Field-doping of C$_{60}$ crystals: A view from theory

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Abstract. The proposal of using the field-effect for doping organic crystals has raised enormous interest. To assess the feasibility of such an approach, we investigate the effect of a strong electric field on the electronic structure of C$_{60}$ crystals. Calculating the polarization of the molecules and the splittings of the molecular levels as a function of the external field, we determine up to what field-strengths the electronic structure of C$_{60}$ stays essentially unchanged, so that one can speak of field-effect doping, in the sense of putting charge carriers into otherwise unchanged states. Beyond these field strengths, the electronic structure changes so much, that one can no longer speak of a doped system. In addition, we address the question of a metal-insulator transition at integer dopings and briefly review proposed mechanisms for explaining an increase of the superconducting transition temperature in field-doped C$_{60}$ that is intercalated with haloform molecules.

The doped fullerenes are materials with very interesting properties. Alkali doped C$_{60}$ with three alkalis per molecule has, e.g., turned out to be metallic, though close to a Mott transition, and superconducting. A problem is, however, that different doping levels can only be realized by preparing separate crystals. Moreover, because of the strong electronegativity of C$_{60}$, no hole-doping has been achieved. In this context the proposal of using a field-effect transistor for doping pristine C$_{60}$ crystals has raised much interest, in particular since such an approach should allow us to continuously change the doping by simply changing the voltage applied to the gate electrode. Sadly the reports of such field-doping and of spectacular values for the superconducting transition temperatures in such devices [1, 2, 3] have been withdrawn [4] after an investigation showed that the publications were based on fraudulent data [5]. Nevertheless, it is an open question whether field-doping of C$_{60}$ crystals could be achieved in principle. In the following we address several aspects of this question.

EFFECT OF A STRONG ELECTRIC FIELD

Reaching substantial charging (of the order of $n$ electrons per C$_{60}$ molecule) in a field-effect device requires enormous electric fields. As the induced charge is basically restricted to one monolayer of C$_{60}$ [6], a rough estimate can be obtained from simple electrostatics: For neutrality the charge on the gate must equal that on the monolayer, hence the field originating from the gate electrode is given by $E_{\text{gate}} = 2\pi n/A_{\text{mol}}$, where $A_{\text{mol}}$ is the area per C$_{60}$ molecule in the monolayer and $n$ is the number of induced electron charges per molecule. Thus the external field is about 1 V/Å per induced charge, corresponding to a voltage drop of about 10 V across the molecule. In such a strong
FIGURE 1. Splitting of the molecular levels in the self-consistent multipole field ($l \leq 2$) for a (001) monolayer (square lattice) of C$_{60}$ molecules oriented such that one of their two-fold axes points in the direction of the external electric field (perpendicular to the layer).

external field the C$_{60}$ molecules are strongly polarized. Nevertheless, we find that their response is still in the linear regime. Furthermore, in the charged monolayer, the field experienced by a molecule is screened by the polarization of the neighboring molecules. Taking this into account, we find that the field is reduced by about a factor of two. Calculating the splitting of the molecular levels in this screened homogeneous field, we find a quadratic Stark effect, with the splitting of both, the $t_{1u}$ and the $h_u$ level, becoming of the order of the band-width for a field corresponding to an induced charge of three to four charges per molecule. This seems to be consistent with the typical doping levels that had been reported.

For a more realistic description of the electrostatics in the field-effect device, we have, however, to go beyond considering only a homogeneous field. Given the spherical shape of C$_{60}$, the natural approach is via a multipole expansion [7]: We choose an external field and the corresponding induced charge per molecule. We determine the multipole expansion of the field generated by all other molecules about the molecule centered at the origin. Using the linear response of a C$_{60}$ molecule to multipole fields (calculated ab initio), we determine the new charge distribution on the molecules and repeat the procedure until self-consistency is reached.

Figure 1 shows the splitting of the molecular levels in the self-consistent multipole field for different doping levels. While for an external homogeneous field ($l = 1$ multipole) the splitting is independent of the direction of the field, including the effect of the induced charge on the neighboring molecules breaks this symmetry. Surprisingly, the asymmetry in the splitting is quite strong, even though the fields that break the symmetry are fairly weak compared to the homogeneous field. This is because the multipole potentials with even $l$ give rise to a linear Stark effect, which changes sign with the external potential and which gives rise to a strong splitting even for weak fields. In addition it turns out [7] that the splitting due to the $l = 1$ and $l = 2$ potentials add or subtract, depending on the sign of the external field: When inducing electrons they add for the $t_{1u}$ level and almost cancel for the $h_u$, while when inducing holes the situation is reversed. I.e., when a molecular level is filled, the splitting is substantially enhanced. It reaches the order of the band width when inducing about two electrons, or somewhat more than
total charge

$11.2 \, e\, a_0$ dipole moment

$h_u$ orbital

$-8.7 \, e\, a_0$

**FIGURE 2.** Polarization of a C$_{60}$ molecule in a homogeneous external electric field of 0.02 a.u. ($\approx 1$ V/Å). The change in charge density compared to the field-free case is indicated by the $\Delta\rho$-isosurface at $0.0020/a_0^3$. It turns out that the dipole moment for the $h_u$ (HOMO) charge density is of the same order of magnitude as that of the total charge — *but of the opposite sign.*

two holes per molecule. Beyond these fillings the effect of the Stark splitting on the electronic structure of the C$_{60}$ monolayer that carries the induced charge will clearly be very large, and one can definitely no longer speak of doping.

**HOMO-ANTISCREENING**

As we have seen, the charge density of the C$_{60}$ molecule is strongly polarized in an electric field, and one might expect that the main contribution comes from the polarization of the highest molecular orbital (HOMO). Calculating the change in the HOMO charge density, we find, however, that the dipole moment of the HOMO charge density is of the same order of magnitude as that of the total charge — *but of the opposite sign* (see Fig. 2). This surprising result can be understood, e.g., in terms of perturbation theory: Expanding the wave function to first order in the external field $V = E_z z$ and calculating the dipole moment $p = ez$, we find that the leading term is given by a sum over the matrix element, squared, with all unperturbed molecular orbitals of different parity divided by the characteristic energy denominator. Hence the main contribution comes from energetically close-by levels, and the sign of their contribution is determined by whether they are energetically above or below the level under consideration. For the HOMO in a molecule with a large HOMO-LUMO gap this means that the contributions mainly come from the molecular levels below — implying antiscreening. We thus see that HOMO-antiscreening should be quite general for molecules with large HOMO-LUMO gap, and, in fact, it can also be found, e.g., in the series of polyacenes: benzene, naphthalene, anthracene, tetracene, and pentacene.
FIGURE 3. Gap $E_g = E(N-1) - 2E(N) + E(N+1)$ with finite-size correction $E_g - E_g(U=0) - U/M$ as calculated by quantum Monte Carlo for the $t_{1u}$ and the $h_u$ band in the (111)-plane of the Pa$\bar{3}$ structure. For the half-filled $t_{1u}$-band the gap opens between $U_c = 0.8 \ldots 1.2$ eV, for the half-filled $h_u$-band between $U_c = 1.2 \ldots 1.6$ eV.

MOTT TRANSITION

Since the bands in the fullerenes are narrow, while the Coulomb repulsion between two electrons on the same molecule is sizable, the doped fullerenes show effects of strong correlation. It is, e.g., only due to orbital degeneracy that $A_3C_{60}$ is metallic and not a Mott insulator [8]. In field-doped fullerenes the electrons are restricted to a monolayer [6]. Hence the number of nearest neighbors to which an electron can hop is reduced and the bands are even more narrow. It is therefore expected that the Mott transition occurs at critical values of the Coulomb interaction $U$ below those found in the bulk. To determine the transition point, we have performed quantum Monte Carlo calculations [9] for a doped (111)-layer (without Stark splitting) and find that the Mott transition occurs between $U_c = 0.8 - 1.2$ eV for doping with three electrons, and $U_c = 1.2 - 1.6$ eV for the half-filled $h_u$ band (see Fig. 3). For integer dopings other than half-filling the transition is expected to occur for even smaller values of $U$ [9]. Furthermore, the splitting of the molecular levels in the electric field should weaken the effect of the degeneracy on the Mott transition and lead to still smaller values of $U_c$ [10]. In particular for the $h_u$ orbital, the strong electron-phonon coupling might lead to a further reduction of $U_c$ [11]. One has, however, to keep in mind that the Coulomb interaction $U$ depends on the environment of the molecule. Screening due to the polarization of the neighboring molecules is, e.g., responsible for a large reduction of $U$ in the crystal as compared to the value for an isolated molecule [12]. Likewise, it is to be expected that for a molecule in the monolayer next to the gate dielectric, $U$ might be substantially changed from the bulk value. This effect is, however, hard to quantify without knowing the microscopic structure of the oxide-$C_{60}$ interface. Nevertheless it seems likely that field-doped $C_{60}$ should be insulating at integer fillings.
ENHANCEMENT OF TRANSITION TEMPERATURE

In A$_3$C$_{60}$ the superconducting transition temperature $T_c$ increases with increasing lattice constant, i.e., with increasing density of states at the Fermi level [13]. It is therefore natural to try the same for field-doped C$_{60}$. The simplest way to increase the distance of the molecules in the conducting monolayer is to apply uniaxial stress [14]. An alternative approach is the intercalation of the crystal with inert molecules. In fact, for field-doped C$_{60}$ intercalated with haloform molecules spectacularly increased transition temperatures have been reported [3, 4]. A subsequent analysis of the lattice structure of these crystals revealed, however, that the lattice is mainly expanded perpendicular to the conducting layer, and that the density of states in the doped layer shows no correlation with the reported $T_c$ [15]. Therefore, the additional coupling to the vibrations of the haloform molecules has been proposed as an alternative explanation of the enhancement of the transition temperature [16]. It has, however, turned out that such a coupling is very small and, for the two-fold degenerate modes, is even excluded by symmetry [17]. The reported enhancement of $T_c$ in haloform intercalated C$_{60}$ is therefore not understood.

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