Theory of the Metal-Paramagnetic Mott-Jahn-Teller Insulator Transition in $A_4C_{60}$

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We study the unconventional insulating state in $A_4C_{60}$ with a variety of approaches, including density functional calculations and dynamical mean-field theory. While the former predicts a metallic state, in disagreement with experiment, the latter yields a (paramagnetic) Mott-Jahn-Teller insulator.

The alkali fullerides $A_nC_{60}$, based on tightly bound $C_{60}$ molecules, are relatively simple molecular conductors where strong correlations, orbital degeneracy and Jahn-Teller effect intervene at the same time, leading to remarkable physical properties. The three-fold degenerate $t_{1u}$ state of the isolated molecule leads to three bands hosting the valence electrons provided by the alkali metals. Hence all compounds $A_nC_{60}$ with $0 < n < 6$ should in principle be metallic if, as one expects, the alkali metals. Hence all compounds $A_nC_{60}$ with $0 < n < 6$ should in principle be metallic if, as one expects, the bandwidth (of order 0.5 eV), is larger than the relatively small crystal field splittings. The bandwidth is of order 0.5 eV, is larger than the relatively small crystal field splittings. The $n = 3$ fullerides are in fact generally metals, and become superconducting with $T_c$ as high as 40 K. Among the $n = 4$ compounds, however, Na$_4$C$_{60}$, a stable fcc structure at high temperature, is the only one which is also a paramagnetic metal, whereas K$_4$C$_{60}$ and Rb$_4$C$_{60}$, stable bcc structures down to low temperatures, are instead paramagnetic narrow-gap insulators. Understanding in detail this insulating state proves nontrivial, and constitutes the main scope of this work. Known experimental parameters for K$_4$C$_{60}$ are a minimum band gap (probably indirect) between 0.05 and 0.2 eV, and a direct, optical gap of 0.5-0.6 eV. The insulating state is non magnetic with a spin gap to the lowest triplet excitation of 0.1-0.14 eV. Transition to a metal can be provoked by pressure, which rationalizes why Na$_4$C$_{60}$ should be metallic, Na being the smaller cation.

One can invoke at least two possible scenarios for the insulating behavior of A$_4$C$_{60}$: a) a band insulator, due to a strong splitting of the $t_{1u}$ bands, arising for example from the bct distortion, or else from a collective static Jahn-Teller (JT) distortion of the C$_{60}$ molecules, or alternatively b) a Mott-Jahn-Teller insulator, where the hopping between adjacent molecules is first of all suppressed by a strong Coulomb repulsion, an intramolecular JT effect subsequently optimizing the state of the four localized electrons. We have studied first the molecular ion, and then the possible origin of the insulating behavior of A$_4$C$_{60}$ by several theoretical approaches, tight-binding Hartree-Fock, density functional, and Dynamical Mean Field Theory (DMFT), the latter a powerful method to treat the Mott transition.

We start with the single C$_{60}^-$(molecular ion. Within the $t_{1u}$ orbital, assuming rotational (icosahedral) symmetry, a general interaction among electrons can be written as

$$H_{int} = \frac{U}{2} n^2 + \frac{U_z}{6} \left( 3(n_1 - n_2)^2 + 3 \sum_{i<j} \Delta_{ij}^2 + (n_1 + n_2 - 2n_3)^2 \right),$$

where $n_i = \sum \sigma c_{i \sigma}^\dagger c_{i \sigma}$ is the electron number on each orbital ($i = 1, 2, 3$), $n = n_1 + n_2 + n_3$, and $\Delta_{ij} = \sum \sigma c_{i \sigma}^\dagger c_{j \sigma} = H.c.$ At fixed $n$, the second term is responsible for the multiplet splitting. For $n = 2, 4$, the lowest energy state is the $^3T_{1g}$ Hund’s rule triplet, followed at energy $2U_2$ by a $^1H_g$ singlet, and at $5U_2$ by a $^1A_g$ singlet. The exchange coupling $U_2$ is expected not to be significantly screened by the $t_{1u}$ electrons, so that a reasonable estimate can be obtained by optical measurements on solid C$_{60}$, which give $U_2 \approx 0.05$eV. Next, we consider the JT coupling to the eight $H_g$ vibrational modes. In the adiabatic limit, one can use a single-mode approximation

$$H_{JT} = \frac{\hbar \omega \sigma^2}{2} \left\{ (z^2 + r^2) + z(n_1 + n_2 - 2n_3) + r \sqrt{3} (n_1 - n_2) \right\}.$$
strictly applies, for $\hbar\omega_s$ is comparable to all splittings and the coupling is of medium strength, the former limit will yield the right symmetries, while the latter will be quantitatively much more accurate.

In the antiadiabatic limit, the JT term (2) gives rise to a non-retarded electron-electron interaction, which can be absorbed into $U_2 \rightarrow U_2 - (3/4)E_{JT}$, with a change of sign of $U_2$ from 0.05 to $-0.076 eV$. The lowest energy state is now the $A_g$ singlet, followed at 0.23eV by the $A_u$ singlet, and at 0.38eV by the $3T_{1g}$ triplet. The overall JT energy gain in this limit is very large, 0.84eV, about a factor three larger than the bare adiabatic JT energy (see below). This signals a true enhancement, due to the gain in zero point energy corresponding to the frequency collapse of the tangential vibron modes, first pointed out in Ref. [14], as a possible mechanism for explaining the high critical temperature of $A_3C_{60}$ compounds.

In the adiabatic limit we diagonalize (1) plus (2) for $n = 4$, minimizing successively the eigenvalues with respect to $z$ and $r$ treated as classical variables. We find a lowest energy singlet at a classical distortion $z = -1.987$ and $r = 0$, gaining $E_{JT} = 0.293 eV$. Adding the zero point energy gain $\hbar\omega_s$ [1], we obtain a total gain of 0.41eV, the zero-point enhancement still sizable. (A similar total gain of 0.42eV was obtained by uncorrelated eight-mode calculations [13,12].) The lowest triplet state has instead $z = 1.0$ and $r = 0$ and lies above the ground state by $E_t = 0.108 eV$ (spin gap). The lowest singlet, (with $z = 1.0$ and $r = 0$), is at $E_s = 0.208 eV$ above the ground state. Finally, the optical gap, identified with the JT orbital splitting, is $\Delta = (3/2)zE_{JT} \approx 0.504 eV$.

Both limits therefore predict that the $C_{60}^{4-}$ ion should be a singlet. If hybridization between adjacent molecules were much smaller than all the molecular gaps involved, then a lattice of $C_{60}^{4-}$ molecules would indeed be a non magnetic insulator, moreover with an optical gap $\Delta$ and a spin gap $E_t$ remarkably close to the experimental ones. In that case, an electronic structure calculation and total energy minimization for the $A_4C_{60}$ lattice should yield a narrow $t_{1u}$ band split by an insulating gap, in turn supported by a static (uniform or staggered) collective JT distortion of all molecules (scenario (a)).

A tight-binding Hartree-Fock (HF) approximation yields precisely that. The Hamiltonian which we use is

$$H = \sum_{i,j,a,b,\sigma} t_{ij}^{ab} c_{ia\sigma} c_{jb\sigma} + H_{int} + H_{JT},$$

where the hopping amplitudes $t_{ij}^{ab}$ are evaluated along the lines outlined in Ref. [13], and the vibronic terms are treated in the adiabatic approximation, as in Eq. (2). We look for a HF state with a non-zero uniform average of $n_1 = n_2 \neq n_3$ (collective JT state) and find a stable band insulator with direct gap and spin gap of $\sim 1.48 eV$ and an indirect gap of $\sim 1.03 eV$, all of which are much larger that the experimental values. The calculated HF bandstructure is shown in Fig. 1 (upper panel). This indicates that this method, known to overestimate insulating tendencies, is unreliable for this problem, and more realistic first principles calculations are called for in this case.

We have carried out a series of such calculations for $K_4C_{60}$, starting with bct configurations compatible with X-ray data [10], and using state-of-the-art pseudopotential plane-wave density functional techniques [17], with $E_{int} = 35$ Ry (55 Ry for refinements), and careful k-point summations. Confirming previous results [18], we found first of all that intermolecular electron hopping is not small, yielding metallic $t_{1u}$ bands of width $W \approx 0.6 eV$. We searched next for a spontaneous collective JT distortion by relaxing atomic positions based on Hellmann-Feynman forces. In order to check that the calculation could in principle yield such a delicate JT distortion, and also reproduce the molecular limit, we performed test calculations at an artificially enhanced intermolecular spacing of 13.3Å. In that case a distortion appeared spontaneously, leading to a distribution of carbon distances from the $C_{60}$ center between 3.511 and 3.553Å. This distortion magnitude $\Delta R = 0.042Å$, although small, is very close to that reported for [PPN(+)]$_2C_{60}(2-)$ salts [19], namely 0.043Å, and that is very gratifying since JT distortions of $C_{60}^{-}$ and $C_{60}^{4-}$ should be essentially the same. The single-particle gap was only about 0.1 eV, instead of the expected 0.5 eV, a standard density functional shortcoming of no consequence for this case. When carried out for the true structure (bct, intermolecular spacing 9.97Å) however, an extensive search for a JT distortion with one molecule/cell yielded no result, and the system remained undistorted and metallic, as shown in Fig. 1 (lower panel).

Notably, X-rays fail to find a static JT distortion [16], however within a resolution of precisely 0.04Å, which is inconclusive. Selected trial calculations with two molecules/cell also failed to yield a doubling, as would be caused, e.g., by charge-density-waves [18] or by a staggered collective JT state. We temporarily conclude that, since accurate density functional calculations cannot account for its insulating behavior, $K_4C_{60}$ is probably not a band insulator. We will make this statement stronger based on additional reasoning at the end of this paper.

Electron correlations can be strong in these compounds. A realistic estimate [18], of the intra-molecular Hubbard $U$ of Eq.(1) is $\approx 1.0 - 1.6 eV$, which is larger than the full bandwidth. The failure of density functional calculations does not appear surprising in this light. To get a description of the insulating state, and of the insulator-metal transition, we resort to dynamical mean-field theory (DMFT) [10], which is exact in the limit of infinite coordination lattices, and has proved quantitatively successful in describing the Mott transition.

Within DMFT, the Hamiltonian (1) is mapped onto a three-fold degenerate impurity Anderson model, where
the parameters describing the conduction electrons, as well as their coupling to the impurity, are determined self-consistently \[^{10}\]. Band structure enters the calculations via the density of states (DOS) in the self-consistency equations. We approximate the realistic DOS with a semicircular DOS of same bandwidth \(W\), appropriate for a tight-binding model on an infinite-coordination Bethe lattice. This approximation does not change the qualitative behavior of the model and is not expected to significantly influence the value of the gap. The Anderson model is solved by means of exact diagonalization with a finite number \((n_s)\) of conduction electron degrees of freedom \[^{22}\], checking convergence as a function of \(n_s\) by finite-size scaling. We should look for either orbital symmetry broken and unbroken phases, as the capability to describe a true Mott insulator without any symmetry breaking is a unique feature of DMFT, which is not shared by HF or density functional-based calculations, always implying symmetry breaking at metal-insulator transitions. For simplicity, we have restricted our search for insulating solutions either without orbital symmetry breaking or with uniform JT ordering. In order to locate the metal-insulator transition (MIT), we calculate the quasiparticle residue \(Z\) (plotted in Fig. 2 as a function of \(U/W\)), whose vanishing identifies the critical \(U/W\) above which a paramagnetic insulator is stable, and the metallic one is not. Again, we limit our analysis to limiting cases: (i) No JT coupling; (ii) Antiadiabatic JT effect; (iii) Adiabatic JT effect. Case (i) – Orbital degeneracy without JT coupling, is well studied for \(U_2 = 0\) \[^{121}\]. In the presence of a finite \(U_2/W = 0.08\) we find a MIT at \(U/W \simeq 1.414\) for symmetric solutions, much reduced with respect to \(U/W \simeq 1.98\) with \(U_2 = 0\). Case (ii) – The JT coupling renormalizes the dipolar integral, leading to an effective \(U_2/W = -0.127\). The critical MIT \(U/W\) is shifted to a much lower value \(U/W \simeq 0.707\). Case (iii) – Solution of DMFT equations is more involved, since the self-consistency must be required only after averaging over the classical vibrational (five-dimensional) variable \(\vec{Q}\) \[^{22,23}\]. In the broken-symmetry case the average simplifies, at \(T = 0\), as the probability distribution function of \(\vec{Q}\) becomes a single \(\delta\)-function. We obtain a critical \(U/W \simeq 0.9 - 1.0\) (the uncertainty due to convergence difficulty). The orbitally symmetric insulating solution, which becomes stable at \(U/W \simeq 1.237\), is of particular interest since it describes a molecular insulator where each molecule is distorted with equal probability in all possible directions and independently from any other molecule. This state has therefore a very large entropy which could be reduced by including quantum fluctuations, for instance in the form of tunneling between the equivalent local distortions, a way of describing a dynamical JT effect, not included at the adiabatic level. It should be noted that our adiabatic limit does not now include the vibron zero-point energy gain. Because it is present in the symmetric case only, it could lower the true critical \(U/W\) value of this phase, which could in reality prevail over the broken symmetry case. Moreover, temperature would also favor the symmetric state, where entropy is higher.

We can now compare critical \(U/W\)’s with the true ones. As before, we expect the adiabatic values to be quantitatively more accurate. The calculated critical values are in all cases substantially smaller than the actual \(U/W\) value, i.e. 1.7–2.7. We conclude that the insulator is best explained as a Mott-Jahn-Teller state, where orbital degeneracy has becomes split, giving rise to an essentially intra-molecular \(C_{60}^{4-}\) Jahn-Teller state whose calculated gaps (optical, spin) agree very closely with experimental data. In the adiabatic limit the orbital symmetry is broken, but that is likely to change when zero-point energy and temperature are included.

The close agreement between the adiabatic gaps of \(C_{60}^{4-}\) and experimental optical and spin gaps in \(A_2C_{60}\) is perhaps the strongest piece of evidence in favor of a Mott state. Suppose one could even find, by some other band calculation, such as GW \[^{24}\], a stable static collective JT state as in scenario (a). By necessity, the collective JT distortion magnitude would have to be substantially smaller than that of the isolated molecular ion, since electrons leaving the molecule very frequently to hop on other molecules weaken the on-site JT effect. But, in that case, it should not be possible to observe optical and spin gaps of exactly the right molecular magnitude, as one does. They would be much smaller, corresponding to the delocalization, or spillout, of the band Wannier function. In the Mott state, the electron spillout to neighboring molecules is reduced to order \(t/U\), which is very small. Hence this is the only state that can explain why JT electronic gaps are essentially intra-molecular. When the Mott insulator state is destroyed, for example by pressure-induced increase of \(W\) and decrease of \(U\), this intra-molecular physics is expected to disappear rather suddenly (giving way to a density functional-like metal), instead of gradually as in a band MIT transition.

Our conclusion is that the bct \(A_2C_{60}\) are not conventional band insulators, and that both strong correlations and JT effects are crucial for their understanding. That, incidentally, suggests that also the \(n=3\) superconducting fullerides, whose bandwidth is quite similar, are most likely close to a strongly correlated state \[^{11}\]. In that case the metal competes in our picture with a Mott-Jahn-Teller spin 1/2 antiferromagnetic insulator, with the implication that strong correlations should probably not be ignored when discussing superconductivity.

We thank wholeheartedly G. Santoro for his constant support, and S. Ciuchi and FULPROP partners for information and helpful discussions. We acknowledge sponsorship from INFIM (PRA HTSC), and from the European Union, Contract No. ERBFMRX-CT97-0155 (FULPROP).
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FIG. 1. The $t_{1u}$ bands for K$_4$C$_{60}$ according to Hartree-Fock (upper panel) and LDA (lower panel). The HF state sustains a collective JT distortion and is wide gapped, the LDA state is undistorted, and metallic. Both approximations disagree with experiment, indicating a narrow gap semiconductor.

FIG. 2. Quasiparticle residue $Z$ as a function of $U/W$ for the symmetric solution of the purely electronic model (solid line), the symmetric (dotted line) and broken symmetry (dot-dashed line + heavy dots) solutions in the adiabatic limit, and the symmetric solution in the antiadiabatic limit (dashed line). The adiabatic broken symmetry value should be the best numerical approximation. Realistic values of $U/W$ clearly indicate a Mott-Jahn-Teller insulator.