Absence of magic fillings of carrier-doped C$_{60}$ in a field-effect transistor

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(Dated: March 22, 2022)

Motivated by recent experiments of carrier-doped C$_{60}$ in a field-effect transistor (FET), effects of spatial single particle potential variations on Mott-Hubbard (MH) insulators are studied theoretically. It is shown that the presence of strong random potentials leads to a reduced dependence of electronic properties on band fillings and to disappearance of the MH insulating behavior at integer fillings. A simple physical picture to explain this behavior is given using a notion of self-doping of the MH insulator. Our results have important implications on some of the puzzling observations of carrier-doped C$_{60}$ in the FET. It is also discussed that the FET configuration with Al$_2$O$_3$ dielectric provides an “ideal” system with strong disorders.

PACS numbers: 71.10.-w, 71.23.-k, 73.20.-r

Carrier-doped C$_{60}$ has been known to become a Mott-Hubbard insulator (MHI) for most integer fillings of the three (five) fold degenerate lowest unoccupied (highest occupied) molecular orbitals [1, 2], giving a special importance to certain fillings of the system. This is a general property of a Mott-Hubbard (MH) system, a good example of which is the cuprate high Tc’s in which an antiferromagnetic MHI with integer occupation is converted to a metal and superconductor at modest changes of the band filling [3]. It is generally accepted that electron and hole doped C$_{60}$ represents a MH system because the on-site Coulomb repulsion between electrons ($U \sim 1.5$ eV) is considerably larger than the calculated band width ($W \sim 0.5$ eV) [1, 2, 4]. Experimentally it is known that most integer filling C$_{60}$ systems except for perhaps K$_3$C$_{60}$ (see Refs [1, 2, 4, 5]) are in fact insulators contrary to what one finds from a band structure calculation. The explanation for this is generally sought in terms of a MH scenario. The recently developed technique of electron and hole doping using a field-effect transistor (FET) configuration [6] enables one to study a rather wide and continuous range of doping dependence of electronic states of C$_{60}$ with clear advantages over the use of chemical doping. Some recent results [7] have already provided us with spectacular surprises which at least in some cases seem to contradict our general understanding of strongly correlated electrons; they do not show any indications of insulating behavior at or near integer fillings! Here we propose one of the possible and we believe plausible reasons for this behavior which has far reaching consequences regarding the interpretation of the physical properties of such field effect doped, correlated insulators.

The MHI is characterized by a system which, in spite of a partially filled band, has a finite single-particle charge excitation gap defined by $E_{\text{gap}} = E_I - E_A = E_{GS}^{N+1} + E_{GS}^{N-1} - 2E_{GS}^N$ where $E_I = E_{GS}^{N-1} - E_{GS}^N$ ($E_A = E_{GS}^N - E_{GS}^{N+1}$) is the electron ionization (affinity) energy and $E_{GS}^N$ the ground state energy of the system with $N$ electrons as shown in Fig. 1(a) for a non degenerate band. As demonstrated such a system also is characterized by local magnetic moments which may order below some transition temperature. It is also clear from Fig. 1(a) that this gapped situation for charge excitations only occurs for integer filling since both holes in the lower Hubbard band and electrons in the upper Hubbard band can move freely. In Fig. 1(a) we see that the lower and upper Hubbard bands are well-separated in energy by $U$ which is the on-site coulomb repulsion of two electrons on the same site.

The experimental observations in Ref [7] however suggest that nowhere in the electron or hole concentration regime in C$_{60}$ in the field effect set up does such a gap in the minimum charge excitation spectrum occur, since the resistivity versus gate voltage dependence is perfectly smooth with no signs of strongly insulating regions. We believe that this could be a result of a non uniform potential at the C$_{60}$-dielectric interface which led us to study the behavior of a MHI with strong spatial single particle potential variations.

In simple metals we expect a strong random potentials to increase the resistivity and perhaps even lead to localization of charge carriers [8] and insulating behavior. So it may seem strange at first glance that in a strongly correlated MHI strong random potentials can lead to a decrease in the resistivity and turn an insulator into a metal. To understand how this happens we look at a simple model consisting of a MHI with random on-site potentials added as external fields. As will be discussed later, we believe that this is close to what actually occurs in the C$_{60}$-dielectric interfaces in the field effect devices.

In Fig. 1(b)(Fig. 1(c)) we demonstrate what happens if one site for example has a large enough attractive (repulsive) on-site energy to overcome $U$. The physics is simple; this site becomes doubly occupied but the electron (hole) must come from a singly occupied site. Therefore aside from this site the remaining system behaves like a doped MHI which we know has a small or zero energy gap for charge excitations.
The results are shown in Fig. 2 using a constant probability in between these extremes. Take the random potential \( \sigma \) with spin \( \uparrow, \downarrow \). Consider the Hamiltonian for the Hubbard model with a random on-site potential described by the Hamiltonian, systems for the Hubbard model with a random on-site potential energy.

In order to make this more realistic we look at some numerical results using exact diagonalization of finite size systems with on-site repulsions \( U \) between electrons; (a) uniform system, (b) system with one site having a large attractive on-site energy \( A \) \((0 < U < -A)\), and (c) system with one site having a large repulsive on-site energy \((0 < U < A)\). Solid circles with arrows denote electrons and their spins. LHB (UHB) stands for the lower (upper) Hubbard band. The numbers next to the density of states (left) represent the weight of the spectra with \( N \) being the size of the system. These pictures explain self-doping of a Mott-Hubbard insulator induced by a strong on-site potential energy.

![Diagram](image)

FIG. 1: Schematic pictures of energy diagrams (left) and density of states (right) at the atomic limit for single band systems with on-site repulsions \( U \) between electrons; (a) uniform system, (b) system with one site having a large attractive on-site energy \( A \) \((0 < U < -A)\), and (c) system with one site having a large repulsive on-site energy \((0 < U < A)\). Solid circles with arrows denote electrons and their spins. LHB (UHB) stands for the lower (upper) Hubbard band. The numbers next to the density of states (left) represent the weight of the spectra with \( N \) being the size of the system. These pictures explain self-doping of a Mott-Hubbard insulator induced by a strong on-site potential energy.

The variation of the gap for charged excitations with system size and with the size of the random potential is shown in Figs. 3(a) and (b). We see indeed that for a MHI with integer filling the gap rapidly decreases with increasing disorder potential saturating at a value close to what is expected because of the finite size nature of the calculation. The size dependence has been studied systematically in 1D systems (see in Fig. 3(b)), which behaves in a similar fashion in 2D. We also compare the gap as a function of disorder potential for non-integer filling systems consisting of 8 and 6 electrons in 10 sites in Figs. 3(a) and (b), respectively. This system would ideally be metallic for no disorder but for the finite size still shows a gap because of this and then first the gap increases with increasing disorder potential and then turns over and decreases for large disorder potential and ends up close to that of the integer filled system. This result

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FIG. 2: (a) Density of states exactly for a single band 2D Hubbard cluster with \( \sqrt{10} \times \sqrt{10} \) sites and \( U = 8t \) at electron density \( n = 1.0 \). Solid (dashed) lines are for one-particle additional (removal) spectra using width of 0.1t to broaden \( \delta \)-function peaks (denoted by bars in the figure) into Lorentzian. (b) The same as in (a) but for the cluster with the site-dependent on-site random potential extending from \(-A\) to \(+A\), where \( A = 5t \) is taken.

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clearly demonstrates that a MHI with strong disorder has a charge gap which is not or only weakly dependent on the filling and that integer filling is no longer a special case.

FIG. 3: (a) Averaged charge gap $E_{\text{gap}}$ sampling 100 random potential realizations for single band 2D Hubbard clusters with $\sqrt{10} \times \sqrt{10}$ sites and $U = 8t$ at electron densities $n = 1.0$ (solid circles) and 0.8 (open triangles). (b) The same as in (a) but for 1D 10-site (solid marks), 8-site (open squares), and 6-site chains (open diamonds). Densities are indicated in the figure.

Why is this relevant for C$_{60}$ in the FET-like device measurements? We recall how the devices are actually made. One starts with a very pure crystal of C$_{60}$ and evaporates onto this the source and drain electrodes which often is gold. Then using plasma sputtering a thin layer of 10–20 nm of Al$_2$O$_3$ is sputtered onto the C$_{60}$ which serves as the dielectric and on top of this the gate metal electrode. Upon application of a gate voltage calculations show that the charge carriers are concentrated in the first C$_{60}$ layer at the C$_{60}$-dielectric interface. This means that even if the C$_{60}$ surface layer was perfectly smooth the C$_{60}$ molecules at the interface will in fact experience a spatially non uniform potential because the dielectric is not a single crystal. In fact for Al$_2$O$_3$ the interface C$_{60}$ molecules will see in their close vicinity a variety of crystallite orientations and crystal faces. We now recall that Al$_2$O$_3$ is an ionic insulator stabilized to a large extent by the Madelung potential set up by the ionic charges. It is easy to see that the Madelung potential fields in the vicinity of the crystallite will leak outward to distances of at most several Al$_2$O$_3$ lattice spacings and that the strength of these fields will depend strongly on the crystallite orientation and termination. The potential at distances of 0.3 nm from the interface can easily be as large as $\pm 2$ eV and can also vary by that amount depending on the crystal orientation and termination. The Hubbard $U$ has been measured on the C$_{60}$ (111) surface and is found to be 1.6eV [4] and the band width is about 0.5 eV. Therefore indeed the spatial variation of the potential can be expected to be of the order of the MH gap resulting in a strongly disordered system with a charge excitation gap which will be nearly independent of the charge concentration.

This may be the answer to the question related to the absence of insulating regions in the regions where integer doping is expected but it also then raises a lot of other questions. For example why is the mobility so high and why does the charge motion look like coherent band motion? We do not pretend to know the answer but it is important to note that we do not need a large density of potentials with variations of 1 eV or so. If 10% of the interface C$_{60}$ molecules experienced such potential fluctuations this is enough to wipe out the MHI regimes. This could still leave enough space for percolating regions of weak scattering. Another very interesting thought could be that strong disorder in the first layer could cause some charge carriers to actually move to the second layer and that the high mobility is caused by motion in the second layer. We note that the Madelung potential like effects decay exponentially as one moves away from the interface so the second layer would experience at most weak scattering effects. The question as to the influence on superconductivity remains an open question. Why would doped carriers in such disordered systems favor a superconducting state rather than a glassy-like state which is likely the case in “dirty” boson systems [10].

To summarize, we have studied the effects of on-site potential variations on a MHI and shown that strong disorder leads to a reduced dependence of electronic properties on band fillings and to disappearance of the MH insulating behavior at integer fillings. We also discussed that carrier-doped C$_{60}$ in the FET configuration with Al$_2$O$_3$ dielectric may provide an ideal situation for a strongly disordered MH system. Our results explain some of the most puzzling experimental observations for carrier-doped C$_{60}$ in the FET.

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