Metallic screening and correlation effects in superconducting fullerenes

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Abstract

We consider the frequency dependent Coulomb interaction between electrons in a molecular metal in the limit in which the conduction bandwidth is much less than the plasma frequency, which in turn is much less than intramolecular excitation energies. In particular, we compute the effective interactions at the Fermi energy in alkali-doped C_{60}, to second order in the screened interactions. The frequency dependence of the screening substantially reduces the effects of the long-range part of the Coulomb interaction,
leading to the possibility of an effective attraction between electrons.
The alkali- and alkaline-earth-doped fullerenes [1] are molecular solids, characterized by strong intramolecular electron-phonon and electron-electron interactions, but weak intermolecular hybridization. They can exhibit metallic, magnetic, insulating, or superconducting behavior; the $A_3C_{60}$ compounds are superconductors with transition temperatures as high as 33 K.

Electrons at the Fermi energy are strongly coupled to intramolecular phonons, especially the high frequency tangential modes with energy $\hbar\omega_c \approx 200$ meV. A variety of microscopic calculations [2,3] yield estimates of the BCS effective attraction produced by these intramolecular modes of roughly 75 meV-C$_{60}$. Since the bands at the Fermi energy are narrow (bandwidth $W \approx 200$ meV), the electronic density of states at $E_F$ is correspondingly large: $N(E_F) \approx 15/\text{eV-spin-C}_{60}$. The dimensionless electron-phonon coupling constant $\lambda \equiv N(E_F)V_{\text{BCS}}$ is then of order unity. The implications of this coupling are unclear, however, since the electronic bandwidth and characteristic phonon energies are comparable, preventing the straightforward application of the Born-Oppenheimer/Migdal-Eliashberg approximation.

Electron-electron interactions are also important in the doped fullerenes: the typical intramolecular Coulomb energy is $e^2/\epsilon_\infty R_b \approx 2$ eV, where $R_b = 3.5\text{Å}$ is the fullerene radius. The importance of Coulomb scattering in the doped fullerenes was emphasized by Chakravarty et al., [3] who calculated the effective interaction at the Fermi energy [1] using an on-site Hubbard repulsion $U$ to model the screened Coulomb interaction. Although the bare Hubbard interaction is repulsive, Chakravarty et al. found that for moderate $U$ both second order perturbation theory [3] and exact diagonalization studies of small fullerene analogs [4] exhibit an effective interaction at the Fermi energy which is anomalously small or even negative (indicating an effective attraction). The possibility of an effective attraction suggests an electronic pairing mechanism due to intramolecular correlation effects. Much of the phenomenology of fullerenes can be understood in the context of such correlation effects. [3,5]

How do longer-range Coulomb interactions affect these considerations? Goff and Phillips
have shown, also using second order perturbation theory, that moderate-range (e.g., several bond-lengths) bare interactions lead to effective interactions at the Fermi energy that are substantially more repulsive. They argue that an electronic mechanism is thereby ruled out. Similar arguments have been made by Auerbach and Murthy. Such arguments misrepresent the complexity of the electron-electron interactions in the fullerenes, since such a strong effective repulsion would overwhelm the phonon mechanism as well! (There can only be a limited renormalization of the electronic repulsion since the phonon frequencies are comparable to the conduction bandwidth. [9])

While these calculations raise the important issue of long-range Coulomb effects, the extended Hubbard models of refs. and omit the crucial effects of metallic screening. In this note we consider a simple, physical model for this frequency dependent screening, and study its effect on the energetics of pairing. Our model relies on the separation of energy scales corresponding to intermolecular hopping ($W$), metallic screening ($\hbar \omega_p$), and intramolecular hopping ($W_\pi$), as shown schematically in fig. and discussed in detail below. Although correlation effects cannot be computed exactly, they can be studied in a controlled manner using second-order perturbation theory. This permits a comparison with the perturbative calculations of refs. , , and .

We find that a long-ranged but frequency dependent screened interaction strikingly reproduces the results obtained from the Hubbard model. Frequency dependence is a crucial ingredient in this somewhat surprising result, which can be understood heuristically as follows: The direct repulsive interaction of electrons at the Fermi energy (see fig. a) occurs at a frequency below the plasma frequency, and is therefore heavily screened. The higher-order corrections (which can be attractive in second order, fig. b-e), however, involve excitations above the plasma energy, and are therefore unscreened. The weakening of the first order repulsion relative to the second order attraction explains the physics of our results. Similar considerations may also apply to cluster compounds known as Chevrels, although these superconductors are not as strongly molecular as the doped fullerenes.

**Frequency dependent screening.** In alkali-doped $C_{60}$, the bands at the Fermi energy
are derived from a set of three symmetry-related molecular orbitals. Due to their narrow bandwidth, electronic hopping between molecules is sluggish compared with the screening response of the surrounding metal: the bandwidth, $W \approx 0.2 \text{eV}$, is an order of magnitude smaller than the Drude plasma energy, $\hbar \omega_p \approx 1 - 1.5 \text{eV}$. Interactions within the conduction bands are therefore well screened. The intra-molecular virtual fluctuations to the rest of the $\pi$-complex, spread over $W_\pi \approx 15 \text{eV}$, however, occur too rapidly to be screened by the surrounding metal. The corresponding Coulomb matrix elements are therefore largely unscreened. (Intra-molecular plasmon-like excitations at 6 eV of the carbon $2p\pi$ orbitals will be explicitly taken into account below. Screening due to carbon $2p\sigma$ orbitals can be absorbed into a frequency independent dielectric constant because the characteristic energy for such excitations is larger than $W_\pi$.)

The separation of energy scales $W_\pi > \hbar \omega_p > W$ (see fig. [1]) suggests a simple model for the frequency-dependent screened Coulomb interaction. We treat the intra-band repulsion at the Fermi energy as fully screened, since the bandwidth $W$ is considerably smaller than the plasma energy $\hbar \omega_p$. Scattering matrix elements to states away from the Fermi energy, however, cannot be screened by the surrounding metal, since the plasma frequency is significantly smaller than typical intra-molecular excitation energies.

We therefore approximate the screened Coulomb interaction by its high and low frequency parts:

$$V(r, \omega) = \begin{cases} V_{lo}(r) & \text{if } \omega < \omega_p; \\ V_{hi}(r) & \text{if } \omega > \omega_p, \end{cases}$$

(1)

where $r$ is the distance between a pair of $\pi$ electrons on a given fullerene molecule.

The high frequency part of the effective Coulomb interaction is simply the unscreened Coulomb interaction:

$$V_{hi}(r) = \frac{e^2}{\epsilon r}.$$  \hfill (2)

The dielectric constant $\epsilon \approx 2$ is determined by the polarizeability of degrees of freedom which are omitted from our model, especially the carbon $2p\sigma$ complex.
The low frequency interaction $V_{lo}(r)$ between electrons on a single molecule can be estimated by considering a molecule of radius $R_b$ at the center of a spherical cavity of radius $R_c$ inside a metal (fig. 2). This approximation can be justified diagramatically. The image charges formed in the metal result in a screened interaction

$$V_{lo}(r) = \frac{e^2}{\epsilon} \left[ \frac{1}{r} - \frac{R_c}{\sqrt{(R_c^2 - R_b^2)^2 + R_c^2 r^2}} \right].$$

(3)

Since the distance from the center of one molecule to the nearest carbon nucleus of a neighboring molecule is 6.5 Å, and the carbon 2p$_z$ orbitals extend roughly 1 Å from the nucleus, we estimate the effective cavity radius to be $R_c \approx 5-6$ Å. While the geometric radius of an individual fullerene molecule is 3.5 Å, the 2p$_\pi$ orbitals are squeezed to the outside of the molecule by its curvature. The effective radius $R_b$ at which the electrons move is therefore somewhat larger than the geometric radius of the molecule, perhaps by as much as half an Angstrom.

The on-site interaction is an atomic property of the carbon 2p orbitals, and must be treated separately. For a carbon 2p orbital, the unscreened Coulomb integral $V_{ui}(0)$ is roughly 7-10 eV. Metallic screening of this atomic Coulomb integral should be negligible, so for simplicity we present here results for $V_{lo}(0) = V_{ui}(0) \equiv V(0)$, where $V(0)$ corresponds roughly to the “Hubbard $U$.” Eqns. (2) and (3), plus the high and low frequency on-site interactions, complete the specification of our model for frequency dependence in the screened Coulomb interaction of metallic fullerenes.

**Calculation of pairing interaction.** To calculate the effective interaction arising from eqns. (1-3), we start with a simple tight-binding model for the $\pi$ molecular orbitals of $C_{60}$. The matrix elements $t$ and $t'$ corresponding to nearest-neighbor intra-pentagon (“single bond”) and inter-pentagon (“double bond”) hopping are 2.0 and 2.6 eV, respectively.

The three partially occupied molecular orbitals in the alkali-doped fullerenes transform as the $t_{1u}$ representation of the icosahedral group. The pair state favored by both the intramolecular phonon and the electronic pairing mechanisms is the unique spin and orbital singlet.
\[ |A_y, S = 0 \rangle \equiv \frac{1}{\sqrt{3}} (|xx\rangle + |yy\rangle + |zz\rangle), \tag{4} \]

where the filled sea is implicitly included and \( x, y, \) and \( z \) label the three orthogonal states of \( t_{1u} \) symmetry.

We calculate the effective singlet pair interaction energy in this state, \([4]\) which corresponds to the negative of the pair binding energy of ref. \([3]\). This and other renormalized interactions can in turn be added to a model for intramolecular hopping and phonons to describe the low-energy behavior of the metal and superconductor. \([4]\)

Explicitly, we compute the Feynman diagrams shown in fig. \([3]\). The double dashed lines represent the screened Coulomb interaction of eqns. (1-3); the incoming and outgoing thin lines are propagators for the singlet pair state eq. (4). We sum over all intermediate states with at least one particle or hole in orbitals away from the Fermi energy. Such propagators are represented by thick lines in fig. \([3]\). There are over 60,000 distinct terms in this sum. In this manner, all virtual particle-hole fluctuations involving the higher-lying states are included to second-order in the interaction. Our calculation includes (a) the first-order scattering at the Fermi energy and (b) the usual second-order ladder, as well as (c) the crossed ladder, (d) screening from an intra-molecular particle-hole bubble (\(i.e.,\) the 6 eV \(2p\pi\) intra-molecular plasmon), and (e) the leading vertex correction. Due to the explicit frequency dependence of our model interaction, one cannot easily sum even the ladder diagrams, as can be done when frequency dependence is neglected.

Fig. \([4]\) shows the second-order effective interaction calculated using the screened Coulomb interaction discussed above. The results are plotted \emph{versus} the on-site interaction \( V(0) \). Results for cavity radii \( R_c = 5 \) Å and 6 Å are shown. For comparison, we show the second-order calculations of Chakravarty \emph{et al.} for the Hubbard model and of Goff and Phillips for the exponentially screened interaction \( V(r) = U e^{-\lambda r} \). In these two models the frequency-dependence of screening effects have been neglected, and interactions are instantaneous.

The effects of the long-range part of the screened Coulomb interaction are substantially reduced by the properly accounting for their frequency dependence, as seen by comparing
our results with Goff and Phillips. Within second-order perturbation theory, we find that the effective interaction changes sign near $V(0)$ of order 7-8 eV, which is close to the value obtained for the Hubbard model. The effective Coulomb interactions for the Hubbard model and the present frequency-dependent model are quite similar, except at small $U$, where the present model includes longer-range Coulomb interactions that yield a repulsive effective interaction even when the bare on-site interaction vanishes.

The suppression of the effects of the long-range part of the Coulomb interaction can be understood schematically as follows. In the usual ladder sum, the first- and second-order terms (fig. 3a,b) both involve the screened Coulomb interaction. In a molecular metal, however, second- and higher-order terms are not screened, since they involve virtually excited states above the plasma frequency. These higher-order terms are therefore stronger (i.e., more attractive) than one might naively expect. Thus screening reduces the (repulsive) first-order term, but not the (attractive) second-order term.

In conclusion, we stress that strong intramolecular correlation effects are necessarily present in a molecular metal such as $C_{60}$. We have shown that a combination of intermolecular screening and intramolecular correlations leads to a dramatic reduction of the Coulomb repulsion between electrons. Such a reduction is necessary for a consistent theory of phonon-mediated superconductivity in the fullerenes in the presence of strong electron-electron repulsion. To the extent that second-order perturbation theory is valid, frequency-dependent screening may even result in an effective pair binding arising purely from electronic correlation effects.

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FIGURES

FIG. 1. The electronic excitations of metallic fullerenes are characterized by three energy scales: the bandwidth $W$ due to interfullerene hopping, the plasma frequency $\omega_p$, and the width of the $\pi$ complex $W_\pi$.

FIG. 2. We model the low-frequency effects of metallic screening by considering a single $C_{60}$ molecule inside a spherical cavity of radius $R_c$ in a metal.

FIG. 3. The first-order contribution to the effective interaction between two electrons in the spin singlet, orbital singlet channel is represented by (a) direct scattering by the screened interaction. There are four second-order terms: (b) the uncrossed ladder, (c) the crossed ladder, (d) the vertex correction, and (e) screening due to on-ball particle-hole pairs. In the second order diagrams (b-e), at least one of the thick propagators must lie away from the Fermi energy.

FIG. 4. Second order calculations of the effective singlet interaction at the Fermi energy. The two solid lines are the results of the present work, corresponding to cavity radii $R_c = 5$ Å and $R_c = 6$ Å. The dotted line is the Hubbard model calculation of ref. [3]. The dashed lines are the results of Goff and Phillips. [7] The horizontal axis is the on-site Coulomb repulsion, $V(0)$, or equivalently the Hubbard $U$. For comparison, the phonon mediated attraction $V_{BCS}$ is roughly 75 meV.
\[ W_\pi \]

\[ \hbar \omega_p \]

- empty bands

- plasma frequency

- \( W \) 1/2-filled band at Fermi energy

- filled bands
