-site nature of electron interactions and correlations in many of these systems, a fact that poses large technical difficulties. In this light, identifying a superconductor family where correlations are at the same time strong, simple, and on-site is welcome.

A more crucial element is one of perspective. It has been a widespread prejudice to distinguish between superconductors where (as in BCS theory) pairing of electrons takes place in the s-wave channel and is mediated by phonons, from those where the mechanism may be electronic and not phononic, and where pairing instead takes place in the d-wave channel. Whereas it is widely held that strong repulsive correlations are essential to superconductivity in the latter (Anderson, 1987), they are not considered crucial in the former. The conventional BCS scenario and its extensions, namely the Migdal-Eliashberg theory (Eliashberg, 1960) Migdal, 1958, Parks, 1969) – a controlled approximation valid when the typical phonon frequency is much smaller than the Fermi-energy – are more or less automatically accepted, and used to account for the superconducting properties. In this theory, electron-electron repulsion merely renormalizes the electron-phonon parameters, lowering the critical temperature $T_c$ rather than enhancing it.

The trivalent alkali fullerides superconductors, excellently reviewed, e.g., by Gunnarsson (1997, 2004) and Ramirez (1994), are among the systems where this conventional logic seemingly applies. Fullerides are solid state compounds of generic composition $A_3C_{60}$, where $C_{60}$ is the fullerene molecule (Gunnarsson, 2004) and $A = K$, Rb, and Cs are alkali cations. The three alkalis donate a total of $n=3$ electrons to each fullerene, half filling its threefold degenerate $t_{1u}$ molecular level. Electron hopping between first neighboring fullerenes gives rise to a metal, where conduction is restricted to the three narrow $t_{1u}$-derived bands, with a total energy bandwidth of no more than 0.6 eV (Erwin, 1993; Satpathy et al., 1992). Metallic fullerides are generally superconducting, with critical temperatures $T_c$ reaching $\sim 40$ K, depending on various factors. An empirically important factor appears to be the cell volume. When the fulleride lattice is chemically expanded, by either increasing cation size or by insertion of neutral molecules, or else physically expanded by removing pressure, $T_c$ undergoes a definite and systematic change. It rises initially with a good correlation with the $C_{60}-C_{60}$ distance (Gunnarsson, 1997; Yildirim et al., 1995). Further expansion however causes $T_c$ to drop, ending eventually, through a first order transition, in an insulating state, as we shall discuss later.

A wealth of evidence indicates that superconducting pairing in fullerides is phononic and that the relevant phonons are the $s$-type intra-molecular $H_g$ vibrations of the $C_{60}$ molecule, Jahn-Teller coupled to the $t_{1u}$ conduction electrons (Gunnarsson, 1997). Further support to the apparent BCS nature of superconductivity in fullerides comes from specific-heat jumps that scale linearly with $T_c$ in agreement with BCS theory (Burkhart and Meingast, 1996; Kortan et al., 1992; Ramirez, 1994), as well as a regular (i.e., not exceedingly high) normal phase magnetic susceptibility. (Kortan et al., 1992; Robert et al., 1998) Superconducting energy gaps are less clearly defined, (Gunnarsson, 1997) the gap ratio $2\Delta/T_c \approx 3.4 - 4.2$ in K$_3$C$_{60}$ and Rb$_3$C$_{60}$ (Gunnarsson, 1997; Ramirez, 1994), but not far from the BCS value of 3.53. These elements suggest viewing the $A_3C_{60}$ compounds as weakly correlated Fermi-liquid conductors (Ramirez, 1994), though with unusually narrow electron bands, with a large effective mass roughly three free electron masses (Robert et al., 1998). Even the observed decrease of $T_c$ under applied pressure in K$_3$C$_{60}$ and Rb$_3$C$_{60}$ is in qualitative agreement with an increasing bandwidth and decreasing density of states at the Fermi level, which further supports a standard BCS picture.

These reassuring, conventional looking facts are however contrasted by a number of conflicting elements that are strong enough to cast serious doubts on the general applicability of the BCS scenario to superconductors in this family. These elements are especially apparent in the more expanded ful-
lerides including \((\text{NH}_3)_2\text{NaK}_2\text{C}_{60}\) \cite{Ricco2003} and \(\text{Li}_3\text{C}_{60}\) \cite{Durand2003}, and in the alloys \(\text{Cs}_3–\text{K}_2\text{C}_{60}\) and \(\text{Cs}_3–\text{Rb}_2\text{C}_{60}\) \cite{Dahlke2000}. For these expanded compounds \(T_c\) decreases upon expansion, contrary to BCS theory. The electron density of states extracted by NMR Knight shift is at the same time an increasing function of lattice parameter, smoothly connecting with that of the unalloyed compounds under pressure \cite{Dahlke2000}. Within BCS theory, that increase should lead to a rise of \(T_c\) and not to a drop as observed. The same unconventional behavior is observed in \(\text{Cs}_3\text{C}_{60}\), the fulleride compound with the highest \(T_c \sim 40\) K attained under pressure \cite{Palstra1999}. A novel A15 superconducting phase of \(\text{Cs}_3\text{C}_{60}\) with expanded structure has very recently been synthesized \cite{Ganin2008} corresponding to a body-centered cubic arrangement of fullerenes. Superconductivity emerges under pressure through a first order non-structural transition at 4 Kbar. The critical temperature \(T_c\) first increases with pressure, reaching a dome-shaped maximum of 38 K around 7 Kbar, above which \(T_c\) drops. Since no structural changes are observed under pressure, the appearance of superconductivity as well as the dome-shaped \(T_c\) vs. pressure behavior must be ascribed solely to the volume contraction \cite{Ganin2008}. This non-monotonic behavior of \(T_c\) with pressure finds no apparent explanation within the conventional theory.

The basic and striking anomaly of expanded fullerides occurs in the compounds with the largest inter-molecule distances. In these materials a relatively modest additional lattice expansion (and minor change of symmetry due to intercalated ammonia) is enough to dramatically turn them from metallic and superconducting to antiferromagnetic and insulating \cite{Durand2003, Iwasa2003}⁷. With temperature, antiferromagnetic order in the ammoniated compound \(\text{NH}_3\text{K}_3\text{C}_{60}\) changes to paramagnetic disorder at a Néel temperature slightly above \(\sim 40\) K \cite{Prassides1999}. Even above the Néel temperature, the microwave conductivity in \(\text{NH}_3\text{K}_3\text{C}_{60}\) remains several orders of magnitude below that of \(\text{K}_3\text{C}_{60}\) \cite{Kitano2002}, testifying the Mott insulator (correlation driven) nature of the insulating phase. Electrons in a lattice give rise to a Mott insulating state when electron electron repulsion stops their free propagation and the lattice appears as a collection of molecular ions. Correlations lead to an energy gap in their spectrum, even if their number density per cell is odd, instead of even as in regular band insulators \cite{Mott1990}. Proximity of a Mott insulator phase in fullerides had long been advocated in different contexts \cite{Baskaran1991, Chakravarty1991, Chakravarty1991, Lof1992}.

\footnote{We expect that below the superconducting pressure of 4 kbar, the new compound A15 \(\text{Cs}_3\text{C}_{60}\) \cite{Ganin2008}, yet to be characterized in this respect, should also be an insulating antiferromagnet.}

\section{II. Electron Interactions in Fullerides}

The electrons donated by the alkalis to the \(\text{C}_{60}\) molecule enter the threefold degenerate \(t_{2u}\) former lowest unoccupied molecular orbital (LUMO). In a degenerate molecular orbital, electrons interact through a variety of mechanisms. The first is overall Coulomb repulsion, which we will associate later below with the Hubbard parameter \(U\). The second is Coulomb exchange energy, minimized when the molecular state has the highest total spin, and the highest total orbital angular momentum compatible with it (Hund’s rules) \cite{Landau1958}. The third is the Jahn-Teller (JT) interaction, caused by coupling of the electron levels to symmetry lowering molecular distortions \cite{Landau1958, chap. 13}. Contrary to Hund’s rules, in a JT distorted molecule the ground state maximizes double occupancy of levels, thus favoring low total spin instead of high spin in the isolated

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{FIG.1.png}
\caption{Schematic representation of a planar projection of the crystal structure of \(\text{NH}_3\text{K}_3\text{C}_{60}\). Green dots are potassium atoms, blue dots surrounded by three grey dots are \(\text{NH}_3\) molecules, and \(\text{C}_{60}\) molecules are shown according to their actual spatial orientation. (Courtesy of Kosmas Prassides).}
\end{figure}
molecular ion. In molecular C$_{60}^{3-}$, the strength of these interactions has been evaluated in the past, and the JT effect has been estimated to prevail narrowly over Hund’s rule exchange (Lüders et al., 2002). This narrow balance favors a low-spin ground state, with a relatively small “spin gap” – the energy between the low spin ground state and the lowest high-spin excited state, expected to be of the order of 0.1 eV (Capone et al., 2001, Lüders et al., 2002). In agreement with this expectation, local moments indicate that in antiferromagnetic Mott insulating NH$_3$K$_3$C$_{60}$ the C$_{60}(3^-)$ sites are in a low-spin state, $S = 1/2$ (Prassides et al., 1994), their high spin state $S = 3/2$ lying about 100 meV higher in energy. A low-spin qualifies the overexpanded fullerenes as “Mott-Jahn-Teller” insulators – that is, Mott insulators whose sites are in a JT stabilized low-spin state (as opposed to a Hund’s rule stabilized high-spin state) (Fabrizio and Tosatti, 1997). Under hydrostatic pressure, NH$_3$K$_3$C$_{60}$ undergoes a transition to a metallic state where superconductivity re-emerges with a rather large $T_c$ (Prassides et al., 1999). It is important to note that this superconducting phase still belongs to the “expanded” family, as signaled by the fact the $T_c$ here increases further with increasing pressure (reaching 28 K at 14.8 kbar (Zhou et al., 1995)) at variance with non-expanded fullerenes, where $T_c$ drops under pressure.

A lateral, but relevant additional element comes from tetravalent compounds A$_4$C$_{60}$, which are insulators or near insulators. By comparison with the trivalent fullerenes, the slight reduction of band-energy gain per particle caused by adding one more electron per molecule and by slightly changing the crystal structure is sufficient to turn the metallic trivalent metals into tetravalent insulators even in non-expanded materials. Careful density-functional electronic structure calculations indicated that it is not possible to describe the tetravalent compounds such as K$_4$C$_{60}$ as statically distorted Jahn-Teller band insulators (Capone et al., 2000). A static JT distortion and the associated orthorhombic state is actually present only in Cs$_3$C$_{60}$ (Dahlke and Rosseinsky, 2002), and in Rb$_4$C$_{60}$ above a critical pressure (Huq and Stephens, 2000), while it never shows up in K$_4$C$_{60}$ (Huq and Stephens, 2000) (with the exception of monolayers, see Wachowiak et al., 2003). The persistence of insulating or near insulating behavior and the recovery of molecular symmetry observed in the high temperature phase of tetravalent fullerenes suggests that these compounds too are Mott-Jahn-Teller insulators (Capone et al., 2000, Klupp et al., 2000, Knupfer and Fink, 1997), like the overexpanded trivalent materials. The dynamic JT effect in each C$_{60}^{4-}$ ion associated with Mott localization of carriers is crucial in explaining the low spin ground state and the spin gap of A$_4$C$_{60}$, exactly as for the expanded trivalent compounds.

From the above discussion one might be tempted to conclude that strong correlations play a role only in tetravalent and expanded trivalent compounds, while face-centered cubic (f.c.c.) K$_3$C$_{60}$ and Rb$_3$C$_{60}$, where superconductivity was originally discovered, could still be viewed as weakly correlated systems, and as BCS type superconductors. We do not believe in this conclusion. A final, independent and strongly unconventional signal is provided by NMR. In fact, NMR data show direct evidence of a spin gap of order 0.1 eV, appearing as an anomalous activated increase of inverse relaxation time. Most likely this gap between a low spin ground state and a high spin excited state reflects the multiplet behavior of the localized C$_{60}^{3-}$ molecular ion. It shows up ubiquitously in all alkali doped fullerenes, including superconducting f.c.c. compounds (Brouet et al., 2002, Thier et al., 1995). The existence of the spin gap signifies that the magnetic response of fullerenes is very far from Fermi-liquid behavior, which has no such feature. Magnetically, the fullerenes behave as if localized molecular multiplet excitations coexisted with delocalized propagating quasiparticles. As discussed, the recovery of molecular physics is characteristic of Mott insulators, suggesting that the fingerprint of Mott physics is strongly present already in the non-expanded superconducting f.c.c. compounds. This suggests that the f.c.c. compounds are somehow the analog of the overdoped cuprates, whereas the expanded trivalent materials are analogous to the underdoped cuprates. The conclusion is that both are crucially, even if differently, influenced by electron correlations.

We believe that the above elements are strong enough to call for a new physical picture for the whole family of A$_3$C$_{60}$ superconductors. Proximity of the Mott insulator strongly suggests that the anomalies of expanded fullerene superconductors most likely originate from strong repulsive electron correlation in the narrow $t_{1u}$ bands. The prevalence in the Mott localized state of molecular physics, with its orbital degeneracy, JT effect and intra-molecular exchange must be taken into account along with itinerant electron band physics. Upon expanding the cell volume, the intermolecular hopping of electron weakens, whereas all the on-site correlation terms – Coulomb and exchange electron-electron interactions as well as molecular JT effect – are likely to become increasingly relevant. We are led to a picture where the Mott insulator physics of weakly coupled molecular ions progressively prevails over band physics for increasing lattice expansion. In particular, superconductors that operate in this regime are bound to deviate from the standard Migdal-Eliashberg scenario, the more so as the lattice spacing increases. To investigate that regime, we need to start with a broader theoretical scheme for trivalent fullerenes, capable of describing their behavior under lattice expansion and near the Mott transition. While that has been the scope of our work for several years, previous work was for practical technical reasons limited to tetravalent systems (Capone et al., 2002, 2000). The study of A$_3$C$_{60}$ systems, computationally much heavier due to the simultaneous relevance of magnetic and orbital ordering, has only now been completed, and we offer here an outline of the main results.
III. MODEL AND INTERACTIONS

Our theoretical model of trivalent fullerides assumes a lattice of molecular sites, each representing a C_{60} molecule. The C_{60} t_{1u} threefold degenerate LUMO can for all purposes be treated as an atomic p level. An average of three electrons per molecule are donated by alkali atoms and partially fill these orbitals, which can host up to six electrons. The electrons hop from site to site giving rise to half-filled bands of width \( W \sim 0.6 \text{eV} \). On each site the electrons experience a Hubbard repulsion \( U \sim 1 \text{eV} \) (corresponding to the Slater integral \( F_0 \propto U \)),

\[
\mathcal{H}_U = \frac{U}{2} (n - 3)^2 , \tag{1}
\]

together with a weaker, yet crucial, inter-orbital Hund’s rule exchange coupling term \( J_H \) proportional to the Slater integral \( F_2 \). Under the sole assumption of full rotational orbital symmetry, this exchange term takes the form \( \mathcal{H}_J = J \left( 2\mathbf{S} \cdot \mathbf{S} + \frac{1}{2} \mathbf{L} \cdot \mathbf{L} \right) + \frac{5}{6} J(n - 3)^2 , \tag{2} \)

where \( J = -J_H < 0 \), while \( n, \mathbf{S} \) and \( \mathbf{L} \) are the density, spin and orbital angular momentum operators, defined as for p-orbitals, on the given site. This exchange term favors high \( \mathbf{S} \) and \( \mathbf{L} \) molecular multiplets, and has been overlooked or neglected in most treatments so far. The next interaction is the JT intra-molecular coupling of electrons in the t_{1u} orbital to \( H_g \) intramolecular vibrations. This interaction has on the contrary been very widely discussed (see e.g. Auerbach et al. 1994; Gunnarsson et al. 1995; Varma et al. 1991; Lannoo et al. 1991; Lüders et al. 2002; Martin and Ritchie, 1993), whereas \( J_{JT} \sim 0.06 - 0.12 \text{eV} \) (Auerbach et al. 1994; Gunnarsson et al. 1995; Lannoo et al. 1991; Lüders et al. 2002; Varma et al. 1991). The total result – and the only one compatible with s-wave superconductivity, with a spin 1/2 Mott insulator, and with a moderate spin gap near 0.1 eV – is a relatively weak unretarded attraction which has the form of an inverted Hund’s rule coupling (Capone et al. 2002; Granath and Ostlund, 2003). This is the approximation we shall adopt, keeping in mind that it is strictly valid only when \( ZW < \hbar \omega \), that is, close enough to the Mott transition.

The lattice expansion characterizing the expanded fullerides is believed to have little effect on either \( J_H \) or \( J_{JT} \). On the other hand, expansion will surely decrease \( W \) and increase \( U \), so it can be modeled as a gradual increase of \( U/W \), reflecting both the band narrowing due to smaller overlap between molecular wave functions, and a decreased screening strength. As discussed above, this Hamiltonian model, even if not really simple, has many body interactions that are strictly on site, an ideal situation for Dynamical Mean-Field Theory (DMFT) (Georges et al. 1996), one of the most popular and powerful tools in the field of strongly correlated electron systems that we briefly describe in the next subsection.

A. Dynamical Mean-Field Theory

DMFT is a quantum version of classical mean-field theory, which provides an exact description of the local dynamics, at the price of freezing away all spatial fluctuations. The mean-field scheme is formulated by a mapping of the lattice model onto an Anderson impurity model (AIM) embedded in a free-electron Fermi “bath” subject to a self-consistency condition (Georges et al. 1996). In our model, the effective AIM is three-fold orbitally degenerate, with p-like levels representing the t_{1u} orbitals, each hybridized with a bath. The Hamiltonian is

\[
\mathcal{H} = \mathcal{H}_U + \mathcal{H}_J + \sum_{k\alpha \sigma} \varepsilon_{k\alpha} c_{k\alpha \sigma}^\dagger c_{k\alpha \sigma} + \sum_{k\sigma} V_k (c_{k\alpha \sigma}^\dagger p_{\alpha \sigma} + H.c.), \tag{3}
\]

where \( \mathcal{H}_U \) and \( \mathcal{H}_J \) are (1) and (2) for fermions on the impurity orbitals, \( \varepsilon_{k\alpha} \) are the bath energy levels labeled by the index \( k \) and by an orbital index \( a = x, y, z \), \( V_k \) are the hybridization parameters between the bath fermions, created by \( c_{k\alpha \sigma}^\dagger \), and the impurity fermions, created by \( p_{\alpha \sigma}^\dagger \). The mean-field scheme implies a self-consistency condition that depends on the impurity Green’s function and on the bare density of states of the original lattice. Throughout our calculations, we use an infinite-coordination Bethe lattice, whose density of states is
The impurity model Hamiltonian can be diagonalized in the finite resulting over the low-lying eigenvectors where the thermal Green’s function is expressed as a sum temperature extension of Lanczos (Capone et al., 2007), the exception. They are obtained by means of the finite- temperature results for the Hamiltonian. The finite temperature results for the bital. Most of the results we shall present are at zero degenerate AIM by exact diagonalization. That requires iteratively the AIM until the impurity Green’s function satisfies Eq. (5). In this work, we solved the threefold degenerate AIM with error on the Green’s function to be of order of a few per cent, a level of accuracy that does not allow to fully determine thermodynamic properties such as the critical temperature. Luckily though, this error affects much more the absolute specific heat value than its relative changes, including the superconducting jump in units of $T_c$ which we shall discuss further below (see Sec. V). We underline that this limitation does not affect by any means the $T = 0$ calculations. The above DMFT equations refer to a paramagnetic phase where no symmetry breaking occurs. However, in this work we shall be crucially interested in s-wave superconducting and in antiferromagnetic solutions, where symmetry is broken. Superconductivity is conveniently studied in the Nambu-Gor’kov representation by introducing spinors

$$\psi_{\mathbf{k}a} = \begin{pmatrix} p_{\mathbf{k}a} \tau \, \frac{p_{\mathbf{k}a}}{p_{\mathbf{k}a}} \end{pmatrix},$$

and defining accordingly the Green’s function $G_{\mathbf{k}a}(\tau) = -\langle T_\tau \psi_{\mathbf{k}a}(\tau) \psi_{\mathbf{k}a}^\dagger(0) \rangle$ in imaginary time as a $2 \times 2$ matrix that satisfies the Dyson equation in Matsubara frequencies

$$G_{\mathbf{k}a}(i\omega) = G_{\mathbf{k}a}^0(i\omega) + \Sigma_{\mathbf{k}a}(i\omega) G_{\mathbf{k}a}(i\omega),$$

with $G_{\mathbf{k}a}^0(i\omega)$ the non-interacting value. The single-particle self-energy $\Sigma(i\omega)$ is also a $2 \times 2$ matrix whose off-diagonal element $\Delta(i\omega)$, when finite, signals a superconducting phase. The DMFT self-consistency can be written now as

$$G_{\mathbf{k}a}^{-1}(i\omega_n) = i\omega_n \tau_0 + \mu \tau_3 - t^2 \tau_3 G(i\omega_n) \tau_3,$$

where $\tau_0$ and $\tau_3$ are Pauli matrices.

Analogously, antiferromagnetism in a bipartite lattice is conveniently described using the spinor

$$\psi_{\mathbf{k}a\sigma} = \begin{pmatrix} p_{\mathbf{k}a\sigma} \\ p_{\mathbf{k}a\sigma} \end{pmatrix},$$

with $\mathbf{k}$ in the magnetic Brillouin zone and $\mathbf{Q}$ the modulation vector. This leads once more to a $2 \times 2$ Green’s function and self-energy matrices related by the Dyson equation (8). Here too, a finite off-diagonal element signals an antiferromagnetically ordered phase. The self-consistency equation for antiferromagnetism exploits the bipartite property of the lattice. Indicating one sublattice with A and the other with B, the general self-

$$G_{\mathbf{k}a\sigma}(i\omega) = G_{\mathbf{k}a\sigma}^0(i\omega) + \Sigma_{\mathbf{k}a\sigma}(i\omega) G_{\mathbf{k}a\sigma}(i\omega),$$

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$$G_{\mathbf{k}a\sigma}^{-1}(i\omega_n) = i\omega_n \tau_0 + \mu \tau_3 - t^2 \tau_3 G(i\omega_n) \tau_3,$$

where $\tau_0$ and $\tau_3$ are Pauli matrices.
consistency condition is
\[ G_0^{-1}(i\omega_n)_{\sigma A} = (i\omega_n + \mu) - t^2 G(i\omega_n)_{\sigma B}, \tag{10} \]
which becomes Eq. (6) if \( G_{\sigma A} \equiv G_{\sigma B} \), i.e. if the system is nonmagnetic. When the system is antiferromagnetic, then \( G_{\sigma A} \equiv G_{-\sigma B} \). Thus we can eliminate the sublattice B from Eq. (10), and obtain the following result for the self-consistency equation:
\[ G_0^{-1}(i\omega_n)_{\sigma A} = (i\omega_n + \mu) - t^2 G(i\omega_n)_{-\sigma A}. \tag{11} \]
This equation is valid for a Bethe lattice with nearest neighbor hopping, a case with perfect nesting that is rather exceptional in realistic antiferromagnets. A way to simulate imperfect nesting typical of more realistic situations, while still taking advantage of the Bethe-lattice simplifications, is to add a next-nearest-neighbor hopping \( t'/z \) in the Cayley tree (merely a device to eliminate nesting, not meant to suggest next nearest neighbor hopping, small in fullerides). In the limit \( z \to \infty \) of the Bethe lattice, the self-consistency equation becomes
\[ G_0^{-1}(i\omega_n)_{\sigma A} = (i\omega_n + \mu) - t^2 G(i\omega_n)_{-\sigma A} - t^2 G(i\omega_n)_{-\sigma A}. \tag{12} \]
For both broken-symmetry phases, if the diagonal elements of the self-energy matrix at low Matsubara frequencies follow the conventional Fermi-liquid behavior – which we always find to be the case,
\[ \Sigma_{\text{diagonal}}(i\omega_n) \simeq \left( 1 - \frac{1}{Z} \right) i\omega_n, \tag{13} \]
the actual value of the spectral gap in the single particle spectrum is given by \( Z \Delta(0) \), the zero frequency anomalous (superconducting or antiferromagnetic) self-energy multiplied by the so-called quasiparticle weight \( Z \).

We end by noting that, within DMFT, one can search for solutions with different symmetries by simply allowing/preventing symmetry breaking order parameters, even in regions where the chosen phase is not the most stable. When two or more solutions coexist, the stable one is determined by an explicit energy calculation. As we shall discuss, for a wide range of \( U/W \) values we do find coexisting superconducting and antiferromagnetic solutions, the former prevailing at smaller \( U \), the latter at larger \( U \). The physical phase diagram thus exhibits a first-order transition between these two symmetry broken phases – a nonmagnetic \( s \)-wave superconductor, and an insulating spin 1/2 antiferromagnet – taking place when the respective energy curves intersect.

B. \( T = 0 \) Phase Diagram

Modeling lattice expansion of fullerides as a gradual increase of \( U/W \), we can proceed to analyze the theoretical zero temperature “phase diagram” of our model obtained by DMFT as a function of \( U/W \). Starting with the uncorrelated system with \( U = 0 \) the model initially exhibits straight BCS superconductivity driven by JT phonons (i.e., the attractive \( J \) we introduced above) with an \( s \)-wave \( (S = L = 0) \) order parameter.
\[ P_{\text{SC}} = \frac{1}{N} \sum_i \sum_{a=x,y,z} \langle p_{i,a}^{\dagger} p_{i,a} \rangle, \tag{14} \]
where \( N \) is the number of molecules and \( p_{i,a}^{\dagger} \) creates an electron on molecule \( i \), with spin \( \sigma \) and in orbital \( a = x, y, z \). The Fermi-liquid scattering amplitude in the Cooper channel, measuring the strength of the effective attraction, is \( A = -10 J/3 \). We note that owing to fairly strong JT interactions \( Auerbach \ et \ al. \ 1994 \) \( Gunnarsson \ et \ al. \ 1993 \), if Hund’s exchange \( J_H \) were neglected, the dimensionless JT coupling constant of fullerenes controlling superconductivity would be numerically very large, \( \lambda = \rho_0 |A| \simeq 0.6 - 1.0 \), where \( \rho_0 \simeq 2.4 \ eV^{-1} \) is the bare density of states per spin and orbital. Turning on a weak Coulomb repulsion \( U \) on top of that will reduce the pairing attraction in this regime. Perturbatively one obtains for small \( U \) that \( A = -10 J/3 + U \). Since \( J \) is insensitive to expansion while \( U/W \) increases, this implies that in this picture, where Hund’s rule exchange is neglected, \( T_c \) should always decrease upon expansion, a prediction which is at odds with experiments.

In fact, as anticipated, Hund’s rule exchange is not negligible, and its effect is to introduce a substantial cancellation in \( J \) leading to a largely reduced effective coupling \( \lambda_{\text{eff}} \simeq \frac{10}{2} (J_{\text{JT}} - J_H) / \rho_0 \). Should we interpret the ubiquitous spin gap of 0.1 eV \( \text{Brouet et al. 2002a} \) \( \text{Thier et al. 1995} \) as the \( C_{60} \) molecular excitation energy between its low spin ground state with \( S = 1/2 \) and \( S = 0 \) for \( n = 3 \) and \( n = 4 \), respectively, and its high spin excited state, with \( S = 3/2 \) and \( S = 1 \) for \( n = 3 \) and \( n = 4 \), respectively, we would conclude that, to be consistent with our model where both gaps are equal to \( 5 J \) \( \text{Capone et al. 2004} \), the total effective inverted exchange \( J \), comprehensive of both JT and Hund’s rule exchange, should be approximately \( J \simeq 0.02 \ eV \). In reality, the qualitative scenario we will describe is relatively independent of the precise value of \( J \) provided it is inverted, i.e., negative and small.

Once exchange is included, the resulting \( \lambda_{\text{eff}} \simeq 0.16 \) is now much smaller – in fact way too small to explain within conventional BCS or Migdal-Eliashberg theory any of the observed values of \( T_c \) in fullerides (let alone the non-monotonic behavior of \( T_c \) versus the density of states for expanded fullerides \( \text{Dahlke et al. 2000} \) \( \text{Ganin et al. 2008} \)). Things get worse when we increase the on-site Coulomb repulsion \( U \) closer to realistic values, \( U \sim W \)

\(^2\text{Since gauge symmetry is broken, we are allowed to assume } P_{\text{SC}} \text{ real.}\)
sured for example in the DMFT spectral function (not
creasing becomes a normal metal as expected. Upon further in-
importance of electron correlations increases with
Beginning from zero, the increase of \( U \) vanishes at roughly the mean-field value
stroys the weak BCS superconductivity . The supercon-
tor. Panel (b) corresponds to the case in the presence of a
between the two phases is indicated by a vertical line separating
the superconductor from the antiferromagnetic Mott insula-
tors. The full DMFT solution of the model for
Superconducting solution (triangles) and antiferro-
magnetic solution (squares) zero-frequency anomalous self-
energies \( \Delta(0) \) as function of \( U/W \). Solid symbols are used
when the corresponding symmetry broken phase is stable, while open symbols when it is metastable, i.e. has lower
energy then the other phase. The first-order transition be-
 tween the two phases is indicated by a vertical line separating
the superconductor from the antiferromagnetic Mott insula-
tor. Panel (b) corresponds to the case in the presence of a
frustrating next-nearest neighbor hopping \( t' = 0.3t \), absent in
(a).

and beyond. In the conventional weakly correlated pic-
ture \( U \) would provide in the electron pairing problem a repulsive “Coulomb pseudopotential” whose bare value is \( \mu_u = U \rho_0 \simeq 3 \) (Parks, 1969). Simply comparing these bare values of \( \lambda \) and \( \mu_u \) we should conclude that s-wave
BCS superconductivity in fullerenes is simply impossible
(with the obvious proviso that for small \( U \) an unretarded treat-
ment of JT phonon interactions is not really justi-
ified).

The full DMFT solution of the model for \( J = 0.05 \) \( W \) and increasing \( U/W \) yields the phase diagram in Fig. 2
While confirming the above expectations for moderate \( U \), it has a surprise in reserve at larger \( U \) values, where the Mott transition is approached.

Fig. 2 shows the zero frequency anomalous single-
particle self-energies calculated within DMFT for the su-
perconducting and for the antiferromagnetic solution. At
\( U = 0 \), the model is an s-wave BCS superconductor,
with an exponentially small superconducting \( \Delta(0) \). It
is too small to be visible in the figure, since the effec-
tive exchange-reduced \( \lambda \sim 0.2 \) is as said very weak.
Beginning from zero, the increase of \( U \) first rapidly de-
strouts the weak BCS superconductivity. The supercon-
ducting \( \Delta(0) \) vanishes at roughly the mean-field value
\( U = 10/3J \), and above this value of \( U \) the ground state
becomes a normal metal as expected. Upon further in-
creasing \( U/W \) the model remains a normal metal – no
superconductivity, no antiferromagnetism. However, the
importance of electron correlations increases with \( U \), as
signaled for example in the DMFT spectral function (not
shown) by the gradual formation of incoherent Hubbard
bands on both sides of the Fermi level. The metallic
character persists until a hypothetically continuous Mott
transition eventually reached near \( U/W \sim 1.5 \), where
\( Z = 0 \) and the metallic character is extinguished.

Before this happens however, s-wave superconduc-
ity re-enters from the normal metal state. The anomalous
self energy \( \Delta(0) \), proportional to the superconducting
order parameter has, as a function of \( U \), a bell-shaped
behavior – a “superconducting dome” as it is called in
cuprates – hitting a large maximum before dropping
again. The re-entrant superconductive behavior is a clear
realization of phonon-induced strongly correlated super-
conductivity (SCS) (Capone et al., 2002). The sharply
rising order parameter edge with increasing \( U/W \) can in
our view explain the strong rise of \( T_c \) upon lattice ex-
ansion in non-expanded compounds, previously (and we believe incorrectly) attributed to a BCS-like increase of
density of states upon band narrowing. Past the dome
maximum, and upon increasing expansion, the SCS su-
perconducting order parameter declines, and would even-
tually drop to zero at the continuous metal insulator
transition near \( U/W \sim 1.5 \). This continuous decline of
superconductivity is preempted by a first order transition
to a lower energy antiferromagnetic Mott insulating
phase, with order parameter

\[
P_{AFM} = \frac{1}{N} \sum_i (-1)^i (n_{i\uparrow} - n_{i\downarrow}),
\]

where \( n_{i\sigma} = \sum_{a=x,y,z} P_{i,\sigma}^a P_{a,\sigma} \) is the full occupation
number with spin \( \sigma \) at molecule \( i \). The exact location of
the superconductor-insulator transition depends on de-
tails. For strong nesting (\( t' = 0 \)) it takes place even be-
fore the superconducting dome maximum. In Fig. 3 we
show \( \Delta(0) \) of Fig. 2 in comparison with the spectral gaps
\( Z \Delta(0) \), as well as the order parameters \( P_{SC} \) and \( P_{AFM} \).
Notice that \( Z \) for the superconductor is smaller and van-
ishes at the continuous metal insulator transition, while \( Z \) for the antiferromagnet is of order 1. In both cases
the dimensionless order parameter essentially follows the
behavior of the spectral gap.

When we add a next-nearest neighbor hopping \( t' \) to
mimic imperfect nesting (as we expect to find generi-
cally for realistic band structures, in particular in the
face-centered cubic \( A_3C_{60} \) materials), we find that the
superconducting phase is only weakly affected but anti-
ferromagnetism is strongly frustrated. As a result the
superconducting region expands at expense of the magnetic
insulator, and the superconducting dome may emerge in
full panel (b) of Fig. 2. We propose that the grad-
ual drop of superconducting order parameter past the
dome maximum now naturally explains the decline of
\( T_c \) of expanded fullerenes (Dahlke and Rosseinsky, 2002;
Durand et al., 2003; Ganin et al., 2008).

Finally, past the first-order Mott transition, we find
that the antiferromagnetic insulator is formed mainly
by spin-1/2 local configurations, which is in agreement
with experiments in \( NH_3K_3C_{60} \) (Iwasa and Takenobu,
2003). We also predict that ambient pressure \( A15 \)
\( Cs_3C_{60} \), yet to be characterized, should similarly be a
fluctuations are gradually frozen away near the Mott transition, the effective repulsion between quasiparticles is also renormalized down to some smaller value $U_s < U$. In particular, the Fermi-liquid description provided, e.g., by the Gutzwiller variational approach (Gutzwiller, 1963) and supported by the DMFT behavior of the average charge fluctuations $\langle (n - 3)^2 \rangle$, suggests that $U_* \approx U \Gamma_U Z(U)^2 \sim U Z(U)$, where $\Gamma_U$ includes all the so-called vertex corrections (Abrikosov et al., 1962). This implies that the vertex function $\Gamma_U$ diverges close to the Mott transition, but does not compensate the vanishing of $Z$ (Capone et al., 2002). The pairwise Jahn-Teller and exchange based attraction $J$ between quasiparticles, even if small, here is restricted to spin and orbital space, and has nothing to do with charge fluctuations. In other words, Hund’s rule exchange and the JT coupling only influence the internal splitting of each molecular multiplet without affecting its center of gravity. As a result, this attraction should remain unrenormalized $J_* = J \Gamma_U Z(U)^2 \sim J$ close to the metal insulator transition, thus implying a strongly divergent vertex correction $\Gamma_U$ that cancel the vanishing $Z$. Therefore the electron pair scattering amplitude $A_e$ in the Cooper channel should renormalize as $A = U - U_0^2 J \rightarrow A_* = Z(U) U - U_0^2 J$. When $U/W$ is small, $Z \lesssim 1$, the main effect of $U$ is to suppress superconductivity, as was noted earlier. However, if $U$ is close to the critical metal-insulator value $U_c$, then $Z \sim (U_c - U)/U_c \ll 1$ and the scattering amplitude turns negative in spite of a large $U$. This is qualitatively the reason for the SCS re-entrance of superconductivity (though in this region of course the actual pair scattering amplitude might deviate from this simple formula (Capone et al., 2002)).

In addition, the Fermi-liquid argument suggests an explanation for the large value of superconducting order parameter, implying a large $T_c$, in the SCS regime, see Fig. 2 compared to the $U = 0$ BCS values. In fact, when $A_* \approx ZW$, and $Z$ is dropping sharply, the quasiparticle attraction $A_e$ will at some point $U = U_*$ equal the coherent quasiparticle bandwidth $ZW$. That very uncommon situation, of metallic quasiparticles with a pair attraction equal to their energy bandwidth, is known to yield maximum superconductivity for a given attraction. As shown by studies of purely attractive models (Micnas et al., 1990), the maximum superconducting temperature $k_B T_c$ attainable in that case is about 7% of the pair attraction energy itself. In our model of trivalent fullerenes, this estimate yields $k_B T_c \sim 0.07 A_* \sim 0.2 |J|$, which has the correct magnitude of roughly 40 K for $J \sim 20$ meV – a value in turn fully consistent with the observed spin gap 0.1 eV $\sim 5J$. While this coincidence of numbers is probably fortuitous, it does indicate that orders of magnitude implied by our model with realistic parameters are quite consistent with experimental facts. At face value, it also suggests that 0.07 $|J|$ could be the maximum attainable $k_B T_c$ in fullerenes. We conclude that strong correlations play a crucial role in bringing the superconducting gap magnitude to the right

![Superconducting solution (SC, left) and antiferromagnetic solution (AFM, right) anomalous self-energies (top) and order parameters (bottom) as a function of $U/W$. The top panels also show (green diamonds) the spectral gaps obtained multiplying $\Delta$ by the quasiparticle weight $Z$ of each solution. The gaps are in units of the bandwidth $W$ (the order parameters are by definition dimensionless). Dashed vertical lines mark the first-order phase transition between the two solutions.](image-url)

**FIG. 3** Superconducting solution (SC, left) and antiferromagnetic solution (AFM, right) anomalous self-energies (top) and order parameters (bottom) as a function of $U/W$. The top panels also show (green diamonds) the spectral gaps obtained multiplying $\Delta$ by the quasiparticle weight $Z$ of each solution. The gaps are in units of the bandwidth $W$ (the order parameters are by definition dimensionless). Dashed vertical lines mark the first-order phase transition between the two solutions.
range of values as compared with the experimental ones, see Fig. 4. Such values and large critical temperatures would never be attained within conventional BCS theory using a value of \( \lambda \approx 0.16 - 0.2 \), including as it should the large cancellation of JT by exchange. They could in point of fact be attained if the cancellation due to exchange were (incorrectly) neglected; but then a lattice expansion should always lead to a decrease of \( T_c \), contrary to experiment.

To appreciate further the effect of exchange-JT cancellation, it is instructive to consider, as was done for a simplified model by Capone et al. (2004), the behavior with \( U/W \) of the superconducting self-energy \( \Delta(0) \) (proportional to the \( T = 0 \) gap, and roughly speaking to \( T_c \)) starting with pure JT and without exchange, and then proceeding to turn on exchange and gradual cancellation, see Fig. 5. For the bare JT, \( \lambda \approx 1 \) (a strong coupling value) the superconducting self-energy decreases monotonically with increasing \( U \), in agreement with the Migdal-Eliashberg prediction of an increasing Coulomb pseudo-potential. Above a critical value, the system turns directly, via a second-order or weakly first-order phase transition, to a Mott insulating phase. This result is fully consistent with previous calculations by Han et al. (2003), where the same type of Hubbard model was studied within DMFT at finite temperature. Treating explicitly the electron-phonon coupling (including the full phonon dynamics) with \( \lambda = 0.6 \) and neglecting exchange they obtained a superconductor with monotonically decreasing gap.

Through a progressive reduction of \( \lambda \) (mimicking JT cancellation by exchange) we find that a non-monotonic superconducting behavior makes its appearance as a function of \( U \). Initially there is still a single superconducting phase for all \( U/W \) values; but two different regions near zero and near \( U_c \) begin to materialize. (Note that \( U_c \) simultaneously shifts to higher \( U \) as \( \lambda \) decreases). When the cancellation is so strong that \( \lambda \) is still positive but small, the two superconducting regions break apart to form two separate pockets, leaving a normal metal phase in between. In the leftmost pocket near \( U/W = 0 \) the anomalous self-energy has a BCS-like exponential dependence on \( \lambda \) and indeed superconductivity in this corner is BCS. Superconductivity in the rightmost pocket near the metal insulator transition behaves quite differently. Here the \( \lambda \) dependence of superconductivity is much weaker, and the superconducting gap much stronger, than in the BCS pocket. Superconductivity in this pocket can in fact be characterized as SCS (Capone et al. 2002), due to narrow quasiparticle pairing as described above. A similar behavior to Fig. 5, with two separate BCS and SCS regimes emerging from a single initial one when the effective pairing attraction is progressively weakened by exchange, was derived and illustrated in a simpler twofold degenerate model in Capone et al. (2004).

The SCS superconducting pocket near the Mott transition is expected to differ from the BCS pocket even in its normal state properties. The normal state underlying a BCS superconductor is Fermi-liquid-like. On the other hand, previous analysis suggest that the Fermi-liquid picture is likely to break down in our model when the Mott transition is approached. The key reason for the breakdown of the Fermi-liquid is precisely that, when
$Z \to 0$, the attraction between quasiparticles must eventually reach and exceed in magnitude the quasiparticle bandwidth $ZW$, a situation difficult to sustain.\(^3\) Possible deviations from the Fermi-liquid paradigm were in fact overlooked in Ref. (Capone et al. 2002) as they are related to the very-low energy behavior of the normal phase close to the Mott transition, not explored in that work. Later, the non-Fermi-liquid behavior was discovered in the two-orbital model where the physics is very similar (Capone et al., 2004).

A. Anderson Impurity With a Rigid Bath

The DMFT calculations described above involved two steps, one solving the Anderson impurity model (AIM), the other making that selfconsistent with the bath. Following a reasoning proposed by Fabrizio et al. (2003), one may start off with the first step alone, namely analyzing the bare AIM without imposing any self-consistency constraint. The conduction bath can be assumed to have a flat density of states, and the bath-impurity hybridization to be structureless, a situation which avoids numerical uncertainties and yields accurate low-energy properties. This kind of analysis applied to the AIM shows (De Leo and Fabrizio, 2005) that two different impurity phases are stabilized according to the ratio between the attraction $J$, and the Kondo temperature $T_K$ (Hewson, 1997). Below this temperature and when $J = 0$, the spin of an impurity coupled to a Fermi sea is screened out and absorbed in the conduction sea (Hewson, 1997). In the lattice context within DMFT, the Kondo scale measures metallic coherence and corresponds to the renormalized quasiparticle bandwidth $ZW$. For finite $J \neq 0$ but smaller than $T_K$, Kondo screening remains, thus still implying a Fermi-liquid behavior in DMFT. In fullerides, the impurity represents the $C_{60}^-$ ion, carrying three orbitals and three spins. In the Kondo phase each of the three spins is separately screened by the bath and thus incorporated in the Fermi sea. Conversely, when $J > T_K$ the Kondo screening is lost, and that was shown to imply a non Fermi-liquid phase characterized by a pseudogap in the single-particle spectrum and by several other singular properties (De Leo and Fabrizio, 2005). A very qualitative description of this phase is that, unlike the Kondo phase, two spins out of three pair off antiferromagnetically at any given time, leaving out a single spin 1/2 available for Kondo screening. However, since orbital degeneracy is unbroken, this residual spin $S = 1/2$ also carries orbital momentum $L = 1$, which corresponds to an overscreened non-Fermi liquid situation (De Leo and Fabrizio, 2007). In this regime, it was predicted that the impurity contributions to the specific-heat coefficient and to the pair susceptibility in the s-wave channel diverge as $T^{-1/5}$ at low temperature $T$. In addition, the conduction electron scattering rate has a non-analytic temperature-behavior $T^{2/5}$. The local response functions to either a quadrupolar field, which splits the orbital degeneracy, or to a magnetic field which polarizes both spins and orbitals also diverge as $T^{-1/5}$. The two phases, the Kondo screened phase and the pseudogap phase, are separated by a critical point at $J = J_{cp} \simeq T_K$. It is endowed with a finite entropy $1/2 \ln 3$, and with a divergent superconducting susceptibility with an exponent $1/3$. As shown in Fig. 6 the single-particle spectral function displays strong deviations from a normal metal in the pseudogap phase and at the critical point.

Near this critical point it has been found that the low-energy dynamics around the impurity is controlled by two separate energy scales (De Leo and Fabrizio, 2005), $T_+$ and $T_-$, whose behavior is very different as a function of increasing $U/W$. A higher energy scale $T_+$ is set by the critical $J_{cp} \sim T_K$ and represents the width of a broad incoherent resonance; it evolves smoothly and uneventfully as the critical point is crossed (See Fig. 6). A lower energy scale $T_- \propto |J - T_K|^3$ measures instead the distance from the critical point, and leads simultaneously to

\(^3\) Note that the high-energy Hubbard bands are unaffected by the small attraction $J$; superconductivity is just a matter of quasiparticles (Capone et al. 2002). Therefore, a quasiparticle attraction exceeding their bandwidth cannot correspond to an instability towards a Mott insulator, which must involve also the Hubbard bands, but at most towards a breakdown of a quasiparticle-based Fermi liquid.
a narrow resonance in the Fermi-liquid region, and to an equally narrow spectral density dip (the “pseudogap”) in the pseudogap phase \cite{De Leo and Fabrizio, 2005}. Since in this phase the impurity still carries a residual spin-1/2, there remains a finite value of the spectral function at the chemical potential, and the gap is not complete. The pseudogap widens if $J$ is increased, and the cusp-like dip in the impurity spectral function smoothly turns into a cusp-like peak, the value at the chemical potential staying fixed and constant. This behavior is shown by the dotted curve in Fig. 6 corresponding to a very large pseudogap (see top inset), possessing a very tiny peak at the chemical potential. This indicates the existence of yet another energy scale besides $T_+$ and $T_-$ that sets the width of the cusp peak.

B. Anderson Impurity with a Self-Consistent Bath in DMFT

The rigid bath AIM behavior and its critical point briefly reviewed above provide a guide to the DMFT results once the impurity-bath coupling is self-consistently determined. First of all, since $T_K$ coincides within DMFT with the renormalized $ZW$ which in turn vanishes when the continuous Mott transition is approached, the impurity critical point is inevitably met before the metal insulator transition as $U/W$ is increased, at some $U_{cp} \lesssim U_c$. This entails several important consequences:

- The normal state may be a Fermi liquid only far below the continuous metal insulator transition, such as perhaps may be the case in the non-expanded fullerenes. Expanded compounds on the other hand are expected to have a non Fermi-liquid normal state, and eventually a pseudogap, possibly developing before the first order transition to the antiferromagnetic insulator.

- The SCS superconducting pocket near the Mott transition reflects the leading instability of the impurity critical point. In other words SCS superconductivity is the way in which the lattice model responds to impurity criticality and avoids it.

- The lower energy scale vanishes right at the critical point, $T_- = 0$. Here $T_+ \simeq J$ thus remains as the only energy scale controlling the magnitude of the superconducting energy gap. Away from $U = U_{cp}$, $T_- \neq 0$, and the amplitude of the superconducting gap should decrease monotonically with $(T_+ - T_-)/T_+$ \cite{Capone et al, 2004}, since $T_-$ cut-offs the local pairing instability. Therefore the gap should be maximum right at the impurity critical point (the top of the dome).

- Even though the normal phase is non-Fermi liquid, well defined Bogoliubov quasiparticles should exist inside the SCS superconducting pocket.

The last statement comes from the fact that, at the impurity critical point, superconductivity provides a new screening channel which helps the system get rid of the finite residual entropy at the critical point, thus eliminating non-Fermi liquid singularities \cite{De Leo and Fabrizio, 2005; Schirò et al, 2008}. The role of superconductivity as a novel screening channel close to the impurity model critical point should reflect, in the lattice model, into a gain of band energy (the tight binding “kinetic energy”) at the onset of superconductivity. Owing to a sum rule connecting kinetic energy and zero-frequency optical conductivity (sometimes referred to as “Drude weight”) \cite{Scalapino et al, 1993} the onset of SCS superconductivity close to the Mott transition should lead to a Drude weight increase. This prediction is well borne out by the full DMFT solution of our Hamiltonian. In Fig. 7 we plot the $\omega = 0$ (d.c.) optical conductivity of our model superconductor (where it coincides with the superfluid stiffness), defined by \cite{Toschi et al, 2005}

\begin{equation}
D_s = -E_{kin} + \chi_{jj}(q \rightarrow 0, \Omega = 0),
\end{equation}

where $E_{kin}$ is the kinetic energy and $\chi_{jj}$ the static limit of the paramagnetic part of the electromagnetic kernel

\begin{equation}
\chi_{jj} = \frac{2}{\beta} \sum_n \int d\epsilon N(\epsilon) V(\epsilon) \times [G(\epsilon, \omega_n)G^*(\epsilon, \omega_n) + F(\epsilon, \omega_n)F(\epsilon, \omega_n)],
\end{equation}

where $V(\epsilon) = (4t^2 - \epsilon^2)/3$ is the current vertex in the Bethe lattice, while $G(\epsilon, \omega_n)$ and $F(\epsilon, \omega_n)$ are the normal and anomalous lattice Green functions, respectively. In the same figure we also plot the zero-frequency d.c. conductivity (the Drude weight) of the underlying metastable solution where superconductivity is inhibited.
FIG. 8 Energetic balance underlying superconductivity. \(\Delta E_{\text{pot}} = E_{\text{pot}}^S - E_{\text{pot}}^N\) is the difference between the potential energies of the superconducting and the normal solution, while \(\Delta E_{\text{kin}} = E_{\text{kin}}^S - E_{\text{kin}}^N\) is the same difference between the kinetic energies of the two solutions.

this state meant to provide a cartoon of the real normal phase above \(T_c\). The Drude weight is given by Eq. \((16)\) and \((17)\) with \(F(\epsilon, \omega_n) = 0\). Upon entering the SCS dome from the low \(U/W\) side, the superconducting phase initially loses kinetic energy over the normal state as in ordinary BCS theory. However, upon increasing \(U/W\) at and beyond the dome maximum, the loss reverts over to a gain, and indeed most of the SCS superconducting pocket is predicted to have a larger weight of the zero-frequency optical absorption than the non superconducting state. The same behavior is displayed (Fig. 8) by the energetic balance between the two solutions. Only far below the Mott transition the superconductor is stabilized by a potential energy gain, as is the case in BCS theory. In the pseudogap regime, corresponding to the expanded fullerides near the Mott transition, the stabilization is associated with a kinetic energy gain.

A similar phenomenon is well known in the optical conductivity of high-\(T_c\) copper oxides (Carbone et al., 2006). Our calculations show that an increase in the zero-frequency optical conductivity or a kinetic energy gain do not actually exclude an electron-phonon pairing mechanism, but rather demonstrates the key importance of strong electronic correlations. Thanks to pairing, the motion of carriers in the superconducting phase is facilitated with respect to the pseudogap nonsuperconducting metal. In that anomalous metal – a non Fermi liquid – the interaction constraints jam the free propagation of quasiparticles, causing a kinetic energy cost, partly released with the onset of superconductivity. It would be of extreme interest if the optical conductivity increase demonstrated in cuprates could be investigated in fullerides, both regular and expanded, since that would help discriminate between conventional BCS and SCS.

V. DISCUSSION OF EXPERIMENTAL PROBES

In the following we discuss whether and how the dominance of strong correlation we propose for the superconducting fullerides can be reconciled with the list of experimental facts given earlier, apparently supporting a conventional BCS behavior. The first quantity we discuss is the specific heat jump at \(T_c\). Within BCS theory, the specific heat jump \(\Delta C_V\) at \(T_c\) is approximately

\[
\frac{\Delta C_V}{T_c} \simeq 1.52 \gamma_*,
\]

where \(\gamma_*\) is the specific heat coefficient of the metallic phase \((C_V = \gamma_* T)\), proportional to the mass enhancement \(m^*/m\), in our case \(1/Z\). The measured specific heat jump leads, through \((18)\), to an estimate of \(\gamma_* \simeq 3\gamma_0\). This is indeed a rather low and regular value which has been commonly advocated as evidence of weak correlations in fullerides. However, the standard argument only holds provided the normal phase is Fermi-liquid, which is not applicable close to a Mott transition, independently of any models.

In Fig. 9 we plot the jump in \(C_V\) at \(T_c\) for increasing \(U/W\), compared with the Fermi-liquid estimate \(1/Z\). After a region where the calculated quantity closely follows \(1/Z\), \(\Delta C_V/T_c\) flattens out and stays roughly con-

FIG. 9 Specific heat jump, in units of \(T_c, \gamma_0\), as function of \(U/W\). For comparison we also show the behavior of \(1/Z(U)\), which should correspond to the same quantity if Fermi liquid theory were valid.

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4 As mentioned in Sec. III.A, for the present three-orbital model it has not been practical to include in Eq. \((3)\) a number of excited states sufficient to make the truncation error in the Green’s function negligible. For the data reported in Fig. we have an average error of 3-4% which does not allow us to determine \(T_c\) with sufficient accuracy. Yet, the jump of the specific heat relative to \(T_c\) turns out to be almost independent on the truncation error and on the details of the calculations.
constant around $4\gamma_0$ up to the Mott transition, despite a diverging $1/Z$ (See Fig. 9). This shows that the energy scale that controls the superconducting instability is constant near the Mott transition, consistent with the single-impurity prediction that this scale should be identified by $T_+$, a quantity of order $J$. The bottom line conclusion here is that a normally sized specific-heat jump does not imply BCS superconductivity in fullerides.

Another physical quantity which seemingly pointed towards weak correlations in fullerides is the magnetic susceptibility measured in the normal phase, apparently consistent with a weakly correlated a Fermi liquid and a Stoner enhancement of about a factor 2 to 3. This argument again becomes inconclusive once the Fermi-liquid scenario is abandoned. In Fig. 10 we plot as function of $U/W$ the uniform magnetic susceptibility in the normal phase calculated by DMFT. After an initial Stoner enhancement of about a factor 2 to 3, the susceptibility flattens out and remains almost constant before a rapid growth which takes places extremely close to the Mott transition. In the plateau region the susceptibility enhancement of a factor between 2 and 3 with respect to $U = 0$, surprisingly close to the experimental enhancement, covering the whole superconducting domain. Physically, the origin of this susceptibility plateau for increasing $U$ is quite instructive. It corresponds to the gradual crossover of the maximum spin available at each site from $S=3/2$ in the Fermi liquid to $S=1/2$ near Mott and large $U > U_{cp}$, where Fermi liquid behavior is lost. In essence, at large $U$ each molecule is effectively in a (dynamically) JT distorted state, where two out of three electrons are spin paired (Auerbach et al., 1994). We are thus led to conclude that the relatively weak observed enhancement of susceptibility does not correspond at all to a Stoner enhanced, weakly correlated Fermi liquid – in fact quasiparticles do not even exist in most of the plateau region.

Finally, we wish to address signatures of the strongly correlated scenario which we expect should show up in important spectroscopies including the tunneling I-V characteristics and angle resolved photoemission spectroscopy (ARPES). This is initially embarrassing on two accounts. First, ARPES spectroscopies are k-vector resolved, whereas in DMFT we do not have access to any spatial structure. Second, tunneling spectroscopies are extremely well resolved near zero voltage, whereas our Lanczos method yields a much poorer spectral function resolution in this region.

Let us addressing tunneling first. Although Fig. 10 refers to the impurity C$_{60}$ molecule, we believe that similar features would remain after full DMFT self-consistency in the normal phase – if we only had a better low-frequency numerical resolution than we presently have. Hence, we suggest that tunneling I-V spectra of expanded fullerides be measured and examined, in order to bring out the expected rich structure of the kind sketched in Fig. 9.

Next, let us consider photoelectron spectroscopy. Again according to the single-impurity analysis (De Leo and Fabrizio, 2003), the imaginary part of the single-particle self-energy should be finite and of order $T_+$ almost everywhere in the non-Fermi liquid normal phase above $T_c$. This has the following implications for ARPES:

- the fulleride photoemission spectrum should show $t_{1u}$ bands dispersing in the Brillouin zone with nonzero bandwidth, governed by the energy scale $T_+$. The value of $T_+$ decreases with increasing $U/W$ (increasing expansion), from $W$ at $U = 0$ to (larger than) $J$ at the Mott transition;

- there should be a spectral peak broadening of the same order of magnitude $T_+$ as the apparent k-resolved band dispersion. In particular the broadening should remain constant approaching the Fermi surface – unlike a Fermi liquid phase where quasi-particle peaks become narrower and narrower.

The momentum-independence of the DMFT self-energy implies that, in this approximation, the k-modulation of the electronic dispersion is assumed to remain unaffected by interactions. Within this assumption and without requiring too high frequency-accuracy, we can compute a toy k-resolved spectral function according to

$$A(k,\omega) = -\frac{1}{\pi} \text{Im} \frac{1}{\omega - \varepsilon_k - \Sigma_{DMFT}(\omega)},$$ (19)

where $\varepsilon_k$ is the non interacting dispersion and $\Sigma_{DMFT}(\omega)$ is the DMFT self-energy calculated with a finite number of baths. The effect of the local self-energy will be to change the effective bandwidth and to give rise to finite lifetime effects, even if the k-modulation of the dispersion is unrenormalized. For our Bethe lattice,
there is no straightforward definition of momentum, and
we remedy that by computing \( A(\varepsilon,\omega) \), which corresponds
to Eq. \((19)\) with \( \varepsilon_k \to \varepsilon \).

In Fig. 11 we show theoretical ARPES results for some choices of \( \varepsilon \) obtained by using the DMFT self-energy for temperatures above \( T_c \), both for a value of \( U/W = 1.1 \) which lies close to the maximum of the superconducting dome, but still on the less correlated side, corresponding to unexpanded (or moderately expanded) fullerides, and for a value which lies in the downward branch of the dome (\( U/W = 1.3 \)), corresponding to a very expanded fulleride. We note in both cases the existence of an incoherent low-energy feature dispersing with a reduced but nonzero electron bandwidth of 0.1 \( W \). In the expanded case the pseudogap feature is clearly present.

Recent photoemission spectra of \( K_3C_{60} \) (Goldoni, 2007) indicate an overall dispersion bandwidth of about 160 meV, about a quarter of the bare calculated bandwidth in the local-density approximation. The experimental spectral peak does not show the usual Fermi-liquid-like narrowing on approaching the Fermi level, a fact which is in agreement with our expectation for a non Fermi liquid (although a non expanded fulleride like \( K_3C_{60} \) probably lies at the beginning of the SCS dome, where deviations from Fermi liquid are not massive). Experimentally the peak does not appear to cross the Fermi level, and the intensity instead drops, suggestive of a pseudogap. Unfortunately the spectrum shows very strong vibronic effects, reflecting the retarded strong electron Jahn-Teller coupling. This aspect is not covered by our unretarded approximation, but it heavily affects the line shape and hampers the extraction of purely electronic features. Treatment of the vibronic effects, and a quantitative description of dispersion, will require abandoning in the future our approximation of infinitely fast phonon dynamics, as well as a possible extension to cluster extensions of DMFT which allow for different renormalizations of different momenta (Hettler et al., 2000).

VI. CONCLUSIONS

Summarizing, we addressed the apparently contradictory properties of expanded trivalent fullerides superconductors and insulators – and to some extent of the whole family of fullerides – and presented a theoretical scenario emphasizing the role of strong electron correlations. That is especially designed and appropriate for the more expanded members of the family, such as (NH\(_3\))\(_2\)NaK\(_2C_{60}\), Li\(_3\)C\(_{60}\), Cs\(_3\)−\(\frac{1}{2}\)K\(_2C_{60}\) and Cs\(_3\)−\(\frac{1}{2}\)Rb\(_2C_{60}\), and the recently discovered A15 \( C_{83}C_{60} \) that are near or past the Mott transition.

Our model explains the dome-shaped increase and subsequent decrease of \( T_c \) upon expansion of the lattice spacing in fullerides; the coexistence of metallic behavior and of Mott insulator features such as the large NMR spin gap in all fullerides, and the \( S = 1/2 \) spin in the insulating state (identified as a Mott-Jahn-Teller insulator). It explains why the \( s \)-wave \( T_c \) can be as high as 40 K even though the Coulomb interaction strength is prohibitive, and why \( T_c \) does not automatically decrease upon increase of \( U/W \). It also accounts for more standard observations, such as regular specific heat jumps and moderately high spin susceptibilities, facts that were so far construed as evidence for conventional BCS superconductivity.

Besides those listed in the previous Section, one can anticipate a number of additional experiments that could provide “smoking gun” evidence for strongly correlated superconductivity in fullerides. The tunneling \( I-V \) characteristics observable, e.g., by a scanning tunneling spectroscopy tip should, in an expanded fulleride, develop the low energy features typical of the Kondo impurity spectral function. The isotope effect upon carbon substitution should also behave very unconventionally, and eventually get smaller as the superconducting dome is passed and the Mott transition is approached upon expansion. In this regime, as the quasiparticle bandwidth \( ZW \) gradually falls below the typical energy \( \hbar \omega \) of an increasing fraction of the eight \( H_j \) Jahn Teller modes, the associated retardation effect should in fact disappear. The expanded fullerides and related materials, clearly not enough investigated so far, deserve in our view the strongest experimental attention. They combine elements that make them members at large of the high temperature superconductor family. They combine neighborhood of the Mott transition and predominance of strong electron correlations, with conventional elements such as electron-phonon \( s \)-wave pairing, that are typical of BCS systems. Our study identifies a pseudogap and other features in the IV tunneling spectrum, an increase of zero-frequency optical weight in the optical response of the superconducting phase, and the emergence of two separate energy scales in ARPES as the most urgent experimental undertakings that could confirm of falsify our claims.
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