Metal-Insulator Transitions in Degenerate Hubbard Models and A_xC_{60}

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Abstract

Mott-Hubbard metal-insulator transitions in N-fold degenerate Hubbard models are studied within the Gutzwiller approximation. For any rational filling with x (integer) electrons per site it is found that metal-insulator transition occurs at a critical correlation energy $U_c(N,x) = U_c(N,2N-x) =$ $\gamma(N,x)|\bar{\epsilon}(N,x)|$, where $\bar{\epsilon}$ is the band energy per particle for the uncorrelated Fermi-liquid state and $\gamma(N,x)$ is a geometric factor which increases linearly with x. We propose that the alkali metal doped fullerides $A_x C_{60}$ can be described by a 3-fold degenerate Hubbard model. Using the current estimate of band width and correlation energy this implies that most of $A_x C_{60}$, at integer x, are Mott-Hubbard insulators and $A_3 C_{60}$ is a strongly correlated metal. PACS numbers: 71.10.+x,71.30.+h,74.70.W

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The discovery of superconductivity in A_3C_{60} [1] has spurred great interest in alkali metal doped fullerides [2]. Beside A_3C_{60} , stable phases such as Rb_1C_{60} , Na_2C_{60} , K_4C_{60} were synthesized [2,3]. One unusual property is that except A_3C_{60} all integer x phases are found to behave like insulators [4]. This contradicts the band structure calculations which imply that all of them are metals due to the 3-fold degeneracy of the t_{1u} molecular orbitals which forming the conduction bands [5]. In this letter we show that the strong (compared with the band width) intramolecular electron-electron correlation is responsible for this unusual property. The results we have obtained also shed light on the instability of the non-integer x phases [6].

The existence of strong correlation in pure C_{60} is supported by spectroscopy experiments. Photoemission shows an insulating gap of 2.6eV, while the photo-conductivity and absorption indicate excitation at 1.6eV. This discrepancy is interpreted as due to strong correlation which results in a large excitonic binding energy. The estimated correlation energy $U \sim 1eV$ [4,7,8] is much larger than the conduction band width $W \sim 0.2 - 0.4eV$ [5,10]. Thus, it has been suggested that that A_3C_{60} is a Mott-Hubbard insulator and the superconducting phase is non stoichiometric [7]. However, structural, transport and spectroscopic measurements show that the superconducting phase is stoichiometric and there is no evidence of insulating behavior in A_3C_{60} . Even more interesting is that for $x \neq 3$ integer stoichiometric phases no metallic behavior have been observed so far. Therefore neither a simple Hubbard model which prefers insulating at half filling (x = 3), nor the simple band filling model which predict metallic behavior for all phases, can explain the unusual metal-insulator transitions observed.

Clearly the 3-fold degeneracy of the conduction band can not be neglected. This leads us to study the general N-fold degenerate Hubbard model at rational fillings. We find that the unusual metal-insulator transitions observed can be understood in term of Mott-Hubbard transition in the degenerate Hubbard model. It is found that for a general N-fold degenerate Hubbard model at rational filling x/2N, where the average number of electrons per site (x)is an integer, the metal-insulator transition occurs at a critical U_c which increases with both x and N. U_c is found to be the largest at half filling x = N for a given degeneracy N (except N = 2). Therefore it is possible that the system is a metal at half filling while insulating away from it. Our results lay a solid theoretical foundation for the interpretation that A_xC_{60} are either Mott-Hubbard insulators or strongly correlated metals and provide a rationale to understand the unusual metal-insulator transitions in this family of materials and molecular metals in general.

Consider the general N-fold degenerate Hubbard model with the correlation energy U independent of orbitals and spins

$$H = \sum_{i,j,\alpha,\beta} t_{i,j}^{\alpha,\beta} c_{j,\beta}^{+} c_{i,\alpha} + \frac{U}{2} \sum_{i,\alpha\neq\beta} n_{i,\alpha} n_{i,\beta} , \qquad (1)$$

where $\alpha = (r, \sigma)$ include both spin (σ) and orbital (r) indices; $n_{i,\alpha} = c_{i,\alpha}^+ c_{i,\alpha}$ are number operators. Let L be the size of the lattice and M be the total number of electrons. By rational filling we mean that the average number of electrons per site x = M/L is an integer. For such a filling there exists a well defined insulating state where there are exactly x electrons localized at each site. Obviously for a sufficiently large U hopping is forbidden, and the the ground state is insulating. As U decreases a metal-insulator transition, at a certain critical U_c , is expected. For the case of the non-degenerate Hubbard model the only rational filling is the half filling (N = x = 1); in this case it is well known that the ground state at large U is an ordered magnetic insulator [9]. For the degenerate Hubbard model, in general, the insulating state could also be ordered. However, we will consider the paramagnetic (or disordered) insulating state only because our primary interest is $A_x C_{60}$, where the lattice is non bi-partile and large amount of intrinsic disorders are known to exist [10,11].

In the insulating state, the kinetic energy is zero and the total energy per site E_0 is given by the correlation energy $PE = \frac{U}{2}x(x-1)$. Imagining a situation very close to the metalinsulation transition such that only one site has x+1 electrons, the correlation costs U while the kinetic energy gained for the excitation is of the order W. Since there are x electrons per site, there are x possible ways of making such an excitation. Therefore one might expect $U_c(x) \sim xW$ [12].

In the case of the non-degenerate Hubbard model at half filling the rigorous result $U_c = 8|\bar{\epsilon}| = 2W$ was obtained by Brinkman and Rice [13] within the Gutzwiller approximation [14]. The central point of Gutzwiller approximation is to associate a projection factor η with every doubly occupied site, assuming that the many-body wavefunction can be written as a superposition of states with different numbers of doubly occupied sites ν . The optimal ν is determined variationally by calculating the expectation value of the Hamiltonian. In the thermodynamic limit the summation over ν is dominated by the optimal ν term, then the kinetic and potential energies can be calculated by counting the number of configurations which contribute.

We have carried out similar calculations rigorously for the general N-fold degenerate Hubbard model in a limit close to the metal-insulator transition. The details of counting are rather tedious and will be published elsewhere [15]. Here we will simply state assumptions and results and discuss their implications for A_xC_{60} .

Let x be the average number of electrons per site and L be the total number of sites. We assume that there is complete permutation symmetry between all orbitals and spins, so the number of electrons occupying each $\alpha = (r, \sigma)$ state is $m = \frac{xL}{2N}$. Near the metalinsulator transition the probability that a site is occupied by more than x + 1 electrons is very small as it costs 2U or more energy. Thus we assume that each site can only be "empty" (x - 1 electrons), "singly-occupied" (x electrons) or "doubly-occupied" (x + 1 electrons). Let $2N\nu \ll L$ be the total number of doubly occupied sites, then by symmetry the number of empty sites is also $2N\nu$. Every doubly occupied site costs a correlation energy U with respect to the insulator state where there are exactly x electrons on every site. The Gutzwiller wavefunction is constructed from the uncorrelated Slater determinant $|SL >= |\{k_1, \alpha_1, ..., k_n, \alpha_n\} >$ by projecting out doubly occupied states with a weighting factor η

$$|\phi\rangle = \prod_{i,\alpha,\beta} (1 - \eta c_{i,\alpha}^+ c_{i,\beta}^+) |SL\rangle .$$
⁽²⁾

This wave function is a linear combination of a large number of states with different ν . Following the original calculation of Gutzwiller, the expectation value of the Hamiltonian is dominated by the state with the optimal ν which is to be determined variationally. After a lengthy derivation the average energy per particle with respect to the paramagnetic insulating state is found to be [15]

$$E(N,x) = Q(N,x,\nu,m)\overline{\epsilon}(x) + \frac{\nu}{m}U, \qquad (3)$$

where $\bar{\epsilon}(x)$ is the kinetic (band) energy per particle in the uncorrelated state with the center of the band chosen to be zero, $\bar{\epsilon}(x=2N)=0$. The quotient Q, which reflects the reduction of the hopping term in the correlated state [14,15], is given by

$$Q(N,x) = \frac{\alpha_{N,x}\nu(m-2x\nu)}{m^2} \left(1 + \eta \frac{(m-2x\nu)}{\alpha_{N,x}\nu}\right)^2,$$
(4)

where

$$\alpha_{N,x} = \begin{cases} \frac{2Nx}{2N-1} & \text{if } x = 1 \text{ or } 2N - 1\\ x & \text{if } 2 \le x \le 2N - 2 \end{cases},$$
(5)

and the projection parameter η is

$$\eta = \begin{cases} \frac{2x\nu}{m - 2x\nu} \sqrt{\frac{N}{2N - 1}} & \text{if } x = 1 \text{ or } 2N - 1\\ \frac{x\nu}{m - 2x\nu} & \text{if } 2 \le x \le 2N - 2 \end{cases}$$
(6)

Substituting eqs.4-6 into Eq. (3) and minimizing the energy with respect to $\bar{\nu} = \nu/m$ leads to

$$\bar{\nu} = \frac{1}{4x} \left(1 - \frac{U}{U_c}\right) \tag{7}$$

and the energy per particle

$$E_0 = \frac{\gamma(N, x)\overline{\epsilon}}{8x} (1 - \frac{U}{U_c})^2 , \qquad (8)$$

where U is given by

$$U_{c}(N,x) = \gamma(N,x)|\bar{\epsilon}(N,x)| = \begin{cases} \frac{2Nx}{2N-1} \left(1 + \sqrt{\frac{2N-1}{N}}\right)^{2} |\bar{\epsilon}(N,x)| & \text{if } x = 1 \text{ or } 2N - 1\\ 4x|\bar{\epsilon}(N,x)| & \text{if } 2 \le x \le 2N - 2 \end{cases}$$
(9)

As U increases toward U_c , the number of doubly occupied states approach zero. Thus the Mott-Hubbard transition occurs at U_c .

Eq.9 is the main result of this paper. Several points are worth mentioning. a) The particle-hole symmetry is preserved if $|\bar{\epsilon}(N, x)| = \frac{x}{2N-x}|\bar{\epsilon}(N, 2N - x)|$; this is expected because the starting Hamiltonian Eq. (1) contains particle-hole symmetry. b) For N = 1 the only rational filling is half filling x=1, the Brinkman-Rice result $U_c = 8|\bar{\epsilon}|$ is recovered. c) Regardless of the band structure, U_c generally increases with x reaching the maximum at half filling x = N (N = 2 is an exception); thus, for a degenerate Hubbard system it is more difficult for it to become a Mott insulator. d) The above results apply only to integer x. For non-integer x, if U is larger than U_c , there will be tendency for the system to phase separate into integer phases to lower the total energy. This may explain the experimental observation that non-integer x phases 1 are not stable $A_x C_{60}$ where the alkali ions can segregate together with electrons which screen out the long range Coulomb repulsion. Details of this issue will be explored elsewhere.

To make a quantitative estimate, one needs to know the band structure. In the case of a flat band with the bandwidth W, $\bar{\epsilon}(N, x) = \frac{x-2N}{4N}W$. One obtains the simple result $U_c(N, x) = \frac{x(2N-x)}{N}W$ ($x \neq 1, 2N - 1$). This agrees qualitatively with the simple argument discussed earlier. Fig.1 shows plots of U_c/W vs x/2N for several N values.

Now let us turn to the specific application of the above results to the metal-insulator transitions in $A_x C_{60}$. It is known that each alkali metal donates one electron and that the conduction band is formed by overlap of the 3-fold degenerate t_{1u} molecular orbitals. For x = 1, 3, 4 structures are known to be rhombohedral, face-center-cubic and body-center-tetragonal, respectively [3]. For all these structures LDA *ab initio* calculations suggest that all of them are metals [5]. Experimentally, except x = 3, all phases with integer x are found to be insulating. It has also been shown that the band structure can be accurately represented by a 3-band tight-binding model, in particular the density of states was shown to be approximately flat due to the intrinsic orientational disorder [10]. The band width W determined from both experiments [16] and calculations [5,10] is very small, $W \sim 0.2-0.4eV$.

On the other hand, spectroscopic studies [4,7] and theoretical calculations [8] suggest that the intramolecular electron correlation energy is around $U \sim 1 eV$. The value of U is expected to remain unchanged with doping because the screening is provided by the large number of molecular orbitals above t_{1u} , which is not affected by the doping. From Eq. (9) and assuming a flat band one obtains $U_c(x, N = 3)/W = 2.6, 2.67, 3$ respectively for x = 1, 2, 3. Thus if the parameters are such that 2.67W < U < 3W, which is where the current best estimate of W and U fall, then the whole family of A_xC_{60} for x = 1, 2, 4, 5 are Mott-Hubbard insulators while x = 3 could be a strongly correlated metal. Of course we caution that the U_c calculated here only represents the lower bound; however, we expect the qualitative results $U_c(N, x) \leq U_c(N, N), U_c(N, N) \sim NW$ will hold for the exact U_c .

In conclusion we have studied Mott-Hubbard transitions in the N-fold degenerate Hubbard model within the Gutzwiller approximation. It is shown that for any integer number of electrons per site there exists a critical correlation energy U_c above which the system is a Mott-Hubbard insulator. U_c is found to be sensitive to both the degeneracy and filling. We propose that the family of materials A_xC_{60} can be described by a 3-fold degenerate Hubbard model. With reasonable estimates for the band width and the intramolecular correlation energy, we show that it is possible that for most integer phases (x = 1, 2, 4, 5) the materials are Mott-Hubbard insulators and A_3C_{60} is likely a strongly correlated metal despite the fact that U is several times of the band width.

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- [12] Notice that in the Hartree mean field approximation it is straightforward to show that the expectation of Hubbard U term is $x\frac{2N-1}{4N}U$ per particle, while the average kinetic energy is $\epsilon(x) = \frac{x-2N}{4N}W$ for a flat band with the band width W. Thus, the energy gain with respect to the disordered insulating state is $\Delta E = \frac{x-2N}{4N}(W-U)$. Thus $U_c = W$ independent of N and x.
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FIGURES

FIG. 1. Phase diagrams for Mott-Hubbard metal-insulator transitions in N-fold degenerate Hubbard models. Shown are results for N = 2, 3, 4, 5. For $U > U_c(N, x)$ the system is a Mott-Hubbard insulator. Note that only the points, corresponding to integer (x) number of electrons per site, are meaningful.