Superconductivity in molecular solids with Jahn-Teller phonons

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We analyze fulleride superconductivity at experimental doping levels, treating the electron-electron and electron-phonon interactions on an equal footing, and establish the existence of novel physics which helps explain the unusually high superconducting transition temperatures in these systems. The Jahn-Teller phonons create a local (intramolecular) pairing that is surprisingly resistant to the Coulomb repulsion, despite the weakness of retardation in these low-bandwidth systems. The requirement for coherence throughout the solid to establish superconductivity then yields a very strong doping dependence to $T_c$, one consistent with experiment and much stronger than expected from standard Eliashberg theory.

The discovery of superconductivity in alkali-doped $C_{60}$, persisting up to unexpectedly high temperatures ($T_c = 33$ K [2] or $T_c = 40$ K [3]), raises interesting questions about superconductivity in low-bandwidth molecular solids. Superconductivity arises from an effective attractive interaction between the electrons. In conventional superconductors a net attractive interaction survives, in spite of the strong Coulomb repulsion, thanks to retardation effects [3]. However, retardation is small for the fullerides [4,5], since the molecular vibration frequencies are comparable to the bare electron bandwidth. We show that the combination of molecular solid character and coupling to Jahn-Teller phonons produces a local pairing, important for superconductivity, which is not strongly suppressed by the Coulomb repulsion. In addition, the transition temperature depends anomalously strongly on the doping level. The superconducting mechanism in fullerides therefore differs in important ways from that of conventional superconductors.

Conventional superconductors are studied in the Migdal-Eliashberg theory, assuming a band width $W$ much larger than a typical phonon frequency $\omega_{ph}$. For the fullerides, $\omega_{ph} \sim W$, so the Eliashberg theory is of questionable accuracy. This failure of Eliashberg theory is typically thought to lower $T_c$ [2] (although the opposite has also been argued [6]). Metallic fullerides have very large, nonsaturating resistivities in the normal state [7], suggesting “bad metal” behavior [8] which is also expected to reduce $T_c$ [9]. However, we find that $T_c$ in the fullerides is not generally lower than expected from Eliashberg theory due to an unusual cancellation of countervailing effects. The violation of Eliashberg theory asserts itself explicitly in a very strong doping dependence of $T_c$.

In $A_3C_{60}$ (A = K, Rb), the three-fold degenerate $t_{1u}$ level is partly occupied and couples strongly to eight $H_g$ intramolecular Jahn-Teller phonons. We capture the essential physics using a model with one $t_{1u}$ level and one $H_g$ mode per molecule, with a dimensionless electron-phonon coupling strength $\lambda$. We also include the hopping between the molecules and the Coulomb repulsion $U$ between two electrons on the same molecule [10]. The model explicitly includes Jahn-Teller coupling and places no implicit restrictions on the ratio $\omega_{ph}/W$ or the value of $\lambda$. We refer to this model as the $T \times \hbar$ problem. To reveal the novel effects of Jahn-Teller character, we compare this model to a nondegenerate ($a$) or two-fold degenerate ($e$) level interacting with a non-Jahn-Teller $A_g$ or two-fold degenerate ($E_g$) phonon, i.e., $T \times a$, $E \times e$ and $A \times a$ problems, respectively. Typical parameters are $\lambda \sim 0.5 - 1$, $\omega_{ph}/W \sim 0.1 - 0.25$ and $U/W \sim 1.5 - 2.5$ [11].

We circumvent the limitations of Eliashberg theory by using the dynamical mean-field theory (DMFT) [12] with a non-perturbative Quantum Monte-Carlo (QMC) technique [13]. The electron self-energy is assumed to be $q$-independent, allowing a mapping of the lattice problem onto an effective impurity problem. We study superconductivity by applying a perturbation creating electron pairs and calculating the corresponding response function, i.e. the $q = 0$ pairing susceptibility $\chi$. A divergence of $\chi$ below a temperature $T_c$ signals the onset of superconductivity [14]. We write

$$\chi = (1 - \chi_0 \Gamma)^{-1} \chi_0, \tag{1}$$

where $\chi_0$ is obtained from products of two fully dressed electron Green functions describing the propagation of two electrons (holes), which do not interact with each other. Eqn. (1) then defines the effective interaction $\Gamma$. We define a local (intramolecular) pairing susceptibility

$$\chi_{loc}^{\text{loc}}(\tau_1, \tau_2, \tau_3, \tau_4) =$$

$$= - \sum_{mn'm'} \langle c_{m_1}^{\dagger}(\tau_1)c_{m_2}^{\dagger}(\tau_2)c_{m'_3}(\tau_3)c_{m'_4}(\tau_4) \rangle, \tag{2}$$

where $\langle ... \rangle$ denotes a thermal average and $m$ labels the $t_{1u}$ levels on one molecule. Then

$$\chi_{loc} = (1 - \chi_0 \Gamma_{\text{loc}})^{-1} \chi_0 \Gamma_{\text{loc}}. \tag{3}$$

$\chi_{loc}$ and $\chi_{loc}^{\text{loc}}$ can be calculated within DMFT; this defines the local interaction $\Gamma_{\text{loc}}$. $\Gamma \approx \Gamma_{\text{loc}}$ should be a rather good approximation, since the interaction is dominated by intramolecular phonons and an intramolecular

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Coulomb repulsion. Since $\chi_0$ can be calculated within DMFT, $\chi$ follows from Eqn. (3).

Putting $\tau_1 = \tau_2$, $\tau_3 = \tau_4$ and taking the Fourier transform with respect to $\tau_1 - \tau_3$ in the $T \to 0$ limit, we obtain

$$\chi_{\text{loc}}(i\omega_n) = \int_0^\infty \rho_{\text{loc}}(\varepsilon)/(\varepsilon - i\omega_n), \quad (4)$$

where

$$\rho_{\text{loc}}(\varepsilon) = \sum_n \langle \langle n, N - 2 | \sum_m c_m \dagger c_m \downarrow | 0, N \rangle \rangle^2 \times \delta(\varepsilon - E_0(N) + E_n(N - 2)) + \ldots \quad (5)$$

Here $|n, N\rangle$ is the $n$th excited state of the system with $N$ electrons and the energy $E_n(N)$. The term shown describes the removal of an electron pair; "..." indicates the addition of an electron pair.

\[ \text{FIG. 1. The ratios } S/S_0 \text{ and } \chi/\chi_0 \text{ drop as a function of } U/W \text{ for } \lambda = 0.7. \text{ For the non-Jahn Teller model } A \times a, \text{ these ratios drop rapidly as } U \text{ increases. In contrast, the pairing susceptibility for } E \times e \text{ is very resistant to increasing } U. \text{ The results were obtained from exact diagonalization for an impurity model with five host sites.} \]

The new physics can be best understood by examining a sum rule for the spectral function $\rho_{\text{loc}}(\varepsilon)$. In the simplest Jahn-Teller case, $E \times e$,

$$\int_0^\infty \rho_{\text{loc}}(\varepsilon)d\varepsilon \equiv S = 4, \quad (6)$$

for a half-filled band and in the limit of very large $U$ and very small $\lambda$. In this limit the Jahn-Teller phonons produce local singlets on the molecules,

$$\frac{1}{\sqrt{2}} \sum_m c_{m \uparrow} c_{m \downarrow} \downarrow | vac \rangle, \quad (7)$$

with pairing via the molecular quantum number $m$. Although the Jahn-Teller effect competes with intermolecular hopping, a large $U$ reduces hopping, so that singlets form even for small $\lambda$. In contrast, for $\rho_{0\text{loc}}(\varepsilon)$ the corresponding sum rule gives only $S_0 = 1$. Since $\chi_{\text{loc}}$ tends to be larger than $\chi_0^\text{loc}$, the effective interaction $\Gamma_{\text{loc}}$ (Eq. (3)) tends to be attractive. The existence of local singlets (Eq. (5)) means that the probability for removing or adding two electrons with the same $m$ quantum number is very high. In contrast, for $\chi_0$ the electrons’ $m$-quantum numbers are independent and $\chi_0^\text{loc}$ tends to be smaller.

As $U$ increases, spectral weight is shifted upwards in energy, which tends to decrease $\chi_{\text{loc}}$. However, this is partly compensated by an increase of the integrated spectral weight $S$, since the Jahn-Teller effect wins when hopping is reduced (see in Fig. 1 [16]). Increasing $U$ therefore does not rapidly eliminate a negative $\Gamma_{\text{loc}}$, as one might have expected. In contrast, for the $A \times a$ model the Coulomb repulsion $U$ and the electron-phonon coupling directly compete, so $S$ (and therefore $\Gamma_{\text{loc}}$) drops quickly as $U$ is increased. These results illustrate one important aspect of molecular solids with Jahn-Teller phonons: counter-intuitively, Coulomb interactions can in certain respects actually help electron-phonon coupling. Capone et al. [7] have reached similar conclusions for $A_4C_{60}$ using a different approach.

Another important aspect is screening. The Coulomb interaction is well-screened by the transfer of electrons between the molecules [18,19]. Although this helps superconductivity, it also normally implies an equally effective screening of the electron-phonon interaction itself. However, since the $H_g$ phonons do not shift the center of gravity of the electronic levels, they cannot be efficiently screened by charge transfer on and off the molecule [18,19].

Both these effects are missing for $A_g$ phonons. $A_g$ phonons furthermore tend to cause instabilities when coupled to a degenerate level. Within a semiclassical approximation, a molecular solid with $U = 0$ becomes unstable when $\lambda \gtrsim 1/(2N)$, where $N$ is the orbital degeneracy. A QMC calculation for a $T \times a$ model supports this result, whereas in the $T \times h$ case the system stays metallic for $\lambda \lesssim 1$ (and $U = 0$). To be able to use a reasonably large $\lambda$, we therefore study the $A \times a$ system below.

Although it is now clear that Jahn-Teller phonons can cause local pairing, as described by $\chi_{\text{loc}}/\chi_0^\text{loc}$ and $\Gamma_{\text{loc}}$, superconductivity requires the formation of a coherent state through the solid. With a finite coherent metallic weight at the chemical potential and an attractive interaction $\Gamma$, the divergent unperturbed uniform pair propagator $\chi_0$ mediates a pairing instability towards forming the coherent superconducting state.
To obtain explicit results for the superconducting transition, we use DMFT calculations solving the effective impurity problem using QMC [20,21]. We first discuss the case $U = 0$. Fig. 2 shows $T_c$ as a function of $\lambda$ according to Migdal-Eliashberg (dashed line) and DMFT theories for the $T \times h$ (○) and $A \times a$ (∙) couplings at half-filling. The parameters are $\omega_{ph}/W = 0.25$ and $U = 0$. The $T \times h$ results for $U = W$ (●) are also shown.

We next discuss finite $U$, connecting to Fig. 1. The solid points of Fig. 2 show the overall reduction in $T_c$ for finite $U$. Fig. 3 shows $T_c$ as a function of $U$ for the $T \times h$ and $A \times a$ models. For $A \times a$, $T_c$ drops quickly when $U$ increases, as expected. However for $T \times h$, $T_c$ is more resistant to increasing $U$ [27]. This is consistent with the local pairing of Fig. 1 and illustrates the importance of treating explicitly the dynamic interplay between Jahn-Teller phonons and electrons in molecular systems with $W \sim \omega_{ph}$.

Experimentally, $T_c$ drops quickly in fullerides when the doping $n$ is reduced below three electrons per C$_{60}$ molecule [24]. This cannot be explained within Eliashberg theory: reducing $n$ from 3 induces a slight increase of the density of states at the Fermi energy [25], which should increase $\lambda$ and $T_c$. This has been taken as evidence for an electron-electron mechanism of superconductivity [30]. Fig. 4 shows the doping dependence of $T_c$ in DMFT. For small $U$, $T_c$ drops slowly until $n \sim 2$ or 4 and then starts dropping much faster: $\Gamma^{loc}$ drops rapidly here, probably because local pairing is inefficient once the average number of electrons per molecule drops below two. For $U/W > 0.4$, $T_c$ drops more quickly as $n = 2$ is approached. The system can gain a particular large Jahn-Teller energy at $n = 2$ [1,2]; this moves the system towards a metal-insulator transition and shifts spectral weight in the one-electron Green’s function away...
from the chemical potential \[\mu\]. The shift in spectral weight rapidly reduces \(\chi_0\) and therefore \(T_c\). Thus the strong doping dependence can be explained within an electron-phonon mechanism, and there is no need to assume an electronic mechanism.

For conventional superconductors, retardation is important in reducing the effects of the strong Coulomb repulsion \[3\]. For the fullerides, the retardation effects are small, since \(W \sim \omega_{ph}\) \[4,5\]. Local pairing and screening are therefore crucial in reducing the effects of the Coulomb repulsion for the fullerides. An increasing Coulomb interaction does not much damage superconductivity, since the concomitant reduction in hopping favors the Jahn-Teller pairing. This leads to new physics in these strongly correlated low-bandwidth molecular solids.

The importance of local pairing is consistent with the short coherence length, which is only about three times the \(\text{C}_{60}\)-\(\text{C}_{60}\) separation \[8,29\].

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