Superconductivity of K_xC_{60} fullerenes according to the Hubbard model with repulsion

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The electronic structure of the conduction band is analyzed in the limit of an infinitely high positive Hubbard energy. Partial scattering amplitudes are calculated. The results are used to determine the conditions for a Cooper instability. A phase diagram of the existence of the superconducting state is constructed.

Experiments on the resistivity of the compound K_3C_{60} reveal a quadratic temperature dependence[1] and indicate that the electron-phonon interaction is weak. The typical value of the energy which determines the superconducting transition temperature in the BCS formula for the compound A_3C_{60} turns out to be of the same order of magnitude, 0.2 eV, as the half-width predicted for the conduction band in atomic calculations.[2,3] These facts indicate that the electron-electron interaction plays a key role; it is an order of magnitude greater than the width of the filled t_{1u} shell of C_{60}. The number of electrons in the potassium 4*s* shell (n_s) is related to the number of electrons in the C_{60} t_{1u} shell (n_t) by the condition of electrical neutrality: for K_xC_{60},

$$-n_t+xn_s=x. \tag{1}$$

According to Guo *et al.*,[3] the energy of 4*s* states is greater than the energy of *t* states. We therefore assume $n_s<1$, and we examine the filling of the *t* shell, taking account of its triple degeneracy and noting that the Hubbard energy is considerably larger than the Fermi energy. For simplicity we assume that this energy is infinite in comparison with the jump integrals $t^{ik}(r)$, $t^{(i)}(r)$, and $\tau(r)$ in terms of which the Hamiltonian is expressed:

$$H=\sum_{r,r'\sigma}{}' \hat{p}^+_{ir\sigma}p_{jr'\sigma}t^{ij}_{(r-r')}+\sum_{i,r,r'\sigma}[t^{(i)}_{(r-r')}\hat{a}^+_{r\sigma}\hat{p}_{ir'\sigma}+\text{h.c.}]$$
$$+\sum_{r,r'\sigma}{}' \hat{a}^+_{r\sigma}\hat{a}_{r'\sigma}\tau(r-r')+\epsilon_t\sum_{r,\sigma}\hat{p}^+_{ir\sigma}p_{ir\sigma}+\epsilon_s\sum_{r\sigma}\hat{a}^+_{r\sigma}\hat{a}_{r\sigma}. \tag{2}$$

Here *i*, *j* are vector indices corresponding to the t_{1u} states, and ϵ_t and ϵ_s are the energies of one-particle *t* and 4*s* states. We express the creation and annihilation operators in terms of the *X* operators for a transition between *n*- and $(n\pm1)$-particle states:

$$\hat{a}^+_{r\sigma}=X^{\sigma,0}_r;\quad \hat{a}_{r\sigma}=X^{0,\sigma}_r;\quad \hat{p}^+_{ir\sigma}=\sum_\beta \hat{X}^\beta_r b^\beta_i;\quad \hat{p}_{ir\sigma}=\sum_\alpha \hat{X}^\alpha_r b^\alpha_i, \tag{3}$$

where b^α_i are parentage coefficients corresponding to a given α transition.

If the expectation values of n_s and n_t are no greater than one, it is sufficient to consider transitions between a vacant state and eight possible one-particle states. For $1<n_t<2$, we consider transitions between six one-particle states and nine ${}^3A_j^{s_z}$ states, each of which has $S=1$ and an energy ϵ_2. For $2<n_t<3$ we need to consider transitions between two-particle states and four three-particle states ${}^4A_2^{s_z}$, which have a maximum possible spin $S=3/2$ and an energy ϵ_3.

In the zeroth approximation of the Hubbard-1 self-consistent field,[4] the inverse Green's function is expressed in terms of the so-called end factors f_s and f_t, which are equal to the expectation values of the anticommutator of two conjugate Hubbard operators,[5] $\langle\{X_r^\alpha X_r^{-\alpha}\}\rangle$:

$$G_\omega^{-1}(p)=\begin{matrix} s \\ \alpha \end{matrix}\begin{pmatrix} s & \beta \\ \Omega_s-f_s\tau(p); & -f_s t_{(p)}^{(i)} b_i^\beta \\ -f_t^{(k)} t_{(p)}^{(j)} b_j^\alpha; & \delta_{\alpha\beta}\Omega_t^{(k)}-f_t^{(k)} b_j^\alpha t_{(p)}^{ji} b_i^\beta \end{pmatrix}. \tag{4}$$

The diagonal matrix elements are determined in terms of the energies of the one-particle excitations, ϵ_s and ϵ_t, and also in terms of the energy of the lowest-lying particle k states, ϵ_k:

$$\Omega_s=i\omega_n-\epsilon_s, \quad \Omega_t^{(k)}=i\omega_n-\epsilon_t^{(k)}, \quad \epsilon_t^{(-1)}=0, \tag{5}$$

where $\epsilon_t^{(k)}=\epsilon_{k+1}-\epsilon_t^{(k-1)}$, $k=0, 1...5$, and $\omega_n=(2n+1)\pi T$. For an infinite Hubbard energy, the end factors $f_t^{(k)}$ are linear functions of n_t. At the edges of each interval $k<n_t^{(k)}<1+k$ they are equal to the reciprocal of the degeneracy of the lowest k state or particle $k+1$ state:

$$\begin{aligned} &f_s^{(0)}=1-\frac{n_s}{2}, \quad 0<n_s<1; \quad f_t^{(0)}=1-\frac{5}{6}n_t, \quad 0<n_t<1; \\ &f_t^{(1)}=\frac{4-n_t}{18}, \quad 1<n_t<2; \quad f_t^{(2)}=\frac{5n_t-6}{36}, \quad 2<n_t<3. \end{aligned} \tag{6}$$

We find the other coefficients by means of particle-hole symmetry transformations: $n_t\to 2-n_s$; $n_t\to 6-n_t$; $k\to 5-k$.

We can find the relationship among the chemical potential $\mu=-(\epsilon_s+\epsilon_t^{(k)})/2$, the temperature, and the expectation values of the numbers of electrons per cell:

$$n_s=T\sum_{\omega,p,\sigma} f_s G_{\omega(p)}^{ss} e^{i\omega\delta}; \quad n_t=T\sum_{\omega,p,j,\sigma} f_t b_j^\alpha G_{\omega(p)}^{\alpha\beta} b_j^\beta e^{i\omega\delta}. \tag{7}$$

Going through the calculations for each integer interval $k<n_t^{(k)}<1+k$ and $n_s<1$, we find $n_s=2f_s\Sigma_{v,p}a_p^{(v)}n_F(\xi_p^{(v)})$,

$$n_t=k+g_{1+k}f_t^{(k)}\sum_{v,p} a_{jp}^{(v)} n_F(\xi_p^{(v)}). \tag{8}$$

Here $n_F(\epsilon)$ is the Fermi function, and g_k is the degeneracy of the k-particle t states:

$$g_0=g_6=1; \quad g_1=g_5=6; \quad g_2=g_4=9; \quad g_3=4. \tag{9}$$

The four branches of the energy spectrum $\xi_p^{(v)}$ are the eigenvalues of the following 4×4 matrix:

$$\begin{matrix} & 0 & (j) \\ 0 & & \\ (i) & & \end{matrix}\begin{pmatrix} E-\epsilon_s^0-f_s\tau_{(p)} & -f_s t_{(p)}^{(j)} \\ -\bar{f}_t^{(k)}t_{(p)}^{(i)}; & E-\epsilon_t^{(k)}-\bar{f}_t^{(k)}t_{(p)}^{ij} \end{pmatrix}. \tag{10}$$

In contrast with (4), this matrix is expressed in terms of the expectation values of the end factors, which are proportional to the sum of the squares of the parentage coefficients b_k^2: $\bar{f}_t^{(k)}=b_k^2 f_t^{(k)}$,

$$b_0^2=b_5^2=1; \quad b_1^2=b_4^2=3; \quad b_2^2=b_3^2=2. \tag{11}$$

The normal coordinates $a_{sp}^{(v)}$ and $a_{jp}^{(v)}$ depend on the energy of the excitations, $r_k=\epsilon_s-\epsilon_t^{(k)}$, but not on the chemical potential. We find the latter from electrical neutrality condition (1).

At an infinite Hubbard energy, the interaction of s and t excitations is manifested in a scattering and in a strong dependence of the scattering amplitude on the position of the Fermi level. We find the Cooper instability from the condition for the appearance of a singularity in the two-particle Green's function. In the ladder approximation the problem reduces to one of finding the conditions for the appearance of nonvanishing solutions of the homogeneous system of equations[6]

$$\Gamma_{\alpha\beta}=T\sum_{\omega,p} g_{\alpha\bar{\alpha};\beta\bar{\beta}}(p)G_{\omega(p)}^{\beta\gamma}G_{-\omega(-p)}^{\bar{\beta}\bar{\gamma}}\Gamma_{\gamma\bar{\gamma}}. \tag{12}$$

The indices α and $\bar{\alpha}$ distinguish transitions with opposite signs of the change in the spin projection. We find the components of the Green's function $G_\omega^{\alpha\beta}(p)$ in terms of inverse matrix (4). According to Dyson,[7] the scattering amplitude $g_{\alpha\bar{\alpha};\beta\bar{\beta}}$ is determined by the double commutation relations $\{X_r^\alpha[X_r^{\bar{\alpha}}H]\}$. It is ultimately expressed in terms of the structure constants $N_{\alpha,\beta}^{(\pm)}$ of the corresponding superalgebra:[8]

$$[X_r^\alpha, X_{r'}^\beta]_\pm=N_{\alpha,\beta}^{(\pm)}X_r^{\alpha+\beta}\delta_{r,r'}; \tag{13}$$

$$\hat{H}=\sum_{r,r'}{}' \{X_r^\alpha t_{(r,r')}^{\alpha\beta}X_{r'}^\beta+X_r^{\bar{\alpha}}t_{(r,r')}^{\bar{\alpha}\bar{\beta}}X_{r'}^{\bar{\beta}}\}; \tag{14}$$

$$[\bar{X}_r^\alpha, H]=\sum_{r,r'}[N_{\alpha,v}^{(+)}X_r^{\alpha+v}t_{(r,r')}^{v;\beta}X_{r'}^\beta+(v\to\bar{v};\beta\to\bar{\beta})]. \tag{15}$$

Finally, in the Born approximation (used below), and in the center-of-mass frame, we have

$$g_{\alpha\bar{\alpha};\beta\bar{\beta}}(p)=N_{\alpha,\beta-\bar{\alpha}-\alpha}^{(+)}N_{\bar{\alpha},\beta-\bar{\alpha}}^{(-)}t_{(p)}^{\bar{\beta}-\bar{\alpha}-\alpha,\beta}+N_{\bar{\alpha},\beta-\alpha-\bar{\alpha}}^{(+)}N_{\alpha,\beta-\alpha}^{(-)}t_{(-p)}^{\beta-\alpha-\bar{\alpha},\bar{\beta}}. \tag{16}$$

In our case we have $t_{(p)}^{\alpha\beta}=\Sigma_r b_k^\alpha t_{(r)}^{kj}b_j^\beta e^{ipr}$, so all possible components of $\Gamma_{\alpha\bar{\alpha}}$ differ only by factors $b_i^\alpha b_i^{\bar{\alpha}}$. For this reason, the results can be expressed in terms of normal coordinates and excitation energies determined by matrix (10). At a logarithmic accuracy, the superconducting transition temperature T_c can be written in BCS form: $T_c\propto\exp(-1/2\lambda_k)$, where

$$\lambda_k=-\frac{\epsilon_s}{f_s}\sum_{p,v}(a_{0p}^{(v)})^2\delta(\xi_p^{(v)})-\frac{\gamma_k\epsilon_t^{(k)}}{b_k^2 f_t^{(k)}}\sum_{jpv}(a_{jp}^{(v)})^2\delta(\xi_p^{(v)}). \tag{17}$$

We find the resultant amplitudes γ_k for each integer interval:

$$\gamma_0=-\gamma_5=1;\quad \gamma_1=-\gamma_4=\frac{1}{2};\quad \gamma_2=-\gamma_3=\frac{2}{3}. \tag{18}$$

A superconductivity exists if $\lambda_k>0$. The relation $\gamma_{5-k}=-\gamma_k$ means that there is a pronounced asymmetry with respect to the filling of the lower t_{1u} subband ($n_t<3$) and the upper one ($3<n_t<6$). Through equation of state (8), the condition $\lambda_k(\epsilon_s,\epsilon_t^{(k)})=0$ determines the boundary between the superconducting phase and the normal phase in terms of the variables n_s, n_t and at $T=0$. As the lower half of the t subband is filled ($k\leqslant 2$, $\gamma_k>0$), the condition $\lambda>0$ holds for the finite interval $k<n_{c1}<n_t^{(k)}<n_{c2}<1+k$, within which there is a negative amplitude for $(t-t)$ scattering. Superconductivity does not exist if the number of t electronic excitations is small, and we have $k\leqslant n_t^{(k)}<n_{c1}^{(k)}$. A second, fairly narrow interval, in which there is no superconductivity, exists at small values of n_s ($\epsilon_s>0$); it corresponds to $n_{c2}^{(k)}<n_t^{(k)}<1+k$. Here the contribution of the amplitude for the scattering of t excitations is canceled by the low density of states at the edge of the energy band which is characteristic of cubic crystals. With increasing density of s electrons, the positive-amplitude contribution of $(s-s)$ scattering increases, and it leads to a decrease in the size of the superconducting region. The lower critical density n_{c1} increases, while the higher one, n_{c2}, decreases in that region of the density n_s in which the amplitude for $(s-s)$ scattering is positive, and the lower half of the s band is filled.

In the upper half of the t band, for which we have $3<n_t<6$, and we have $\gamma_k<0$ for all k, a superconductivity can exist at small values of n_s only under the condition $\epsilon_t^{(k)}>0$. At $\epsilon_s>0$, the superconductivity disappears in the region $k<n_t^{(k)}<n_{c1}$, because of the small density of states at the lower edge of the energy band. Again at $n_{c2}<n_t^{(k)}<1+k$ there is no superconductivity, because of the small number of t-hole and s-electron excitations, with $\epsilon_t^{(k)}<0$, $\gamma_k<0$, $\epsilon_s>0$. With increasing density n_s, the lower critical density increases, while the higher one decreases, as long as the condition $\epsilon_s>0$ holds.

In the limit $n_s=0$ there is complete symmetry under the transformation $n_t\to 6-n_t$. All critical values are determined in terms of the sum $S_k=\Sigma_{v,\mathbf{p}}b_p^{(v)}\times\theta(-\epsilon_{tp}^{(v)})$, which is governed by the normal coordinates and the excitation energies of the t electrons at $\epsilon_t=0$ and $\epsilon_s\to\infty$:

$$n_c^{(k)}=k+g_{1+k}f_{tc}^{(k)}S_k. \tag{19}$$

The phase diagram is symmetric under a complete particle-hole transformation: $n_s\to 2-n_s$, $n_t\to 6-n_t$. For $n_s>1$, the phase diagram can thus be found through reflection in the point $n_t=3$, $n_s=1$.

If the number of t electrons is small, a superconductivity might have existed by virtue of a change in the sign of the amplitude for $(s-s)$ scattering, $1>n_s>2/3$.

However, as the density n_t increases, the superconductivity in this region disappears rapidly, because of the high degeneracy of the t states [see (9)].

The quantities of greatest interest are the values of n_s and n_t on the lines of electrical neutrality for the compounds K_3C_{60}, K_4C_{60}, and K_6C_{60}. At small values of n_s, the line $n_t+3n_s=3$ for K_3C_{60} lies entirely in the superconducting region. For the compounds K_4C_{60} and K_6C_{60}, according to (1), the lines of electrical neutrality run through regions with a small number of hole excitations, in which there is no superconductivity under the condition $n_s \ll 1$.

In summary, in the compounds studied here, as in all high-T_c superconductors, the extreme sensitivity of T_c to the dopant concentration is due entirely to a strong dependence of the amplitude for electron-electron scattering on the position of the Fermi level with respect to the middle of the conduction band. The characteristic energy which determines T_c is one of the jump intervals, equal to 10^3 K in order of magnitude. The dimensionless constant $2\lambda_k$ which appears in the exponential function, and which is given by (17), does not exceed 0.5. It depends strongly on the numbers of s and t electrons which are scattered with energies close to the Fermi level. All these facts are in qualitative agreement with experiments on A_xC_{60} compounds.

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