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Superconductivity in hole-doped C_{60} from electronic correlations

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We derive a model for the highest occupied molecular-orbital band of a C_{60} crystal which includes on-site electron-electron interactions. The form of the interactions are based on the icosahedral symmetry of the C_{60} molecule together with a perturbative treatment of an isolated C_{60} molecule. Using this model we do a mean-field calculation in two dimensions on the [100] surface of the crystal. Due to the multiband nature we find that the electron-electron interactions can have a profound effect on the density of states as a function of doping. The doping dependence of the transition temperature can then be qualitatively different from that expected from simple BCS theory based on the density of states from band structure calculations.

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Superconductivity in C_{60} has generally been ascribed to a phonon mechanism due to strong electron-phonon coupling for some C_{60} intramolecular modes.[1] However, due to their high energy and the narrow electronic bandwidth questions have been raised about the effectiveness of retardation for reducing the strong Coulomb repulsion in these materials.[2] In addition, a number of features suggest that these materials are very exotic, including Mott insulating behavior and so-called "bad metal" behavior with resistivities that do not saturate at high temperatures.[3,4] Such behavior is reminiscent of the high-T_c cuprates where electron correlations are generally accepted to play a crucial role.

Another issue which is not well understood is the variation of T_c with doping. The various alkali-doped materials have T_c's that are maximized near the half-filled LUMO (lowest unoccupied molecular-orbital) band, i.e., three electrons per C_{60}, and confined to a narrow doping range around this. This variation of T_c with doping does not correspond to the density of states (DOS) as given by band-structure calculations.[3] Again, a clear indicator that correlation effects are important.

Here we study the effects of electronic correlations on a crystal of C_{60} molecules based on the strong intramolecular electron-electron interactions. Our approach, which expands on earlier work by Chakravarty *et al.*[5] (see also Ref. 6 for similar and independent ideas), can be summarized as follows. We solve the Hubbard model on a truncated icosahedron, i.e., a single C_{60} molecule, in second-order perturbation theory in the on-site repulsion U. We do this for the HOMO (highest occupied molecular-orbital) states given by diagonalizing the tight-binding ($U=0$) Hamiltonian. Based on the perturbative spectrum we formulate an effective interacting Hamiltonian in terms of holes characterized by orbital angular momentum and spin. We then consider a crystal of C_{60} molecules with nearest-neighbor hopping and where this effective Hamiltonian for the interactions on a single C_{60} molecule corresponds to the on-site interactions. Subsequently, we do a standard BCS/Hartree-Fock calculation on the [100] surface of an fcc crystal using this lattice Hamiltonian. The Hartree-Fock calculation on a surface- and hole-doped C_{60} crystal is a model calculation. Nevertheless, we feel that the method presented as well as the qualitative features of the results are relevant also to the alkali-doped materials.

We find that T_c is peaked close to three holes and strongly suppressed at five holes where the DOS based on the band structure is maximized. This striking deviation from the behavior expected from a BCS calculation based on band structure is related to a strong renormalization of the DOS due to the interactions. As a signature of the strong electron-electron interactions we also find that depending on the details of the interactions and band structure there may be non-magnetic Mott insulating states at even integer fillings. Mott insulating behavior is indeed seen in alkali-doped compounds with a doping of two or four electrons per molecule.[7,8] In addition, an equivalent analysis for the LUMO band gives a pair-binding interaction which is roughly 60% of that for the HOMO band in the relevant parameter regime, which suggests a possibility for higher T_c's for a hole-doped material.

Perturbation theory. Let us start by considering the following Hubbard model on a single C_{60} molecule,

$$H_{C_{60}}=-\sum_{ij,\sigma} t_{ij}(c^{\dagger}_{i\sigma}c_{j\sigma}+\text{H.c.})+\frac{U}{2}\sum_{i,\sigma} n_{i\sigma}n_{i-\sigma}, \quad (1)$$

where the only nonvanishing hopping integrals are $t_{ij}=t$ for nearest-neighbor (nn) hopping on pentagons and $t_{ij}=t'$ for nn hopping between pentagons. We use $t=2$ eV and $t'/t=1.2$ in accordance with the values used in Ref. 5 and allow U to vary. Values of $U\sim5-12$ eV have been suggested in the literature.[3]

We do standard second-order perturbation theory in Hubbard U. Since the Hamiltonian is spin rotationally invariant the states fall into degenerate sets corresponding to irreducible representations of the icosahedral group I_h and spin. The states are well characterized by angular momentum and only weakly split by the icosahedral symmetry.

The validity of second-order perturbation theory for the large-U Hubbard model and the neglect of longer-range Coulomb interaction for this problem have been under debate.[3] It has been shown by exact diagonalization that for small Hubbard clusters (e.g., the 12-site truncated tetrahedron) the second-order perturbation theory is qualitatively correct giving positive pair-binding energies for moderately large U.[9] In addition, longer-ranged repulsions are more effectively screened by the metallic environment than the high-energy

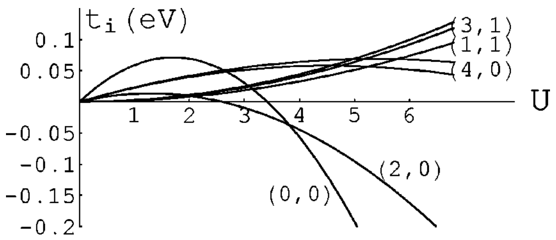

FIG. 1. Coupling constants of the effective interactions labeled according to (L,S). The split due to icosahedral symmetry is not explicitly labeled. (U is in units of $t=2$ eV)

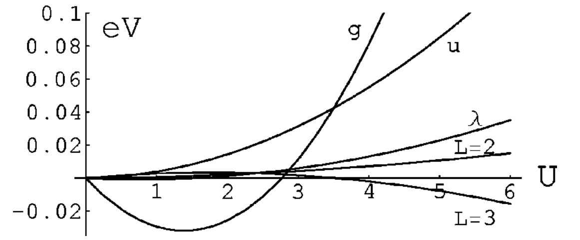

FIG. 2. Magnitude of the coupling constants of $\vec{S}^2$, n^2, and $\vec{L}^2$, respectively, g,u,λ, and the $L=2$ and $L=3$ tensor invariants. (U is in units of $t=2$ eV)

second-order processes that give rise to the attraction.[10] Here, we explore the consequences of this model assuming that it gives a reasonable estimate of the molecular spectrum and the resulting pair attraction.

Effective interactions. Using the perturbation theory results we derive a set of interactions for the crystal. Although the perturbative result contains terms to higher order in fermion operators, we take the effective Hamiltonian

$$H_{eff}=e_0-e_1\sum_{l,\sigma} n_{l\sigma}+t_i T^i_{klmn\alpha\beta\gamma\delta}c^\dagger_{k\alpha}c^\dagger_{l\beta}c_{m\gamma}c_{n\delta}, \quad (2)$$

which acts on a space of one-particle states in the five-dimensional H_u representation of I_h. Here $c^\dagger_{k\alpha}$ creates a hole with quantum number $k=1,\ldots,5$ and spin α, $n_{l\sigma}$ is the number operator and alike indices are henceforth summed over. The e_0, e_1, and t_i are parameters and the $T^i_{klmn\alpha\beta\gamma\delta}$ are tensors chosen to make the four-fermion terms T^i invariant independently under spin and icosahedral symmetry.

Group theory reveals that there are nine such independent four-fermion terms. These can be derived by constructing all two-fermion terms $c_{k\alpha}c_{l\beta}$ transforming in a particular representation of spin and angular momentum and taking the tracing with their Hermitian conjugates. We can write for the product of two fermions in the representation H of I_h and spin-1/2, $H\otimes H=(A\oplus G\oplus 2H)_s+(T_1\oplus T_2\oplus G)_a$, $1/2\otimes 1/2=0_a\oplus 1_s$ where s and a mean the symmetric and antisymmetric parts of the tensor products and where A,T_1,T_2,G, and H are the one-, three-, three-, four-, and five-dimensional representations of I_h, respectively.

The product of two anticommuting fermion operators thus reduces into seven irreducible parts, given by finding the antisymmetric part of the product of angular momentum and spin. We then construct the invariant four-fermion operators T^i, with corresponding coupling constants t_i, labeled according to from which two-fermion operators they are constructed using the composite index

$$i=\{(A,0,0),(H,2,0),(G,4,0),(H,4,0),(T_1,1,1),$$
$$(T_2,3,1),(G,3,1)\}. \quad (3)$$

Here (R_i,L_i,S_i) indicates icosahedral representation, corresponding angular momentum in the case of full rotational symmetry, O(3), and spin, respectively. The tensors $T^i_{klmn\alpha\beta\gamma\delta}$ are normalized such that they are projection operators into the ith irreducible subspace of the two-fermion products. We neglect the additional two invariants that can be constructed from tracing the two different realizations of H together since these are not allowed under O(3) and since the deviance from full rotational symmetry is small.

The effective Hamiltonian (2) is then used to match the spectrum found from the perturbation theory. e_0 is given by the energy of the neutral molecule (filled HOMO), e_1 by the ten-fold degenerate one-hole states and the two-hole spectrum is in one-one correspondence to the seven four-fermion terms with energies $e_0-2e_1+2t_i$, which fixes $t_i=t_i(U,U^2)$ as shown in Fig. 1.

In spite of its relative simplicity this effective model reproduces the trend found in the perturbative calculation, namely, that for moderately large U states with low spin and low "angular momentum" have lower energy, i.e., Hund's rule is not valid. To make this statement more transparent we can consider the conventional four-fermion operators n^2, $\vec{S}^2$, and $\vec{L}^2$, invariant under $O(3)\times SU(2)$. To fit these to the normal ordered four-fermion operators T^i we also need the tensor invariants of angular momentum $\mathcal{Q}^a_L\mathcal{Q}^a_L$ (no sum over L) where $\mathcal{Q}^a_L=Q^a_{L,ij}c^\dagger_{i\alpha}c_{j\alpha}$ transform as the $L=2,3$, or 4 representation of SO(3) $(a=1,\ldots,2L+1)$. We find, $n^2=n+\Sigma_i T^i$, $\vec{S}^2=\frac{3}{4}n+\Sigma_i[S_i(S_i+1)/2-\frac{3}{4}]T^i$ and $\vec{L}^2=6n+\Sigma_i[L_i(L_i+1)/2-6]T^i$, with i, S_i, and L_i as defined in Eq. (3) and with similar expressions for the other operators. Apart from the small split due to icosahedral symmetry, which we average over, we get new coupling constants as shown in Fig. 2. (The $L=2,3$ invariants are normalized as $\vec{L}^2$ and due to overcompleteness we choose not to include the $L=4$ tensor invariant.)

We find that for large U, n^2, $\vec{L}^2$, and $\vec{S}^2$ dominate the energetics and we will subsequently only use these as a minimal model expected to capture the important physics of the interactions.

Lattice Hamiltonian. We can now write down the lattice Hamiltonian

$$H=\sum_{\langle\vec{r}\vec{r}'\rangle} t_{\vec{r}\vec{r}',kl}(c^\dagger_{\vec{r},k\sigma}c_{\vec{r}',l\sigma}+\text{H.c.})$$
$$+\sum_{\vec{r}} g\vec{S}_{\vec{r}}\cdot\vec{S}_{\vec{r}}+\lambda\vec{L}_{\vec{r}}\cdot\vec{L}_{\vec{r}}+un^2_{\vec{r}}, \quad (4)$$

where $\vec{r}$ are the sites of the lattice and $\langle\vec{r}\vec{r}'\rangle$ runs over the range of intermolecular hopping. This model is quite general and could be used also for electron doped systems in two or three dimensions.[11] Here we consider a model where the charge is confined to the [100] surface of the fcc crystal, i.e. a two dimensional system where $\langle \vec{r}\vec{r}' \rangle$ corresponds to nn on a square lattice. From the perturbative calculation (Fig. 2) we take $g,\lambda,u>0$. Note that the confinement of electron propagation to the surface completely breaks the fivefold degeneracy of the HOMO states. This will be manifest in the tight-binding part of the Hamiltonian which reflects the point group symmetry of the surface.

Typical hopping integrals are of the order of 0.1 eV (Ref. 12) which is comparable to the interactions (Fig. 2), the problem is in an intermediate coupling regime. Nevertheless, we do a standard BCS/Hartree-Fock construction, replacing the Hamiltonian (4) by a reduced noninteracting Hamiltonian. We keep only spatially uniform superconducting mean fields $b_{kl\alpha\beta}=(1/V)\Sigma_{\vec{r}}\langle c_{\vec{r},k\alpha}c_{\vec{r},l\beta}\rangle$ and mean fields of the number operators $n_{l\alpha}=(1/V)\Sigma_{\vec{r}}\langle c^{\dagger}_{\vec{r},l\alpha}c_{\vec{r},l\alpha}\rangle$. We can then derive the following effective Hamiltonian in momentum (p) space

$$H_{MF}=H_0+H_{pair}+H_{HF}=\sum_p [t(p)_{kl}-\mu\delta_{kl}]c^{\dagger}_{p,k\sigma}c_{p,l\sigma} - \sum_{L,S}(c^{\dagger}_{p,l\beta}c^{\dagger}_{-p,k\alpha}\mathcal{O}^{L,S}_{kl\alpha\beta}+\text{H.c.})+h_{HF,kl}c^{\dagger}_{p,k\alpha}c_{p,l\alpha}, \tag{5}$$

where we included a chemical potential μ. We define the components of the order parameter

$$\mathcal{O}^{L,S}_{kl\alpha\beta}=V_{L,S}\sum_{i:L_i=L,S_i=S}T^{i}_{klmn\alpha\beta\gamma\delta}b_{mn\gamma\delta}, \tag{6}$$

where $V_{L,S}=[\frac{3}{4}-S(S+1)/2]g+[6-L(L+1)/2]\lambda-u$ and $V_{L,S}>0$ corresponds to attraction.

Assuming no net magnetization the Hartee-Fock terms can be written (no sum over l),

$$h_{HF,ll}=-\frac{3}{4}gn_l-\lambda\tau_l+u\left(n_l+2\sum_{k\neq l}n_k\right), \tag{7}$$

where $n_l=n_{l\uparrow}+n_{l\downarrow}$ is the total particle number with angular momentum component l and $\vec{\tau}=(3n_4+3n_5,4n_3+n_4+n_5,4n_2+n_4+n_5,3n_1+n_2+n_3+n_5,3n_1+n_2+n_3+n_4)$. (In addition there is one off-diagonal component $\sqrt{3}\lambda(n_5-n_4)(c^{\dagger}_{p,1\alpha}c_{p,2\alpha}+\text{H.c.})$, which is included in our calculations but which will in general be small.)

The tight-binding part of the Hamiltonian for the simplest (unidirectional) crystal structure takes the form

$$t(p)_{kl}\doteq\begin{bmatrix} t_1f_p & t_{12}f_p & t_{13}g_p & 0 & 0\\ t_{12}f_p & t_2f_p & t_{23}g_p & 0 & 0\\ t_{13}g_p & t_{23}g_p & t_3f_p & 0 & 0\\ 0 & 0 & 0 & t_4f_p & t_{45}g_p\\ 0 & 0 & 0 & t_{45}g_p & t_5f_p \end{bmatrix}, \tag{8}$$

where $f_p=\cos(p_x)\cos(p_y)$ and $g_p=\sin(p_x)\sin(p_y)$.

We have taken hopping parameters from Ref. 12. For hole hopping we have, $t_1=-0.107,t_2=0.198,t_3=0.134,t_4=-0.032,t_5=-0.170,t_{12}=0.087,\ t_{13}=0.073,t_{23}=0.162,t_{45}=0.115$ eV. The Hamiltonian has the symmetry $t(p)=-t(p+(\pi,0))$ implying a symmetric band structure around zero energy where all bands will be half filled and there are Van Hove singularities at zero energy at $(p_x,p_y)=(\pm\pi/2,\pm\pi/2)$.

The Hartree-Fock terms (7) have interesting properties related to their multiband nature. For positive g and u it is energetically favorable to fill up as few bands as possible for a given particle number. The term $\vec{S}_{\vec{r}}\cdot\vec{S}_{\vec{r}}$ gives on-site spin-triplet states with higher energy than singlets, so that by putting particles in a single angular momentum state the energy can be lowered by exclusion, and similarly for the on-site charging energy $n^2_{\vec{r}}$, where two particles with the same spin and angular momentum cannot occupy the same site. The $\vec{L}_{\vec{r}}\cdot\vec{L}_{\vec{r}}$ term on the other hand gives rise to an anisotropic attraction between the components.

For positive parameters g, u, and λ the $L=0,\ S=0$ pairing channel of Eq. (5) is the strongest and we can expect this to dominate. But, since the rotational invariance of the C_{60} molecules is broken by the lattice, subdominant order parameters with nonzero angular momentum appear and in general all three $S=0$ order parameters may be nonzero.

What kind of physics can we expect from this model? For large g or u there may be Mott insulating states at even integer $2n$ filling where n bands of angular momentum states will fill up completely. If u is not very large compared to g the insulating state will be nonmagnetic due to the low energy of molecular singlets. (For the regime $u\gg g$, not realized here, there may also be magnetic insulating states at odd integer filling.) The pairing terms compete with a putative insulating state due to the Hartree-Fock terms so that even for large g or λ there may be a superconducting ground state also at even integer fillings, although a suppression of T_c is likely due to the low DOS when the bands are nearly filled or empty. In general we can expect the Hartree-Fock terms to completely recast the DOS compared to that given by the band structure and consequently also T_c's.

Results. By numerical iteration of the mean particle number in the five angular momentum components and the sc mean fields at fixed chemical potential we arrive at self-consistent solutions. For all plots the system size is 100×100 with at least ten sampling points per unit shift in particle number. Figure 3 shows the energy gap 2Δ, the norm of the s.c order parameter (defined as $\sqrt{Tr\mathcal{O}\mathcal{O}^{\dagger}}$ with $\mathcal{O}=\Sigma_{L,S}\mathcal{O}^{L,S}$) at $T=0$ and T_c as a function of doped holes (up to seven holes) for parameters $u=0.09,g=0.06,\lambda=0.02$ eV, both with and without Hartree-Fock (H-F) terms. We find that T_c scales roughly linearly with Δ and the reduced gap $2\Delta/T_c\approx3.2$ is close to the weak coupling BCS value (3.53). For the calculation with H-F terms the magnitude of the order parameter (not in the figure) fits very well with 2Δ. Without H-F terms there is a deviation from this fit around five holes, due to a momentum-dependent gap.

Figure 4 shows the density of states, $\partial n/\partial\mu$, for the same parameters and with Hartree-Fock terms and the DOS from

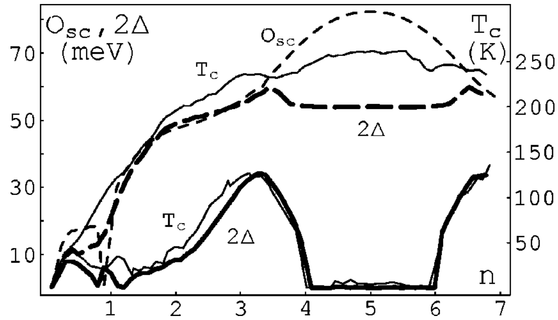

FIG. 3. Spectral gap 2Δ and norm of $\mathcal{O}_{sc}$ at $T=0$ and T_c for parameters $u=0.09, g=0.06, \lambda=0.02$ eV as a function of doped holes. The lower (upper) curves are with (without) Hartree-Fock terms.

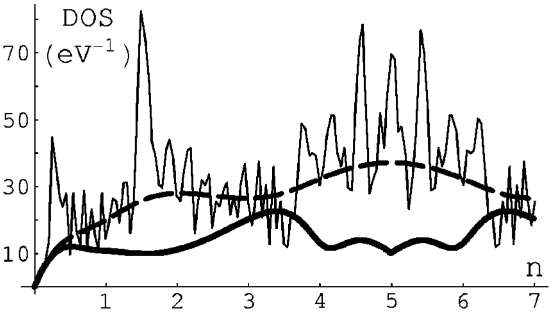

FIG. 4. Density of states. The thick solid line is for parameters as in Fig. 3, calculated at 150 K. The thin (dashed) line is the DOS from band structure at $T=0$ ($T=150$ K).

the noninteracting band structure (8), i.e., the DOS without H-F terms. Since we find self-consistent solutions of both the band fillings and the gaps we calculate the DOS at finite temperature, above T_c, for the realization with H-F terms.

The values of λ and u chosen here correspond roughly to the perturbative spectrum (Fig. 2) at $U=5$, but we have reduced g significantly in order for the pairing attraction not to dominate completely. One could argue that the second-order perturbation theory can be expected to overestimate the core-polarization effect that gives the $\vec{S}^2$ term. Of course, the actual magnitude of T_c and the gap that we find should not be taken too literally since parameters are only rough estimates and we are doing mean-field theory at relatively strong coupling. The important result is the qualitative behavior of T_c as a function of doping.

Without Hartree-Fock terms, T_c follows the DOS of the band structure with a corresponding maximum at the half-filled band. This should be contrasted with the results for the full Hamiltonian which has a T_c that is maximized close to three holes and which is strongly suppressed at five holes. The DOS is suppressed at four and six holes due to the commensurate lock in discussed above. In fact, the influence of these special fillings is such that the DOS is low in the whole region between four and six holes where it is the highest without interactions.

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