Strong Correlations in Electron Doped Phthalocyanine Conductors Near Half Filling

Erio Tosatti,1,2 Michele Fabrizio,3,2 Jaroslav Tóbiek,1 and Giuseppe E. Santoro1,2

1International School for Advanced Studies (SISSA),
and INFM Democritos National Simulation Center, Via Beirut 2-4, I-34014 Trieste, Italy
2International Centre for Theoretical Physics (ICTP), P.O.Box 586, I-34014 Trieste, Italy
3International School for Advanced Studies (SISSA), Via Beirut 2-4, I-34014 Trieste, Italy

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We propose that electron doped nontransition metal-phthalocyanines (MPcs) like ZnPc and MgPc, similar to those very recently reported, should constitute novel strongly correlated metals. Due to orbital degeneracy, Jahn-Teller coupling and Hund’s rule exchange, and with a large on-site Coulomb repulsion, these molecular conductors should display, particularly near half filling at two electrons/molecule, very unconventional properties, including Mott insulators, strongly correlated superconductivity, and other intriguing phases.

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Building novel metals by doping molecular crystals such as polyacetylene, fullerenes, TTF-TCNQ, (TMTSF)$_2$X, (TMTSF)$_2$X and (BEDT-TTF)$_2$X salts, etc., is a well trodden route [1, 2], but remains an exciting and ever moving front. Very recently the Delft group showed that thin films of transition metal phthalocyanines (MPcs) FePc, CoPc, NiPc, CuPc, initially insulating, can be turned genuinely metallic through potassium doping [3]. Electron doping appears to take place largely in the twofold degenerate lowest unoccupied $e_g$ molecular orbital (LUMO) $\mathbf{1}$ of the molecules. The simplest rigid band model naturally explains, according to $\mathbf{3}$, why the MPcs, initially insulating when pristine ($n = 0$) $\mathbf{3}$, become metallic upon increasing doping ($0 < n < 4$), ending up again as insulators at full doping ($n = 4$). It is not yet clear whether stoichiometric compound phases may exist here as they do in alkali doped fullerides, but there is an otherwise striking overall analogy, to the point that even the conductance values reported at optimal doping are similar to those very recently reported, should constitute novel strongly correlated metals. Due

\[ H \approx \frac{U}{2} \sum_i \hat{n}_i^2 + \frac{J}{2} \left( \hat{\tau}_{i,x}^2 + \hat{\tau}_{i,y}^2 \right) + g \left( \hat{q}_{i,1} \hat{\tau}_{i,x} + \hat{q}_{i,2} \hat{\tau}_{i,y} \right) + \frac{\hbar \omega_0}{2} \left( \hat{\tau}_{i,1}^2 + \hat{\tau}_{i,2}^2 \right), \]

where $\hat{n}_i$ is the overall occupation at site $i$, $\hat{\tau}_{i,\alpha}$, with $\alpha = x, y, z$, are pseudo-spin operators spanning the twofold degeneracy $\hat{\tau}_{i,\alpha} = \sum_{a,b=1}^{2} \sum_{\sigma} c_{i,\alpha \sigma} \left( \tau^a \right)_{ab} c_{i,b \sigma}$,
where $\tau^\alpha$ are Pauli matrices. Here $c_{i,a,\sigma}^\dagger$ denotes creation of electrons with spin $\sigma$ at site $i$ in orbital $a = 1, 2$ of the LUMO $e_g$ doublet. The last two terms in $\mathcal{H}$ describe JT coupling of strength $g$ to a doubly degenerate vibration with frequency $\hbar \omega_0$, coordinates $q_{i,1}$ and $q_{i,2}$ and momenta $p_{i,1}$ and $p_{i,2}$, where $E_{JT} = 8g^2/\hbar \omega_0$. A single but degenerate mode is assumed as a simplifying approximation, replacing the actual 14 pairs of nondegenerate JT modes $B_{1g}$ and $B_{2g}$ allowed by the MPc $D_{4h}$ symmetry. As detailed in note 11 an estimate of parameters appropriate to MPcs such as ZnPc, MgPc indicates $U \sim 1$ eV and, for $n = 2$, a singlet energy gain $E_{JT} - 4|J| \sim 0.06-0.07$ eV over Hund’s rule triplet. This prevalence of singlet over triplet, the main ingredient potentially leading to s-wave superconductivity, could be mitigated or even reversed in a solid state compound; we shall therefore examine both possibilities in the rest of this paper.

In the MPc molecular crystal, electrons can quantum mechanically hop between neighboring sites

$$\hat{H}_{\text{hop}} = \sum_{ij} \sum_{\nu,\sigma} \sum_\sigma t_{ij,\nu}^\dagger c_{i,\sigma}^\dagger c_{j,\sigma} + \sum_{ij} \sum_{\nu,\sigma} \sum_\sigma t_{ij,\nu} \sigma c_{i,\nu}^\dagger c_{j,\sigma} \, .$$

(2)

Assuming first a generic three-dimensional structure with $\nu$ neighboring molecules and a weak isotropic first-neighbor hopping $t$, the LUMO $e_g$ orbitals will give rise to a pair of narrow molecular bands of width $W = 2|t|\nu$. (We will discuss the additional signature of a quasi-one-dimensional structure of these compounds in the final part of the paper.) Before doping we generally expect a narrow band $W \sim 0.3$ eV (see below), due to very weak van der Waals bonding between molecules. While $W$ will eventually depend on the intermolecular geometry, including the way that may be altered by doping, we will assume $W$ to remain of approximately the same magnitude after doping. In addition to 11 and 12 we should in principle include additional terms such as the dispersion of vibrations (to account for the coupling between the JT distortion of a molecule and those of other molecules), inter-molecular electron-electron interactions, and more.

We will presently neglect them, concentrating on the basic Hamiltonian

$$\hat{H} = \hat{H}_{\text{hop}} + \sum_i \hat{H}_{i,\text{mol}} \, .$$

(3)

Because $U/W$ is large, and for $n \sim 2$, this system is generally close to a Mott transition. There, the quasiparticle band is very narrow and it is a good approximation to neglect retardation, replacing 12 with

$$\hat{H}_{i,\text{mol}} \to \frac{U}{2} \hat{\rho}^2_i + \frac{J_{\text{eff}}}{2} (\hat{\tau}^2_{x,i} + \hat{\tau}^2_{y,i}) \, ,$$

(4)

where $J_{\text{eff}} = J - E_{JT}/4$.

The further simplifying assumption of nearest-neighbor hopping that are diagonal in the orbital indices 11 brings this Hamiltonian to coincide with that recently studied by Dynamical Mean Field Theory (DMFT) 12 in Refs. 5, 8. Close to $n = 2$ it was shown to display a rich phase diagram including, besides the regular metal, a Mott insulator, a strongly correlated superconductor, and a pseudo-gap metal. Within DMFT, the lattice model 13 is mapped onto an Anderson impurity self-consistently coupled to a conduction electron bath 12. The many-body physics of the Anderson impurity and its fixed points foreshadow that of the infinite many-body system 4, as confirmed by the calculated DMFT phase diagram 5, 8. We exploit here these results to analyse the implications for the phase diagram of half-filling doped MPcs considering both possibilities, namely: (i) singlet ground state or (ii) triplet ground state.

(i) $J_{\text{eff}} < 0$ – The $n=2$ molecular ground state is a non degenerate spin singlet accompanied by a dynamical Jahn-Teller effect. If in the solid $U/W$ is larger than the critical Mott value (between 1 and 2, depending in detail on $J$ and $E_{JT}$) the half filled MPc will realize a non-magnetic, singlet Mott insulator 13. For $U$ just below that value, or for light doping away from $n=2$, the MPc solid will be lightly metallic. In this “doped Mott insulator” regime the Anderson impurity displays instabilities against symmetry-broken phases in both particle-particle and particle-hole channels; which instability will eventually win out depends on band-structure and coupling details. If nesting or other band structure singularities are absent or very weak, the particle-particle instability should dominate leading to an s-wave superconductor with order parameter

$$\Delta_{\text{SC}} = (c_{11}^\dagger c_{21}^\dagger + c_{12}^\dagger c_{12}^\dagger) \neq 0 \, .$$

(5)

This state is a strongly correlated superconductor (SCS) of a kind first pointed out in Ref. 14, further confirmed in the two band model in Refs. 5, 8. It was also suggested 5, 14 – although without a calculation of $T_c$ – that SCS is a “high temperature superconductor” in the sense that the SCS superconducting gap may reach values several orders of magnitudes greater than the corresponding BCS value (that would be attained for $U = 0$), $\Delta_{\text{BCS}} \sim \hbar \omega_0 e^{-1/\lambda}$, where $\lambda = 2\rho_0 |J_{\text{eff}}|$, $\rho_0$ is the density of states at the Fermi level per spin and band.

If, on the contrary, the particle-hole instability channel was favored by some detail of the band structure such as Fermi surface nesting, then one of two alternative symmetry-broken phases can be expected. The first is a trivial one, with order parameter

$$\Delta_{\text{JT}} = \cos \phi \langle \hat{\tau}_x \rangle + \sin \phi \langle \hat{\tau}_y \rangle \neq 0 \, ,$$

(6)

corresponding to a cooperative Jahn-Teller distorted
state, either modulated or uniform, the angle \( \phi \) reflecting \( U(1) \) orbital symmetry breaking. The model in fact possesses \( O(2) \) orbital symmetry, which naturally decomposes into \( Z_2 \otimes U(1) \). \( Z_2 \) is the discrete symmetry \( \tau_z \rightarrow -\tau_z \), while \( U(1) \) represents invariance under rotations around the pseudo-spin z-axis. As a consequence of the static cooperative Jahn-Teller distortion, a conventional insulating band gap or at least a strong lowering of metallic density of states should take place at the Fermi level. More interesting is the alternative instability, associated with a different order parameter in the particle-hole channel

\[
\Delta_{PT} = \sum_{\alpha \beta} \langle c_{1\alpha}^\dagger \sigma_{\alpha \beta} \cdot \vec{S} c_{1\beta} \rangle - \langle c_{2\alpha}^\dagger \sigma_{\alpha \beta} \cdot \vec{S} c_{2\beta} \rangle \neq 0 \, , \quad (7)
\]

breaking both orbital \( Z_2 \) and spin \( SU(2) \) symmetry, \( \vec{S} \) being the direction along which the spin \( SU(2) \) symmetry is broken. We note that the LUMO \( e_g \) orbitals are mainly localized onto the MPc four N-atom ring and have odd parity with respect to the central metal ion. Therefore the discrete \( Z_2 \) symmetry translates into parity in MPcs, whence \( \Delta_{PT} \neq 0 \) represents a spin current flowing on the Pc ring, a very intriguing possibility. This kind of phase should be either insulating or a poor metal like the cooperative JT phase. Unlike the latter, it should break both time reversal and parity, conserving only the \( \text{C}_{1h} \) symmetry. 

(ii) \( J_{\text{eff}} > 0 \) – In this case (less likely in MPcs than (i), as said above) the isolated \( n = 2 \) molecular ion is a spin triplet. The strongest instability here is towards bulk magnetism, ferro or antiferro depending on the band structure, a state which may or may not be accompanied by parity-symmetry breaking or by a Jahn-Teller distortion. If (depending on lattice structure) magnetism was sufficiently frustrated, then it would be possible for spin-triplet superconductivity to appear with order parameter

\[
\Delta_{SC} = \langle c_{1\uparrow}^\dagger c_{2\uparrow} - c_{\downarrow}^\dagger c_{1\downarrow} \rangle \neq 0 \, . \quad (8)
\]

Since orbitals 1 and 2 have opposite parity, this translates into a \( p \)-wave spin-triplet superconducting order parameter. This is an interesting possibility since, at variance with conventional \( p \)-wave superconductors, the pairing function is nonzero on the molecule. According to the DMFT analysis of Ref. [8], where this kind of triplet superconductor was first discussed, this superconducting instability is also enhanced by the proximity of a Mott insulating phase, although not as dramatically as in case (i).

Much of the uncertainty in the above scenario depends on our ignorance of the doped MPc film crystal structure, so far treated generically. A second guess based on the crystal structure of pristine MPcs suggests that the alkali doped crystals could, similar to the undoped alpha-

phase of the CuPc films [8], be made up of quasi-one-dimensional (1D) chains. We carried out density functional electronic structure calculations of MgPc assuming an alpha phase structure with \( n = 0 \) [10], and found an intra-chain \( e_g \) bandwidth \( W \sim 0.3 \text{ eV} \) but an inter-chain bandwidth between one and two orders of magnitude narrower (see Fig. 1). If doped MPcs were indeed this close to 1D, then our earlier DMFT-based analysis, valid for the opposite limit of large coordination lattices, should be replaced by another where the additional effect of quantum fluctuations and other 1D specific anomalies are properly treated.

We studied this 1D model by adapting the two-loop renormalization group (RG) equations derived by Ref. [17] to the two-band model. The fixed point Hamiltonian towards which the model flows under RG was analyzed by means of bosonization [18, 19]. At strict half-filling we found a spin-gapped insulator for any value of \( U \). However, for large \( U \), this was a spin-liquid Mott insulator, i.e. a spin-gapped phase without any symmetry breaking. That corresponds either to the DMFT singlet Mott state found with \( J_{\text{eff}} < 0 \), or to a Haldane spin-1 chain for \( J_{\text{eff}} > 0 \). Here, the DMFT metallic phase at small \( U \) is replaced by a spontaneously dimerized insulator, i.e. a spin-gapped phase with broken translational symmetry, for either sign of \( J_{\text{eff}} \). Away from half-filling the model turns metallic: nonetheless we find that the spin-gap survives. In particular, in the large \( U \) regime likely pertinent to the MPcs, the spin-liquid Mott insulator at \( J_{\text{eff}} > 0 \) turns at low doping into a spin-gapped metal with dominant fluctuations in the SC singlet channel [8] and sub-dominant fluctuations in the particle-hole channel. 

![FIG. 1: Density functional electronic band structure of undoped \( \alpha \) structure MgPc. The molecular stack direction is \( \Gamma - Y \). The crystal structure was taken from Ref. [20]. The monoclinic cell (a = 26.29, b = 3.818, c = 23.92\AA, \( \beta = 94.6^\circ \)) contains four molecules and has symmetry \( \text{C}2/n \).](image-url)
Weak but nonzero interchain interactions will in a hypo-
theoretical doped MPc with alpha phase-like structure
turn all these instabilities into properly long-range or-
dered phases at sufficiently low temperatures. While our
present state of ignorance prevents further in depth dis-
tuction, the expected emerging scenario is parallel to that
obtained by DMFT, apart from those differences specific
to 1D, like dimerization at $n = 2$ or the persistence of a
spin gap away from half-filling for regular Hund’s rules.

Summarizing, we conclude first of all that stoichiomet-
ically doped nontransition MPcs should display Mott in-
sulating phases at all integer fillings, in particular at half
filling. Analysis of a simple model \[11\] revealed a stunning
variety of phases in the immediate neighborhood of the
Mott metal-insulator transition near half filling. The
variety is greater than either that predicted for the three
band case fullerenes \[14\], or that experimentally known in fullerides \[2\] as well as in doped organics (with lower
symmetry than MPcs) near half filling \[1\].

Many of the phases described above will individually
merit an in-depth study. At the theoretical level, ap-
proximations will need to be improved, for example by
treating properly the non-degeneracy of the
approximations will need to be improved, for example by
exploring long-range spin-triplet superconducting correla-
tions. Indeed, in 1D the leading SC fluctuations appear in
a spin-singlet orbital-singlet but space-odd particle-
particle channel \[12\].

The weakly-doped spin-1 chain at $J_{eff} < 0$ feels on the contrary more
the effects of the reduced dimensionality which causes the
spin gap to survive in the metallic phase, hence pre-
vailing long-range spin-triplet superconducting correla-
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4$\hbar F$ channels identified by Ref. \[9\]. The weakly-doped
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In most MPcs described in Ref. \[8\], there is a partly
filled $d$-level. Strongly localized and with a large on-site
Coulomb repulsion, that constitutes a nontrivial mag-
etic complication. The potentially interesting interplay
of metallic conduction in the LUMO with these localized
$d$ electrons is beyond the scope of this work.

$\text{MnPc}$, $\text{FePc}$, $\text{CoPc}$ and $\text{CuPc}$ are open shell molecules
\[4\], so that the pristine parent insulators must themselves
consist of (single-band) Mott-Hubbard insulators.

While the diagonal hopping approximation is not partic-
ularly realistic in the present context, it does not change
the nature of the problem, and provides useful physical
understanding for application to the doped MPcs.

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A_1 - A_2$, where $E_n$ is the total energy of the molecular ion
with $n$ electrons, and $A_n$ its electron affinity. Calculations
for isolated ZnPc$(-n)$ and MgPc$(-n)$ $\[1\]$ find $A_1 \sim 3.7$ eV
and $A_2 \sim 0.7$ eV, whence $U \sim 3$ eV, essentially identical
to that of fullerene in vacuum $\[2\]$. In crystalline MPcs
the screening could be similar to that of fullerene $\[2\]$
suggesting $U = 1 \div 1.5$ eV as a crude estimate. Fits of the
multiplet spectra of ZnPc $\[2\]$ suggest that in the
LUMO $e_\gamma$ orbitals $\|J\|$ could be $\approx 0.15\div0.2$ eV. DFT cal-
culations of ZnPc$(-2)$ and MgPc$(-2)$ yield singlet ground
states, with $E_{JT} - 4|J| \sim 0.06$ and 0.07 eV respectively $\[3\].$
Resonance studies on ZnPc$(-2)$ and MgPc$(-2)$ in solution
$\[4\]$, confirms that these dianions could indeed be singlets.
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