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ELECTRON CORRELATIONS IN DOPED FULLERIDES: EFFECTIVE HAMILTONIAN APPROACH

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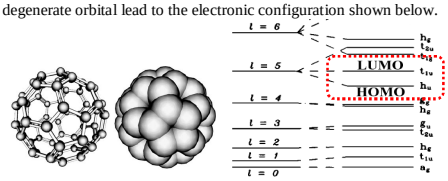
Introduction

Despite the intensive experimental and theoretical studies, the diversity of physical properties of doped fullerides remains unexplained at a microscopic level. Doped systems A_3C_{60} (where A=K, Rb, Cs) turn out to be metallic at low temperatures. According to the theoretical band structure calculations, fullerides with integer band-filling parameter n should be Mott-Hubbard insulators by electric nature, because all of them possess large enough values of intra-atomic Coulomb correlation parameter U. Doping of fullerene C_{60} with alkali metal leads to occurrence of metallic conductivity in fullerides, at low temperature a superconducting transition has been observed (T_c varying from 2.5 K for Na_2KC_{60} to 33 K for $RbCs_2C_{60}$)[1]. Metallic, insulating and superconducting phases have been obtained at different band fillings n ($0< n< 6$) of the lowest unoccupied molecular orbital (LUMO) in C_{60}.

Electronic states in C_{60}.

In single-particle approximation, neglecting electron correlations, the following spectrum has been calculated [2]: 50 of 60 p_z electrons of a neutral molecule fill all orbitals up to L=4. The lowest L=0,1,2 orbitals correspond to icosehedral states a_g, t_{1u}, h_g. All states with greater L values undergo the icosahedral-field splitting. There are 10 electrons in partially filled L=5 state. Icosahedral splitting (L=5 → h_u+t_{1u}+ t_{2u}) of these 11-fold degenerate orbital lead to the electronic configuration shown below.



Microscopic calculations and experimental data shows that the completely filled highest occupied molecular orbital is of h_u symmetry, and LUMO (3-fold degenerate) has t_{1u} symmetry.

The Hamiltonian of doped fulleride electronic subsystem

Within the second quantisation formalism, the Hamiltonian of interacting electrons (with spin-independent interaction $V^{ee}(r-r')$) in crystal field $V^{ion}(r)$, may be written as

$$H = H_0 + H_{int},$$

$$H_0 = \sum_s \int d^3r a_s^+(r)\left[-\frac{\hbar}{2m}\Delta + V^{ion}(r)\right]a_s(r),$$

$$H_{int} = \sum_{s,s'}\int d^3r \int d^3r' V^{ee}(r-r')\hat{n}_s(r)\hat{n}_{s'}(r').$$

Here $a_s^+(r)$, $a_s(r)$ are field operators of electron creation and annihilation, respectively, $\hat{n}_s(r) = a_s^+(r)a_s(r)$. Interaction integral of zeroth-order magnitude is on-site Coulomb correlation (characterized by Hubbard parameter U):

$$U = \iint |j_i(r-R_i)|^2 \frac{e^2}{|r-r'|}|j_i(r'-R_i)|^2 dr dr'$$

In orbitally degenerate system, the on-site (Hund's rule) exchange integral

$$J_H = \iint j_i^*(r-R_i)j_{i'}(r-R_i)\frac{e^2}{|r-r'|}j_{i'}^*(r'-R_i)j_i(r'-R_i)dr dr'$$

is of principal importance, too. The estimations for on-site energy parameters are given in table below.

U	0.8 – 1.3 eV	[3,4]
	1.4 – 1.6 eV	[5,6]
	1.3 eV	[7]
	2.7 eV	[8]
J_H	0.1-0.3 eV	[9]
	0.1 eV	[7]

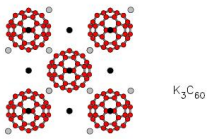
The relevant inter-site parameters are electron hopping integral

$$t_{ijl} = \int d^3r j_{il}^*(r-R_i)\left[-\frac{\hbar}{2m}\Delta + V^{ion}(r)\right]j_{jl}(r-R_i)$$

and inter-site exchange coupling

$$J(ilil'jlil') = \iint j_i^*(r-R_i)j_i(r-R_j)\frac{e^2}{|r-r'|}j_i^*(r-R_j)j_i(r-R_i)dr dr'$$

Estimations of bare half bandwidth (w=2$z|t|$, z being the number of nearest neighbors to a site, t is the nearest neighbor hopping integral) and inter-site exchange parameters are given below.

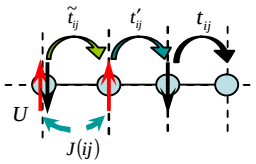


w	0.5-0.6 eV	[2]
	0.6 eV	[7]
J	0.05 eV	[7]

The resulting Hamiltonian of doped fulleride electronic subsystem reads as

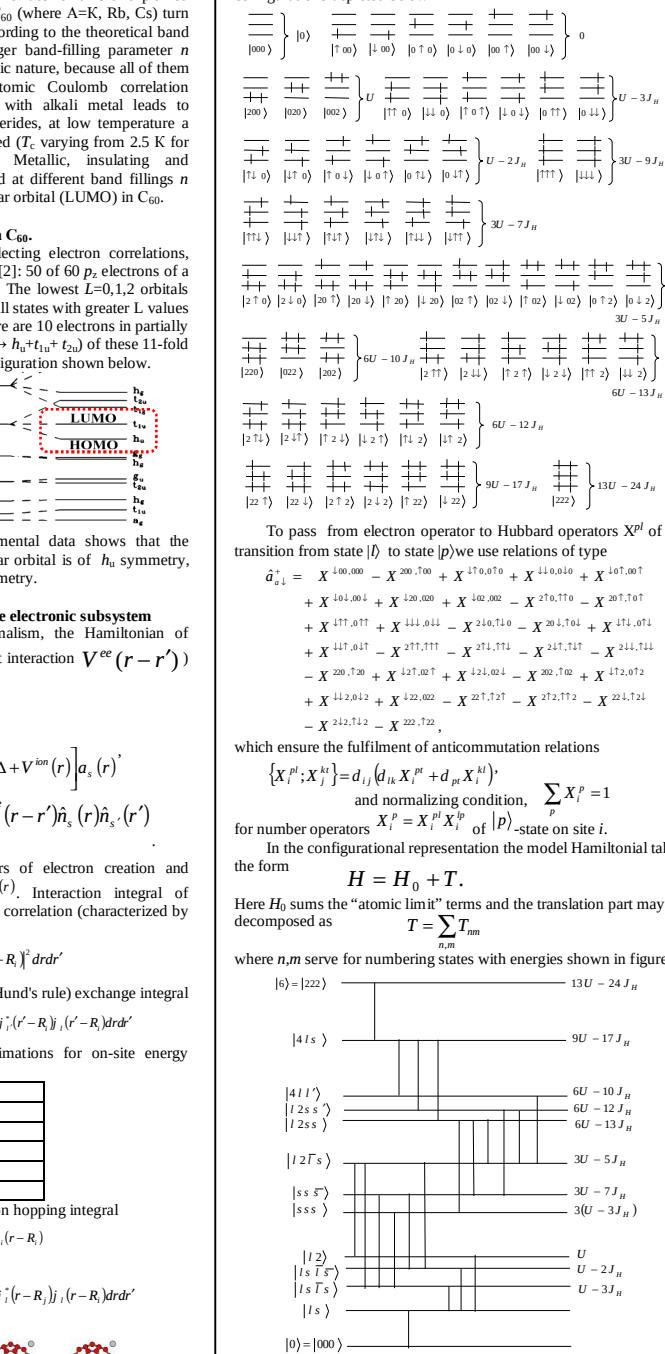
$$H = -m\sum_{ils} a_{ils}^+ a_{ils} + U\sum_{il} n_{il\uparrow}n_{il\downarrow} + \frac{U'}{2}\sum_{ils} n_{ils}n_{il's} + \frac{(U'-J_H)}{2}\sum_{ill's} n_{ils}n_{il's}$$
$$+ \sum_{ijls}{}' t_{ij}(n) a_{ils}^+ a_{jls} + \sum_{ijll's}{}' \left(t'_{ij} a_{ils}^+ a_{jls} n_{il\bar{l}} + h.c.\right) + \sum_{ijls}{}' \left(t''_{ij} a_{ils}^+ a_{jls} n_{il\bar{s}} + h.c.\right)$$
$$+ \frac{1}{2}\sum_{ijlss'} J(ij) a_{ils}^+ a_{jls'}^+ a_{ils} a_{jls},$$

where $U' = U - 2J_H$ and hopping integrals t'_{ij}, t''_{ij} taking into account the correlated hopping of electrons are introduced.



Configurational representation of the Hamiltonian

In a model of triply degenerate band, every site can be in one of 64 configurations depicted below



To pass from electron operator to Hubbard operators X^{pl} of site transition from state $|l\rangle$ to state $|p\rangle$we use relations of type

$$\hat{a}_{a\downarrow}^+ = X^{\downarrow 00,000} - X^{200,\uparrow 00} + X^{\downarrow\uparrow 0,0\uparrow 0} + X^{\downarrow\downarrow 0,0\downarrow 0} + X^{\downarrow 0\uparrow,00\uparrow}$$
$$+ X^{\downarrow 0\downarrow,00\downarrow} + X^{\downarrow 20,020} + X^{\downarrow 02,002} - X^{2\uparrow 0,\uparrow\uparrow 0} - X^{20\uparrow,\uparrow 0\uparrow}$$
$$+ X^{\downarrow\uparrow\uparrow,0\uparrow\uparrow} + X^{\downarrow\downarrow\downarrow,0\downarrow\downarrow} - X^{2\downarrow 0,\uparrow\downarrow 0} - X^{20\downarrow,\uparrow 0\downarrow} + X^{\downarrow\uparrow\downarrow,0\uparrow\downarrow}$$
$$+ X^{\downarrow\downarrow\uparrow,0\downarrow\uparrow} - X^{2\uparrow\uparrow,\uparrow\uparrow\uparrow} - X^{2\uparrow\downarrow,\uparrow\uparrow\downarrow} - X^{2\downarrow\uparrow,\uparrow\downarrow\uparrow} - X^{2\downarrow\downarrow,\uparrow\downarrow\downarrow}$$
$$- X^{220,\uparrow 20} + X^{\downarrow 2\uparrow,02\uparrow} + X^{\downarrow 2\downarrow,02\downarrow} - X^{202,\uparrow 02} + X^{\downarrow\uparrow 2,0\uparrow 2}$$
$$+ X^{\downarrow\downarrow 2,0\downarrow 2} + X^{\downarrow 22,022} - X^{22\uparrow,\uparrow 2\uparrow} - X^{2\uparrow 2,\uparrow\uparrow 2} - X^{22\downarrow,\uparrow 2\downarrow}$$
$$- X^{2\downarrow 2,\uparrow\downarrow 2} - X^{222,\uparrow 22},$$

which ensure the fulfilment of anticommutation relations

$$\left\{X_i^{pl};X_i^{kt}\right\} = d_{ij}\left(d_{lk}X_i^{pt} + d_{pt}X_i^{kl}\right),$$

and normalizing condition, $\sum_p X_i^p = 1$

for number operators $X_i^p = X_i^{pl}X_i^{lp}$ of $|p\rangle$-state on site i.

In the configurational representation the model Hamiltonial takes the form

$$H = H_0 + T.$$

Here H_0 sums the "atomic limit" terms and the translation part may be decomposed as $T = \sum_{n,m} T_{nm}$

where n,m serve for numbering states with energies shown in figure.

Terms of T_{nm} Hamiltonians form the energy subbands and terms of T_{nn} describe the hybridization of these subbands. Different hopping integrals correspond to transitions in (or between) the different subbands. The subbands of higher-energy processes appear to be narrower due to the correlated hopping of electrons. The relative positions and overlapping of the subbands depends on the relations between the energy parameters. At integer values of electron concentration (n=1, 2, 3, 4, 5) in the system the metal-insulator transition is possible.

Partial case of band integer filling n=1

$$H = H_0 + \sum_{l=a,b,g}\left(H_b^{(l)} + H_h^{(l)}\right) + H_{ex}$$

$$H_0 = -m\sum_{is}\left(X_i^{s\,00} + X_i^{0s\,0} + X_i^{00s} + 2\left(X_i^{ss\,0} + X_i^{s\,0s} + X_i^{0ss}\right)\right) +$$
$$+ (U-3J)\sum_{is}\left(X_i^{ss\,0} + X_i^{s\,0s} + X_i^{0ss}\right) \qquad \textbf{\textit{"atomic limit"}}$$

$$H_b^{(a)} = \sum_{ij}\left(\tilde{t}_{ij}X_i^{s\,00,000}X_j^{000,s\,00} + \tilde{t}_{ij}X_i^{ss\,0,0s\,0}X_j^{0s\,0,ss\,0} +\right.$$
$$+ \tilde{t}_{ij}X_i^{s\,0s\,,00s}X_j^{00s\,,s\,0s} + \tilde{t}_{ij}X_i^{ss\,0,0s\,0}X_j^{00s\,,s\,0s} +$$
$$\left.+ \tilde{t}_{ij}X_i^{s\,0s\,,00s}X_j^{0s\,0,ss\,0}\right) \qquad \textbf{\textit{"subbands"}}$$

$$H_h^{(a)} = \sum_{ij}\left(t'_{ij}\left(X_i^{s\,00,000}X_j^{0s\,0,ss\,0} + X_i^{ss\,0,0s\,0}X_j^{000,s\,00} +\right.\right.$$
$$\left.\left.+ X_i^{s\,00,000}X_j^{00s\,,s\,0s} + X_i^{s\,0s\,,00s}X_j^{000,s\,00}\right)\right) \qquad \textbf{\textit{"hybridization"}}$$

$$H_{ex} = -\sum_{ijl\bar{l}s} J(ij)\left(0.5X_i^{ls} + X_i^{ls\bar{l}s}\right)\left(0.5X_j^{ls} + X_j^{ls\bar{l}s}\right) - \sum_{ijls} J(ij)X_i^{ls,l\bar{s}}X_i^{l\bar{s},ls}$$

"direct exchange"

Canonical transformation.

We use a variant of the method proposed in paper [10] and apply a canonical transformation

$$\tilde{H} = e^S H e^{-S}$$

To obtain effective form of the Hamiltonian

$$\tilde{H} = H_0 + H_b + H_{ex} + \left([SH_0] + H_h\right) + [SH_b] + [SH_h] + \frac{1}{2}[S[SH_0]] + \mathbf{K}$$

Where the form of S is chosen to exclude hybridization processes

$$S = -\sum_{ijs}\frac{t_{ij}}{(U-3J_H)^2}\left(X_i^{s\,00,000}X_j^{0s\,0,ss\,0} +\right.$$
$$+ X_i^{s\,00,000}X_j^{00s\,,s\,0s} - X_i^{ss\,0,0s\,0}X_j^{000,s\,00} - X_i^{s\,0s\,,00s}X_j^{000,s\,00} +$$
$$+ X_i^{0s\,0,000}X_j^{00s\,,s\,0s} - X_i^{0s\,0,000}X_j^{00s\,,ss\,0} - X_i^{0ss\,,00s}X_j^{000,0s\,0} +$$
$$+ X_i^{ss\,0,s\,00}X_j^{000,0s\,0} - X_i^{00s\,,000}X_j^{s\,00,s\,0s} - X_i^{00s\,,000}X_j^{0s\,0,0ss} +$$
$$\left.+ X_i^{s\,0s\,,000}X_j^{000,00s} + X_i^{0ss\,,0s\,0}X_j^{000,00s}\right)$$

After the canonical transformation, effective Hamiltonian reads as

$$\tilde{H} = H_0 + \sum_{l=a,b,g} H_b^{(l)} + H_{ex} + \tilde{H}_{ex}$$

where the last term represents "indirect exchange" interaction

$$\tilde{H}_{ex} = -\sum_{ijl\bar{l}s}\tilde{J}(ij)\left(X_i^{ls}X_j^{\bar{l}s} + X_i^{ls,l\bar{s}}X_i^{l\bar{s},ls} + X_i^{000}X_i^{ls\bar{l}s}\right)$$

with indirect exchange integral $\tilde{J}(ij) = \frac{2\left(t'_{ij}(n)\right)^2}{U-3J_H}$

$\tilde{J}(ij)$ is of the same order of magnitude as direct exchange integral $J(ij)$ and can enhance considerably ferromagnetic tendencies.

Strong correlation limit

In the limit of strong on-site correlation limit $U - 3J_H >> w$ at partial band filling 0<n<1 one has

$$H_{ex} = -\sum_{ijl\bar{l}s} J(ij)\left(X_i^{ls}X_j^{ls} + X_i^{ls,l\bar{s}}X_i^{l\bar{s},ls}\right)$$

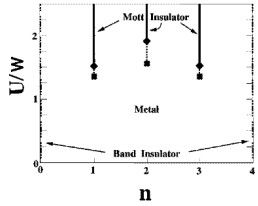
$$\tilde{H}_{ex} = -\sum_{ijl\bar{l}s}\tilde{J}(ij)\left(X_i^{ls}X_j^{\bar{l}s} + X_i^{ls,\bar{l}s}X_i^{\bar{l}s,ls}\right)$$

One can see that in triply degenerate model indirect exchange is of ferromagnetic nature, in contrast to standard "non-degenerate" t-J model

Possible metal-insulator transition in the model

- The obtained effective Hamiltonians allow to classify processes of subbands formation and hybridization, to discover mechanisms of electron localization and possible magnetic ordering stabilization.
- For an explanation of a metallic behaviour of Mott-Hubbard system A_3C_{60} (x=3 corresponds to the half-filled conduction band) three-fold degeneracy of energy levels and Hund's rule coupling has to be properly taken into account.
- The metal-insulation transition in the model is possible also under external pressure (which case is realized, e.g., in Rb_4C_{60}).

Peculiar concentrational behaviour of electrical conductivity in fullerides A_nC_{60} may be an analog to those of dihalcohenides series. For example, within DMFT approach for doubly degenerate band the critical values of correlation parameter depend on band filling [11]. Critical values, obtained [12] within Gutzwiller approximation are $U_c/2w$~2,8 for twofold degenerate half-filled band, $U_c/2w$ ~3,9 for threefold degenerate half-filled band. Correlated hopping also modifies the metal-insulator transition conditions.



References

1. А.В. Елецкий, Б.М. Смирнов УФН, **165**, 977, 1995.
2. N. Manini, E. Tosatti. E-print cond-mat/0602134.
3. M.R. Pederson and A.A. Quong. Phys. Rev. B. **46**, 13584, 1992.
4. V.P. Antropov et al. Phys. Rev. B. **46**, 13647, 1992.
5. R.W. Lof et al. Phys. Rev. Lett. **68**, 3924, 1992.
6. P.A. Brühwiler et al. Phys. Rev. B. **48**, 18296, 1993.
7. R.L. Martin and J.P. Ritchie // Phys. Rev. B. **48**, 4845, 1993.
8. R.L. Hettich et al. Phys. Rev. Lett. **67**, 1242, 1991.
9. R.W.Lof et al. Phys. Rev. Lett. **68**, 3924, 1992.
10. L.Didukh and O.Kramar. Condens. Matter Phys., **8**, 547, 2005.
11. M.J. Rozenberg. Phys. Rev. B. **55**, R4855, 1997.
12. Jian Ping Lu. Phys. Rev. B. **49**, 5687, 1994.