Metallic Screening and Correlation Effects in Superconducting Fullerenes

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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 screening substantially reduces the effects of the long-range part of the Coulomb interaction, leading to the possibility of effective attraction between electrons.

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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 be metals, magnets, insulators, or even 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. Several microscopic calculations [2,3] estimate the BCS interaction due to the exchange of intramolecular phonons to be roughly 75 meV C_{60}. The bands at the Fermi energy are narrow (bandwidth $W \approx 200$ meV), so 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. Since the electronic bandwidth and characteristic phonon energies are comparable, the naive Born-Oppenheimer–Migdal-Eliashberg approximation is no longer justified.

Electron-electron interactions are also important in the doped fullerenes: The typical intramolecular Coulomb energy is $e^2/\epsilon R_b \approx 2$ eV, where $R_b = 3.5$ Å is the fullerene radius. Coulomb scattering in the doped fullerenes was emphasized by Chakravarty and co-workers [3], who calculated the effective interaction at the Fermi energy [4] using an on-site Hubbard repulsion U to model the screened Coulomb interaction. Although the bare Hubbard interaction is repulsive, Chakravarty and co-workers found (using both perturbation calculations [3] and exact solution of small fullerene analogs [5]) that moderate Hubbard U can generate effective interactions at the Fermi energy which are anomalously small or even negative (indicating attraction), suggesting 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 [3,6].

It has been argued [7,8] that the long-range part of the Coulomb potential generates effective interactions at the Fermi energy that are substantially more repulsive than those found with a simple Hubbard model. While these calculations raise the important issue of long-range Coulomb effects, the extended Hubbard models of Refs. [7] and [8] omit the crucial dynamics of metallic screening.

In this Letter we consider *frequency-dependent* metallic screening and its effect on the energetics of pairing. Our approach relies on the separation of energy scales for intermolecular hopping (W), metallic screening (the Drude plasma energy $\hbar\omega_p$), and intramolecular hopping (the width D of the relevant complex of molecular states), as sketched in Fig. 1 and discussed 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 other perturbative calculations.

We find that a long-ranged but frequency-dependent screened interaction strikingly reproduces the results obtained from the Hubbard model [3]. 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. 2(a)] occurs at a frequency below the plasma frequency and is therefore heavily screened. The higher-order corrections [which can be attractive in sec-

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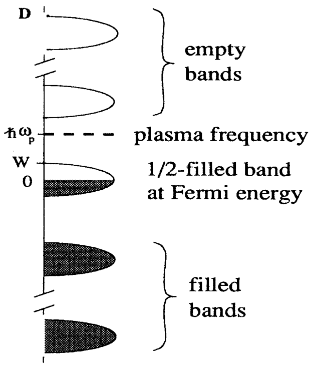

FIG. 1. The electronic excitations of metallic fullerenes are characterized by three energy scales: the bandwidth W due to interfullerene hopping, the plasma frequency ω_p, and the width D of the π complex.

ond order, Figs. 2(b)–2(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 [9].

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. These orbitals are part of a wide $2p\pi$ complex spread over $D \approx 15$ eV. The screening response of the metal is governed [10] by the Drude plasma energy $\hbar\omega_p \approx 1-1.5$ eV.

The separation of energy scales $D > \hbar\omega_p > W$ (see Fig. 1) suggests a simple analytical model for the screened Coulomb interaction. Since the bandwidth W is the smallest frequency in the problem, intermolecular hopping occurs only on long time scales. We therefore neglect intermolecular hopping at this stage of the calculation except insofar as it generates a polarizable metallic environment around each fullerene. The charge fluctuations of these metallic surroundings can then be integrated out exactly to obtain the time-dependent screened Coulomb interaction between electrons on a *single* molecule.

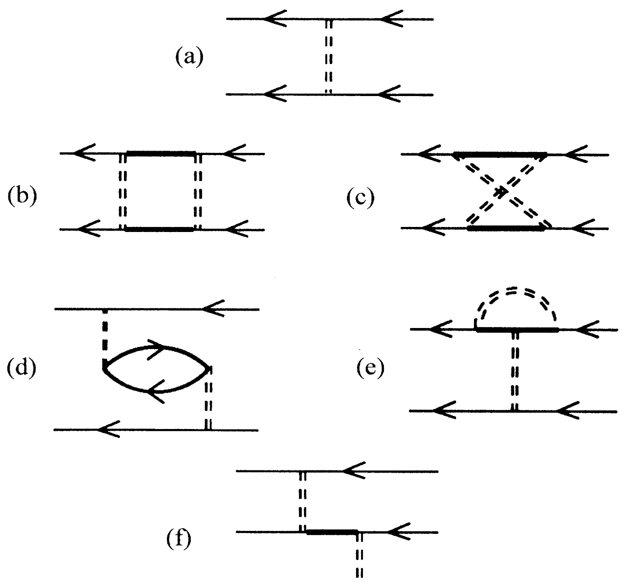

FIG. 2. The first-order contribution to the effective interaction between two electrons in the spin singlet, orbital singlet channel is represented by (a) direct scattering by the screened interaction. There are five second-order terms: (b) the uncrossed ladder, (c) the crossed ladder, (d) the vertex correction, (e) screening due to on-ball particle-hole pairs, and (f) a three-body interaction. In the second-order diagrams (b)–(f), at least one of the thick propagators must lie away from the Fermi energy.

Armed with this screened interaction, we can perturbatively integrate out the π complex to obtain the renormalized interaction at the Fermi energy (the "pair binding energy" discussed below). Note that by accurately treating the frequency dependence of the metallic screening we remove any potential ambiguity [11] in the proper calculation of these renormalizations. It is only when this frequency dependence is neglected that problems can arise, as noted in Ref. [11].

The separation between the plasma frequency and typical intramolecular excitation energies allows us to simplify further. All high-frequency interactions (i.e., interband matrix elements) will be essentially unscreened, since such transitions occur too rapidly for the metal to respond. Low-frequency interactions (i.e., matrix elements between degenerate molecular states), however, will be maximally screened by image charges in the surrounding metal. We therefore approximate the screened Coulomb interaction by its high- and low-frequency parts:

$$V(r,\omega) = \begin{cases} V_{\mathrm{lo}}(r) & \text{if } \omega < \omega_p, \\ V_{\mathrm{hi}}(r) & \text{if } \omega > \omega_p, \end{cases} \tag{1}$$

where r is the distance between a pair of π electrons on a given fullerene molecule.

The *high-frequency* interaction $V_{\mathrm{hi}}(r)$ is simply the dielectrically screened Coulomb potential:

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

The dielectric constant $\epsilon \approx 2$ is determined by the polarizability of degrees of freedom that we have left out of our model, especially the carbon $2p\sigma$ complex.

The *low-frequency* screened interaction $V_{\mathrm{lo}}(r)$ between electrons on a single molecule is calculated by considering a molecule of radius R_b at the center of a spherical cavity of radius R_c inside a metal (Fig. 3). Consideration of the image charges formed in the metal gives

$$V_{\mathrm{lo}}(r) = \frac{e^2}{\epsilon}\left[\frac{1}{r} - \frac{R_c}{\sqrt{(R_c^2 - R_b^2)^2 + R_c^2 r^2}}\right]. \tag{3}$$

Since the distance from the center of one molecule to the nearest carbon nucleus of a neighboring molecule

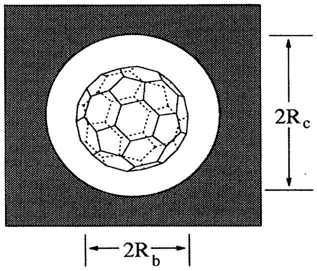

FIG. 3. We model the low-frequency effects of metallic screening by considering a single C_{60} molecule inside a spherical cavity of radius R_c in a metal.

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 $V_{\text{hi}}(0)$ is roughly 7–10 eV. Metallic screening of this atomic Coulomb integral should be negligible, so for simplicity we present here results for $V_{\text{lo}}(0) = V_{\text{hi}}(0) \equiv V(0)$, where $V(0)$ corresponds roughly to the "Hubbard U." Equations (2), (3), and the on-site interaction 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 Eqs. (1)–(3), we start with a simple tight-binding model for the π molecular orbitals of C_{60}. The matrix elements t and t' corresponding to nearest-neighbor intrapentagon and interpentagon 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 (unnormalized) paired states of $C_{60}{}^{n-}$ favored by both the intramolecular phonon and the electronic pairing mechanisms are the unique spin and orbital singlets [4]

$$|A_g, S = 0\rangle \propto [c_{x\uparrow}^{\dagger}c_{x\downarrow}^{\dagger} + c_{y\uparrow}^{\dagger}c_{y\downarrow}^{\dagger} + c_{z\uparrow}^{\dagger}c_{z\downarrow}^{\dagger}]^{n/2}|0\rangle, \quad (4)$$

where $|0\rangle$ represents the neutral state of C_{60} and x, y, and z label the three orthogonal t_{1u} states.

We calculate the "pair binding energy" [3] of these states, which is equal [4] to the effective singlet two-body interaction energy plus a small contribution from three-body terms [Fig. 2(f)]. Our calculation is equivalent to integrating out all electronic states away from the Fermi energy to second order in the Coulomb interaction. The resulting effective interactions at E_F (as well as phonon-mediated interactions) can then be introduced in a model which includes intermolecular hopping to describe the low-energy behavior of the metal and superconductor [4].

Explicitly, we compute the Feynman diagrams shown in Fig. 2. The double-dashed lines represent the screened Coulomb interaction of Eqs. (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. 2. 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 intramolecular particle-hole bubble (i.e., the 6 eV $2p\pi$ intramolecular plasmon), (e) the leading vertex correction, and (f) a small three-body correction.

Figure 4 shows the second-order effective interaction calculated using the screened Coulomb interaction discussed above. The results are plotted versus the on-site interaction $V(0)$. Results for cavity radii $R_c = 5$ and 6 Å are shown. For comparison, we show the second-order calculations of Chakravarty and co-workers for the Hubbard model and of Goff and Phillips for the exponentially screened interaction $V(r) = Ue^{-\lambda r}$. In these latter two models the frequency dependence of screening effects is neglected.

The effects of the long-range Coulomb interaction are substantially reduced by including frequency dependence,

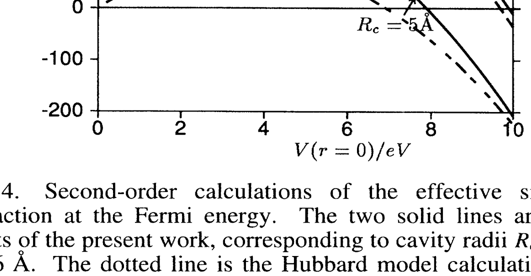

FIG. 4. Second-order calculations of the effective singlet interaction at the Fermi energy. The two solid lines are the results of the present work, corresponding to cavity radii $R_c = 5$ and 6 Å. The dotted line is the Hubbard model calculation of Ref. [3]. The dashed lines are the results of Goff and Phillips [8]. 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.

as seen by comparing our results with Goff and Phillips. In 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.

In conclusion, in a conventional metal the screened Coulomb interaction is essentially instantaneous (i.e., frequency independent) over the bands of interest. Thus in the traditional ladder sum, *all* terms involve the screened Coulomb interaction [11]. In molecular metals like the doped fullerenes, however, second- and higher-order terms are *not* screened, since they involve virtually excited states well above the plasma frequency. These higher-order terms are therefore stronger (i.e., more attractive) than one might naively expect. Screening does reduce the (repulsive) first-order term, but not the (attractive) second-order terms.

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 dramatically reduces 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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