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Effects of static screening on correlation-induced superconductivity in M_3C_{60}

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A recurrent theme among several recently proposed mechanisms for superconductivity in M_3C_{60} (M = alkali metal) suggests that electron pairs bind together because of a subtle intramolecular correlation effect. We have calculated the dependence of such a mechanism on the electron-electron interaction within the framework of perturbation theory. Using a static phenomenological model of screening, we determine the phase diagram for pair binding as a function of an on-site interaction U (in units of the intrafullerene hopping parameter t) and screening length. We find the binding energy to be very sensitive to the range of the interaction. When $U = 4t$, the screening length must be at most one-half of a double-bond length, or approximately 0.7 Å for pair binding to occur. This indicates that a reasonable incorporation of electron-electron correlation strongly suppresses the weak pair-binding effect found when such interactions are neglected.

C_{60} and higher fullerenes and their derivatives have recently been the subject of a flurry of experimental and theoretical work. Among a rapidly growing list of remarkable properties is that of superconductivity. When doped with certain alkali metals, the archetype fullerene C_{60} has been found to superconduct at temperatures as high as 30 K.[1]

In an effort to explain the mechanism responsible for superconductivity in this unusual system, one recurrent theme suggests that pairing of electrons arises from the purely repulsive electron interactions via a subtle intramolecular correlation effect. If superconductivity, which desiderates some effective attraction between electrons, is to ultimately be found at the electronic level, one may conjecture that upon doping with electrons it may be more favorable for electrons to separate unequally and pair off among the fullerenes. We say that pair binding occurs[2] when two noninteracting fullerenes with $n+1$ and $n-1$ electrons, respectively, have lower total energy than two n-electron fullerenes. If an isolated fullerene with n additional electrons has energy Φ_n, then the energy difference

$$E_{\text{pair}}^{(n)} = 2\Phi_n - \Phi_{n+1} - \Phi_{n-1} \tag{1}$$

is the pair-binding energy. A positive E_{pair} implies that pairing is favored and a net effective attraction between electrons exists.

In an intriguing set of articles, Chakravarty, Gelfand, and Kivelson[2] (CGK) found that pair binding may arise if the electron-electron interactions are treated perturbatively in an intramolecular repulsive Hubbard model where long-range interactions are absent. Correlation effects first appear in perturbation theory at second order where CKG found a crucial window in the energy scale where pair binding may arise. Once there is pair binding, one can explain superconductivity using, for example, a negative-U Hubbard model.[2–4] In a different approach, Murthy and Auerbach[3] also found an attractive interaction by treating the electrons as charged particles moving on the surface of a sphere. Their calculations were restricted by the degeneracies intrinsic to the spherical model but they did include electron-electron interactions that interpolated between an on-site delta function and a Coulombic $1/r$ dependence but conclusions from both of these collaborations are highly dependent on the coupling strengths of the interactions.

In this report we describe the dependence of this subtle pair-binding correlation effect in doped C_{60} on the electron-electron interaction. We specifically address the question of long-range interactions while working with the full C_{60} lattice and appropriate electron fillings. For the purposes of this paper we take long range to mean any electron correlation beyond the on-site Hubbard repulsion. We use a phenomenological model for the electron-electron interaction without specific regard to the source of Coulomb screening and work within the framework of perturbation theory. Our work and notation closely follows that of Chakravarty, Gelfand, and Kivelson[2] for ease of putting our results in a specific context. We do not consider higher fullerenes, electron-phonon mechanisms, or aspects of the Jahn-Teller effect.

The undoped fullerite structure is an fcc lattice of C_{60} molecules.[5] We focus on the electronic states of a single molecule spread into bands by weak intermolecular forces, a picture supported by band-structure calculations.[6] The effects of the core and sigma electrons are negligible for our purposes and hence we ignore them. The valence band of 60 π-like electrons is separated by about 1 eV from a band formed from a triply-degenerate set of t_{1u} states. As alkali metals are doped into the lattice, M_xC_{60} (M = K, Rb, Cs, Tl), the lattice is left largely intact and the alkalies easily give up their electrons to the fullerenes. It is these lowest unoccupied molecular orbital t_{1u} states that electrons from the alkalies occupy and we direct our attention toward them. This band in turn is separated above by ~ 0.5 eV from a band of three t_{1g} states[6,7] which will not play a significant role in our analysis. At $x = 3$, the fullerides are found to superconduct.[1]

To model the electronic states of a single fullerene we use the extended Hubbard Hamiltonian

$$H = -\sum_{i,j,\alpha} t_{ij} c_{i\alpha}^{\dagger} c_{j\alpha} + \frac{1}{2}\sum_{i,j} V_{ij} n_i n_j - \frac{U}{2}\sum_{i} n_i \,. \tag{2}$$

The sums are over all independent sites i, j and $V_{ii} = U$ is independent of site i. The hopping matrix element t_{ij} is chosen to be t for all nearest-neighbor single bonds (two adjacent carbon on a pentagon), t' for all double bonds (those bonds that connect the pentagons), and zero otherwise. The fermion operators $c_{i\alpha}^{\dagger}, c_{i\alpha}$ create and destroy electrons of spin $\alpha = \uparrow, \downarrow$ at one of the 60 carbon sites i and $n_i = \sum_\alpha c_{i\alpha}^{\dagger} c_{i\alpha}$ is the number operator at site i. Manousakis[8] has found $t \approx 2.50$ eV which corroborates estimates taken from the conjugated polyacetylene system.[4,9]

The electron-electron potential V_{ij} is the crux of our concern. A Coulombic e^2/r appropriate for bare electrons modified for a finite on-site integral would lead to the Ohno potential[10]

$$V_{ij} = \frac{U}{\sqrt{1 + (r_{ij}/\lambda)^2}} \,, \tag{3}$$

where r_{ij} is the distance between site i and j. This potential interpolates between an on-site ionization energy U, the effective electron repulsion integral between two electrons on the same site, and the Coulombic dependence at large distances. This may be appropriate for an insulating state with little or no electron screening or for the undoped or lightly doped fulleride and has been used for conjugated polymers.[10] However, the doped fulleride M_3C_{60} is a metal and in a metallic environment there will be electron screening which reduces the importance of long-range interactions. The strongly interacting electrons are renormalized to more weakly interacting quasiparticles. We shall consider static phenomenological potentials in order to incorporate these screening effects without particular concern for their precise origin. The extreme case, the Hubbard interaction, assumes the interaction between two electrons is zero except when both electrons are on site: $V_{ij} = U\delta_{i,j}$. This is the potential used by CGK and we use it as a check on our results and a reference point with which to compare other potentials. In the context of polyacetylene, $U \sim 5$–10 eV, and consequently, $U/t \sim 2$–4.[2,9]

The most naive approach to incorporate screening without resorting to the Hubbard model is an exponentially decaying dependence,

$$V_{ij} = U e^{-r_{ij}/\lambda} \,. \tag{4}$$

As $\lambda \rightarrow 0$, one regains the Hubbard model. Primarily out of its simplicity, we shall use this phenomenological potential to determine the binding energy as a function of the on-site integral U and the extent of the long-range interactions as measured by the Thomas-Fermi screening length λ. We consider this to be an overestimation of any power-law behavior found from a more precise treatment, e.g., Lindhard screening. Finally we note that our phenomenological potential (4) neglects any dynamical form of screening.

At zeroth order in perturbation theory, the noninteracting (Hückel) one-electron states are found by simple diagonalization of the hopping term of the Hamiltonian. For $t'/t = 1.2$,[2] we find 60 electronic levels per spin grouped according to the irreducible representations of the icosahedral group as described in earlier work.[2,11] Using these electron levels we find rough qualitative agreement between the location and separation of the bands with the results from full electronic calculations.[6] For an intramolecular bandwidth $\sim 6t \sim 20$ eV,[6] we estimate $t \sim 3.3$ eV, a somewhat larger value, hence smaller U/t, than that of polyacetylene. We use these single-particle eigenstates to build up the low-energy determinantal many-body states using the terminology of pseudoangular momentum.[2] For the neutral half-filled molecule, the ground state consists of occupying the lowest 60 energy states. Upon the addition of one electron to the t_{1u} band, there will be six $L = 1$ (pseudoangular momentum), $S = \frac{1}{2}$ degenerate states in the noninteracting system. The addition of a second electron introduces 15 degenerate states, which can be classified into three irreducible representations according to the addition of spin and the pseudoangular momentum: $L = 0$, $S = 0$ (one state); $L = 1$, $S = 1$ (nine states); and $L = 2$, $S = 0$ (five states). The full classification for the states from zero to six additional electrons has been described in CGK.[2] In general, the degeneracies between different representations for a given number of added electrons n are broken by the interaction.

To obtain ground-state energies through second order in perturbation theory, we diagonalize the operators[12]

$$A_n = H_{\text{int}} + H_{\text{int}} \frac{1 - P_0}{\Phi_n^{(0)} - H_0} H_{\text{int}} \tag{5}$$

in the space of degenerate states where $n = 0, 1, 2, ..., 6$. P_0 projects onto the degenerate noninteracting states. A ground-state energy (Φ_n) with a zero superscript is the noninteracting energy. Using Eq. (5) we calculated the energies for the seven electron fillings for the Hubbard model, the Ohno potential [Eq. (3) with $\lambda = 1.29$ Å (Ref. 10) and U an independent variable], and the exponentially screened potential [Eq. (4)] for the screening lengths $\lambda/l_2 = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, 1, \frac{3}{2}, 2$. Our Hubbard model results reproduce Table 2 of Ref. 2(c). For extended-range interactions, all carbon coordinates were determined as a function of the single- and double-bond lengths $l_1 = 1.45$ Å and $l_2 = 1.39$ Å, respectively.[13]

In order to calculate the binding energies we first determined the stable single-fullerene configurations. The neutral fullerene has one ground state and the singly-charged fullerene has a sixfold degeneracy unbroken by the interaction. For the doubly-, triply-, and quadruply-charged fullerenes, we find for small U/t the maximal spin state to have the lowest energy, consistent with Hund's rule. As U/t increases beyond the range 3.5–1.5 (a value that decreases as the distance of interaction λ increases), a crossover to a lower spin state occurs. The transitions are $L = 1$, $S = 1 \rightarrow L = 0$, $S = 0$; $L = 0$, $S = \frac{3}{2} \rightarrow L = 1$, $S = 1$; and $L = 1$, $S = 1 \rightarrow L = 0$, $S = 0$ for 2, 3, and 4 electrons, respectively. The $L = 2$ configurations are always excited states. We therefore find that increasing U violates Hund's rule. The six five-electron configurations are degenerate and the six-electron configuration is unique. We now use our single fullerene results to look for possible pair binding.

In first-order perturbation theory, charge will tend to separate equally between the two fullerenes in order to minimize the Hartree energies, and no pair binding is expected. In second order, if the correction to the binding energy is positive and higher-order corrections are small, $E_{\rm pair}$ becomes positive beyond a critical $U \equiv U_{\rm pair}$. In Fig. 1 we have plotted $E^3_{\rm pair}$ as a function of U/t for several of the screening lengths λ. Kinks in the curves are symmetry changes in the stable 2^-, 3^-, or 4^- configurations as described above. In all cases the second-order term is positive and, because higher-order terms have been neglected, there exists a $U_{\rm pair}$. We find that $U_{\rm pair}/t$ ranges from 3.432 for the Hubbard model to 12.75 for the Ohno potential (crossing is not shown). This figure demonstrates that $U_{\rm pair}$ is sensitive to the screening length and rapidly increases as longer-range interactions are introduced. From the crossings of the binding energies with $E_{\rm pair} = 0$ in Fig. 1 we plot $U_{\rm pair}/t$ as a function of λ in the phase diagram Fig. 2. This dependence of the critical pairing energy as a function of the screening length is the primary result of our work. From Figs. 1 and 2 we bring together several observations. First, the power-law behavior of the Ohno potential gives an extremely large $U_{\rm pair}$ (not plotted in Fig. 2). We consider such a large value unphysical and so concentrate on the exponential screening dependence. Second, we find that because $U_{\rm pair}/t$ is relatively large for all screening lengths, the pairing energy is always determined by the same single fullerene symmetry configurations, specifically $E^4_{\rm pair} = 2\Phi_3(L = 0, S = 0) - \Phi_4(L = 0, S = 0) - \Phi_2(L = 1, S = \frac{1}{2})$. Third, it appears that for any screening length, there will always be pair binding given a large enough U. This conclusion is of course constrained by corrections due to higher-order terms in the expansion and by what is considered a physically reasonable U/t value. From Fig. 2 we find that only above the value determined by the Hubbard model, $U_{\rm pair}/t = 3.432$, is there a possibility of pair binding. For $U/t = 5$, which is on the upper end of a physically reasonable range if parameters appropriate for polyacetylene are used, we do find pair binding. For a purely on-site interaction, the pairing energy is $0.114t$. This decreases as longer-range interactions are included and a maximum allowed screening length is approximately one double-bond length (1.39 Å). If the Coulomb force is screened any less than this, there will be no pair binding. At $U/t = 4$, there is also pair binding, but only for very short screening lengths. The pairing energy is at most $0.033t$ and decreases for longer-range correlation. For $\lambda > l_2/2$, $E_{\rm pair}$ is negative and there is no binding. This corresponds to a maximum screening length $\sim$ 0.7 Å. In terms of off-site energies, the nearest-neighbor repulsion would be $\sim$ 14% of the on-site value. These results show that long-range interactions significantly constrain the permissible parameter window for pair binding.

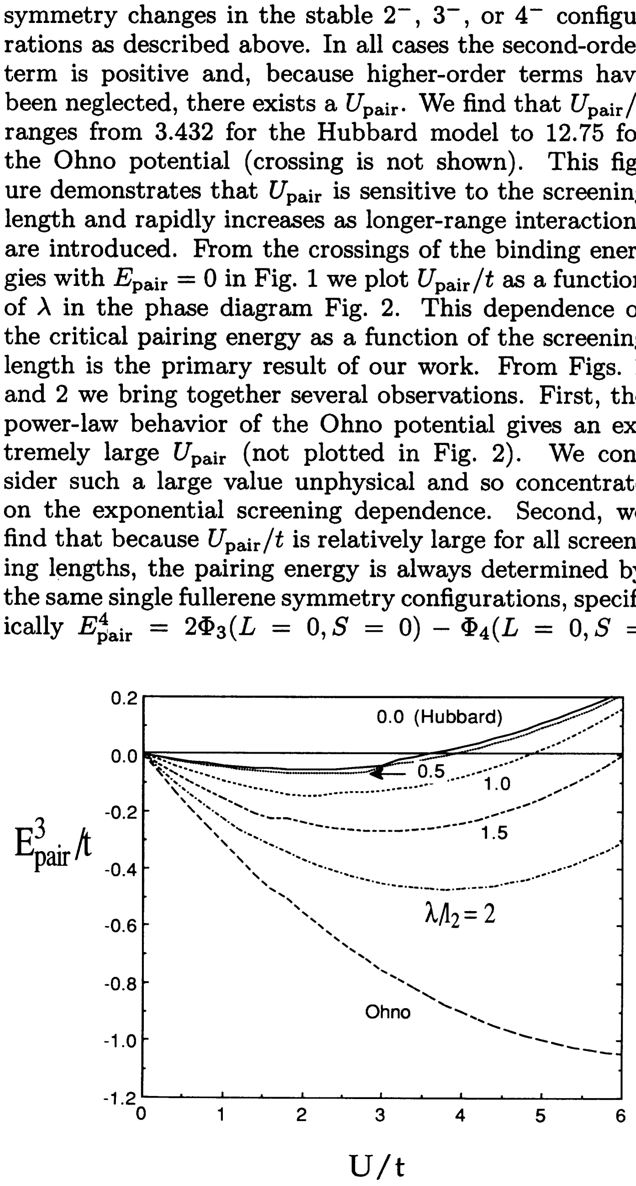

FIG. 1. Pairing energy as a function of U/t for different electron-electron interaction potentials. The screening-length λ is in units of the double-bond length l_2. A positive pairing energy indicates pair binding.

To put these constraints in further perspective we briefly consider possible sources of static screening. At best, lattice effects can give a screening length that may be as short as a lattice constant. According to our results, this means that U/t must be at least $\sim 5t$ for pair binding to occur. On the other hand, because the fulleride is metallic in the normal state, one may argue that it is the valence electrons that play a dual role and provide a source for screening. From an elementary Thomas-Fermi criterion,[14] a screening length obtained by assuming a donation of three valence electrons per fullerene in an fcc lattice with lattice constant 14.24 Å (Ref. 5) is $\lambda = 0.91$ Å. Although shorter than a bond length, this result requires a large though plausible $U \gtrsim 4.2t$. However, a more proper self-consistent approach, by eliminating the dou-

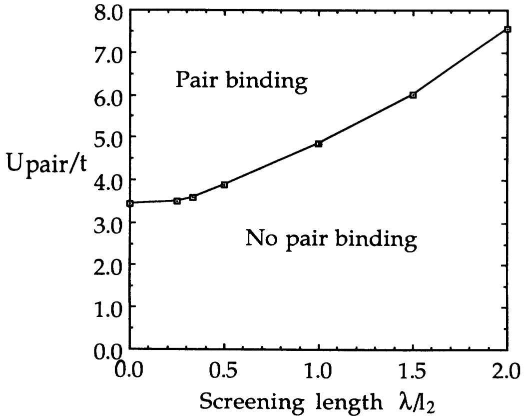

FIG. 2. The electron-electron interaction phase diagram for pair binding (4^-+2^-) and no pair binding (3^-+3^-) as determined by $E^3_{\rm pair} = 0$.

ble counting of the electrons, would likely increase this estimate significantly.

As a check on the validity of perturbation theory, Murthy and Auerbach have estimated contributions from third-order terms.[3] We have attempted to use their result to estimate a range of validity for our results by recalculating the data in Figs. 1 and 2 and $E^{(1)}_{\text{pair}}$ for the case of a singlet state. From their Fig. 4, third-order terms become significant at less than one-half the value where the singlet state shows pair binding in second order. For the *shorter* screening lengths considered in our model we find U_{pair}/t around 3.5–4.0 for the singlet state, meaning second-order perturbation theory should be good when $U/t \ll 2$, a value significantly less than the Hubbard minimum. This estimate, if valid and tied with our results for the screening restrictions at appropriate fillings, virtually closes the window of parameter ranges that could possibly lead to pair binding.

In summary, we have calculated the dependence of a proposed pair-binding mechanism in M_3C_{60} using a phenomenological screened electron-electron interaction. Assuming a conservative exponentially screened electron-electron interaction, we have found that the binding energy is extremely sensitive to the range of the interaction. In particular, for on-site repulsive Hubbard U on the order of $4t$, the screening length due to the valence electrons must be at most one-half of a double-bond length, or approximately 0.7 Å. Such a short screening length seems physically implausible for the fullerene system. Consequently our results indicate that a reasonable incorporation of electron-electron correlation strongly suppresses the weak pair-binding effect found when such interactions are neglected.

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