Degenerate 3-band Hubbard model with anti-Hund’s rule interactions; A model for \( A_x C_{60} \).

Mats Granath
NORDITA
Blegdamsvej 17
DK-2100 Copenhagen
Denmark

Stellan Östlund
Chalmers Technical University
Gothenburg 41296
Sweden

(Dated: November 3, 2018)

We consider the orbitally degenerate 3-band Hubbard model with on-site interactions which favor low spin and low orbital angular momentum using standard second order perturbation theory in the large Hubbard-U limit. At even integer filling this model is a Mott insulator with a non-degenerate ground state that allows for a simple description of particle-hole excitations as well as gapped spin and orbital modes. We find that the Mott gap is generally indirect and that the single particle spectrum at low doping reappears close to even filling but rescaled by a factor \( \frac{2}{3} \) or \( \frac{1}{3} \). The model captures the basic phenomenology of the Mott insulating and metallic fullerides \( A_x C_{60} \). This includes the existence of a smaller spin gap and larger charge gap at even integer filling, the fact that odd integer stoichiometries are generally metallic while even are insulating, as well as the rapid suppression of the density of states and superconducting transition temperatures with doping away from \( x = 3 \).

PACS numbers:

I. INTRODUCTION

The physics of Mott insulators has emerged as a key ingredient in the study of strongly correlated systems\(^1\), largely motivated by the understanding that much of the exotic physics of the underdoped cuprate superconductors has connections to the undoped Mott insulating state. The basic model for a Mott insulator discussed in connection with the cuprates is the large-U half-filled Hubbard model. For this model the low energy spectrum at half-filling is reasonably well understood, but the higher energy spectrum as well as the physics away from half-filling is still very much an open problem. Much of the difficulty seems to trace back to the fact that the Mott insulating ground state for this system is not known.

Here we will study a model of a Mott insulator which has a simple non-degenerate ground state and where we can describe the spectrum of excited states and explore the physics at and near the Mott transition in a well controlled manner. The model is a degenerate three channel Hubbard model which has multiplet splitting on-site interactions that favor low spin and low orbital angular momentum. This model is the simplest model with spin and orbital symmetry which at even integer filling allows for a Mott insulating non-degenerate ground state. Since the ground state is non-magnetic, the spin physics which complicates the single band Hubbard model is absent at low energies. Although interesting in itself as a natural and simplifying extension of the Hubbard model, our main motivation for studying this model is that it very naturally captures some of the most distinctive phenomenology of the alkali doped \( C_{60} \) compounds, the fullerides.

Crystalline \( C_{60} \) is a band insulator with a completely filled molecular orbital.\(^2\) Doping with alkali atoms, forming \( A_n C_{60} \), transfers electrons into the lowest unoccupied molecular orbital (LUMO) which according to elementary molecular theory is threefold degenerate. These form three spin degenerate bands according to the band theory of \( C_{60} \). It is believed that the charge transfer is complete and that the influence of the alkali ions is in general negligible apart from changing the crystal structure and the corresponding band theory.

If these were simple metals, band theory would predict a metallic state for any doping \( 0 < n < 6 \) and possibly superconductivity with transition temperatures which would follow roughly the density of states at the Fermi energy as the doping is varied. Experimentally, however, it turns out that the compounds with even integer doping \( (n = 2, 4) \) are non-magnetic insulators,\(^4\) and superconductivity is only seen in a narrow range around half-filling \( (n = 3) \) and with transition temperatures that are sharply maximized here. Band theory augmented by BCS theory of superconductivity fails to reproduce this behavior.

It is well known that correlation effects are important as these are weakly bound molecular solids with a narrow band
width of approximately \(0.5eV\) and it is believed that the on-site Coulomb repulsion is approximately \(1eV\). One might therefore expect that the system would be a Mott insulator at any integer filling. This, however, does not explain why systems with even integer filling are generally insulating while systems with odd integer filling are generally metallic. A second related question is why the insulating materials at even integer filling are non-magnetic. From Hund’s rule, we would expect the highest spin configuration to be the molecular ground state, \(S=1\) for \(n=2\) and \(n=4\), and consequently some sort of magnetic ground state is to be expected for the solid.

One explanation for the violation of Hund’s rule in the insulating materials is that the Jahn-Teller (JT) effect counteracts Hund’s rule, with the lowest energy JT distorted state of the \(C_{60}\) molecule at even integer occupation being a spin singlet. However, a problem with the naive Jahn-Teller scenario is that static distortions of the \(C_{60}\) molecules have not been detected in solid \(C_{60}\). Indirect evidence has come from the existence of two energy gap scales in the insulating systems, a smaller spin gap of around \(50meV\) and a larger charge gap of the around \(500meV\). The large charge gap is quite clearly a Mott gap related to the intramolecular electron-electron repulsion, whereas the smaller spin gap has been linked to a singlet to triplet gap of JT distorted molecules.

A different scenario for the violation of Hund’s rule suggested by Chakravarty et al.\(^{14,15}\) and Baskaran and Tosatti\(^{11}\) claims that electronic correlations on a \(C_{60}\) molecule can break the degeneracy of any partially filled molecular orbital in such a way as to minimize the spin and orbital angular momentum. Chakravarty and coworkers looked at a Hubbard model on single \(C_{60}\) molecule, with strong electron-electron repulsion (U) on each carbon atom, using second order perturbation theory in U. The linear in U terms give Hund’s rule with a preferred highest spin configuration which minimizes the overlap between electrons. The second order term on the other hand prefers low spin configurations with large overlaps which can take better advantage of virtual excitations of the core electrons. The validity of the qualitative features of the perturbation theory is supported by exact diagonalization of smaller Hubbard clusters.\(^{13}\)

One important feature of the scenario based on intramolecular electronic correlations is that in contrast to the static Jahn-Teller distortions the orbital symmetry of the molecule is preserved. More recently, it has also been emphasized in a series of papers by Tosatti and coworkers,\(^{14,15,16,17}\) that Jahn-Teller phonons treated in the anti-adiabatic limit will also give rise to an effective electronic Hamiltonian with inverse Hund’s rule which preserves the orbital symmetry of the molecule. It may thus be difficult to distinguish the latter scenario from the one based on electronic correlations and a full treatment of both the electron-electron and the electron-lattice interactions to decide which energy scales dominate is asked for. Along these lines a recent density-functional calculation does find that Hund’s rule is valid for an isolated \(C_{60}\) and only counteracted by the JT effect,\(^{18}\) although issues such as electronic screening by the surrounding molecules may also be important.\(^{19}\)

Regardless of the mechanism behind the inversion of Hund’s rule on the \(C_{60}\) molecule it is an interesting problem to study the effective model of solid \(C_{60}\) which this naturally gives rise to, namely the three channel Hubbard model with “anti-Hund’s rule” interactions. Here we study this model in the limit of strong interactions where we can do a rescaling of the hopping by a factor \(1/3\) or 2/3, which this naturally gives rise to, namely the three channel Hubbard model.

We will focus primarily on even integer filling (\(n=2\) or 4) where the problem simplifies significantly because of the resultant non-degenerate strong coupling ground state. Based on this we can describe the spectrum consisting in general of an indirect Mott gap to particle-hole excitations and chargeless spin and orbital modes with a distinct energy gaps. We also derive the spectrum of a single particle or hole doped into the non-magnetic Mott insulator.

We will not, however, discuss the actual mechanism of superconductivity, i.e. the source of pairing. In particular, we will not assume that the intramolecular singlet triplet gap is necessarily large enough to overcome the Coulomb repulsion and give rise to a bare attraction along the lines of the earlier work.\(^{10,11}\) In fact, a fit of the parameters of the model to experiment suggests that this is not the case. Nevertheless, any other mechanism, such as one based on attraction from electron-phonons interactions, certainly needs to include the strong electron correlations which are present as indicated most clearly by existence of Mott insulating phases.

The paper is organized as follows: In Sec. III we define the model and the strong coupling limit we will primarily consider. Then we derive a perturbative effective Hamiltonian valid in the strong coupling limit. In Sec. IV we study...
the Mott insulator at even integer filling and describe the spectrum of excited states. We also discuss the distinction between even and odd integer doping and why at odd integer doping the system is more likely to be on the metallic side of the Mott transition. Then we use the results derived for the model to get an estimate of the parameters by comparing to experiment on $A_2C_{60}$ and $A_4C_{60}$. In Sec. II we study the doped Mott insulator at a filling close to even integer and speculate on the implications of these results to the whole doping range $2 < n < 4$ as well as the properties at higher temperatures. Finally, in Sec. VI we conclude.

II. THE MODEL

We will be studying a three band Hubbard model. The electrons occupy three degenerate p-orbitals ($L = 1$) on every site of the lattice and we define electron creation and destruction operators $c_{r,ls}^\dagger$ and $c_{r,ls}$ with site index, orbital quantum number and spin respectively. We will be working in the $L^z$ basis where $l = -1, 0, 1$.

The Hamiltonian reads

$$H = h + H_I$$

with a nearest neighbor hopping

$$h = \sum_{\langle rr' \rangle} t_{li}^{r,r'} c_{r,ls}^\dagger c_{r',l's'},$$

and on-site interaction

$$H_I = \sum_r \frac{1}{2} U n_r^2 + J_L \vec{L}_r^2 + J_S \vec{S}_r^2,$$

with $U, J_L, J_S > 0$. Here

$$n_r = \sum_{l,s} c_{r,ls}^\dagger c_{r,ls}$$

$$\vec{L}_r = \sum_{l,s} c_{r,ls}^\dagger \vec{L}_{l,s} c_{r,ls},$$

$$\vec{S}_r = \sum_{l,s} c_{r,ls}^\dagger \vec{S}_{l,s} c_{r,ls}.$$

are the number, orbital angular momentum and spin operators respectively.

The lattice is three dimensional and we assume a point group symmetry which is such that the hopping preserves translational degeneracy. It is the topic of the next section to derive an effective Hamiltonian which describes these properties at higher temperatures.

A. Effective strong coupling Hamiltonian.

Let us define the short-hand notation $p = (n, L, S)$ and $\alpha = (L^z, S^z)$. As shown in Table II any single site states $|p, \alpha\rangle_r$ and $|p', \alpha'\rangle_r$ have the same energy, barring accidental degeneracies, if and only if $p = p'$. This implies that any eigenstate of $H_I$ will not mix different representations at a site and can be written as $\prod_r \psi_{p,\alpha}^r |p, \alpha\rangle_r$, where $\psi_{p,\alpha}^r \neq 0$ only for one particular $p(r)$. Consider now the action of the hopping term $h$ on an eigenstate. This will affect two arbitrary nearest neighbor sites $r$ and $r'$, giving $|p, \alpha\rangle_r |p', \alpha'\rangle_{r'} \rightarrow \sum_{q,\beta,\beta'} M_{q,\beta,\beta'} \psi_{q',\beta'}^r |q, \beta\rangle_r |q', \beta'\rangle_{r'},$ where $M$ are
From Table I we can check that in the strong coupling limit this corresponds to \( \Delta E \gg t \) and \( S_{\alpha,b,c,...} \), instance, Fazekas only exchanged particle number and representation between the sites, i.e., the matrix elements of \( h \) between the in and out states. Unless the initial and final nearest neighbor states have different momentum and total spin \( S \).

Let us consider \( h \) as a matrix which acts on nearest neighbor states \(|p,\alpha\rangle|p'\alpha'\rangle\rangle \rightarrow |a\rangle_{rr'} \) which we in a short-hand notation will denote by a single index \( a, b, c, ... \). We write

\[
h = \sum_{\langle rr' \rangle} h_{rr'}^{rr'} = \sum_{\langle rr' \rangle} h_{ab}^{rr'} |a\rangle_{rr'} \langle b|_{rr'},
\]

where

\[
h_{ab}^{rr'} = \langle a|_{rr'} \sum_{l'} \bar{t}_{l'}^{rr'} (c_{l',a}^{|c_{l',b}^{|+ r.l.} h.c.)|b|_{rr'}).
\]

Next we split \( h_{rr'}^{rr'} \) into \( h_{ab}^{rr'} = h_{ab}^{0,rr'} + h_{ab}^{1,rr'} \) where \( h_{ab}^{0,rr'} = h_{ab}^{rr'} \delta_{E(a),E(b)}, \) only connects states with the same energy and \( h_{ab}^{1,rr'} = h_{ab}^{rr'} - h_{ab}^{0,rr'} \) which connects states with different energy. It follows that we can also write \( h = h^0 + h^1 \).

We introduce \( S = S_1 + S_2 \) where \( S_1 \sim O(t/\Delta E) \) and \( S_2 \sim O(t^2/\Delta E^2) \) and expand Eq. 8 to \( O(t^2/\Delta E) \),

\[
\mathcal{H}_{eff} = H_1 + h^0 + h^1 + i[S_1,H_1] + i[S_1,h^0 + h^1] + \frac{t^2}{2}[S_1,[S_1,H_1]] + i[S_2,H_1].
\]

To first order in \( t \) we want to cancel \( h^1 \) by taking \( S_1 \) to solve

\[
i[S_1,H_1] = -h^1
\]

Clearly \( S_1 \) needs to act only on nearest neighbor sites. Defining \( S_1 = \sum_{\langle rr' \rangle} S^{rr'}_1 = \sum_{\langle rr' \rangle} S^{rr'}_1[a]_{rr'} |b|_{rr'} \) gives from Equation 12

\[
i \sum_{\langle rr' \rangle} h_{rr'}^{1,rr'} = \sum_{\langle rr' \rangle} \left[ S^{rr'}_1, H_1^{rr'} \right]
\]

\[
= \sum_{\langle rr' \rangle} S^{rr'}_1 \left[ [a]_{rr'} |b|_{rr'}, H_1^{rr'} + H_1^{rr'} \right]
\]

\[
= \sum_{\langle rr' \rangle} S^{rr'}_1 (E(b) - E(a)) |a|_{rr'} |b|_{rr'},
\]

**TABLE I:** Spectrum of the interaction, Eq. 3 at a single site with states specified by occupation \( n \), total orbital angular momentum \( L \) and total spin \( S \).

| \( n \) | \( (L,S) \) | \( E \) |
|---|---|---|
| 0 | \((0,0)\) | 0 |
| 1 | \((1,\frac{1}{2})\) | \( \frac{1}{2}U + 2J_L + \frac{1}{2}J_S \) |
| 2 | \((0,0),(1,0),(1,1)\) | \( 2U + \{0, 6J_L, 2J_L + 2J_S\} \) |
| 3 | \((1,\frac{1}{2}),(2,\frac{3}{2}),(0,\frac{1}{2})\) | \( \frac{3}{2}U + \{2J_L + \frac{1}{2}J_S, 6J_L + \frac{3}{2}J_S, \frac{5}{2}J_S\} \) |
| 4 | \((0,0),(2,0),(1,1)\) | \( 8U + \{0, 6J_L, 2J_L + 2J_S\} \) |
| 5 | \((1,\frac{1}{2})\) | \( \frac{5}{2}U + \frac{5}{2}J_S \) |
| 6 | \((0,0)\) | \( 18U \) |
where we have used the fact that we work in the eigenbasis of $H_I$ such that $(H_I^0 + H_I^r)|r⟩_r = E(a)|r⟩_r$. We thus arrive at the solution

$$S^r_{ab} = \frac{i\hbar^{1,r'}}{E(b) - E(a)}.$$  \hspace{1cm} (14)

Recall that $\hbar^{1,r'}$ is defined as to only have non-zero entries when $|E(b) - E(a)| \geq \Delta E$ so that $S_1 \sim t/\Delta E$.

Given the solution for $S_1$ obeying Eq. 14 we can rewrite Eq. 15 as

$$H_{eff} = H_I + h^0 + i[S_1, h^0 + h^1] - \frac{i}{2}[S_1, h^1] + i[S_2, H_I]$$

$$= H_I + h^0 + i[S_1, h^0] + \frac{i}{2}[S_1, h^1] + i[S_2, H_I]$$  \hspace{1cm} (15)

In analogy to using $S_1$ to cancel terms linear in $t$ which connect different energy subsectors we can now use $S_2$ to cancel similar terms to order $t^2$ which arise from the commutators of $S_1$ and $h$ in Eq. 15. Technically this is slightly more involved because there is also three site nearest neighbor interactions generated to second order in $t$ and we refer the reader to the Appendix for the details.

The final expression for the effective strong coupling Hamiltonian reads

$$H_{eff} = H_I + \sum_{(r,r'),ab} (\mathcal{H}_{eff})_{ab}^r |a⟩_{rr'}⟨b|_{rr'} + \sum_{(r,r',r''),ab} (\mathcal{H}_{eff})_{ab}^{r,r''} |a⟩_{rr''}⟨b|_{rr''} + O(t^3/\Delta E^2),$$  \hspace{1cm} (16)

with

$$(\mathcal{H}_{eff})_{ab}^{r} = \left(h_{ab}^r - \sum_{c,E(c)\neq E(a)} \frac{\hbar^{r,c}_{ac} h^{r,c}_{ch}}{E(c) - E(a)} \delta_{E(a),E(b)} \right)$$  \hspace{1cm} (17)

$$(\mathcal{H}_{eff})_{ab}^{r,r''} = -\frac{1}{2} \sum_{c,E(c)\neq E(a)} \frac{\hbar^{r,r''}_{ac} h^{r',r''}_{ch} + h^{r',r}_{ac} h^{r,r''}_{ch}}{E(c) - E(a)} \delta_{E(a),E(b)}.$$  \hspace{1cm} (18)

Here $|a⟩_{rr'} = |n, L, S, L^z⟩_r |n', L', S', L^{z'}⟩_r$ and $|a⟩_{rr''}$ are arbitrary nearest neighbor and next nearest neighbor eigenstates of $H_I$ with energy $E(a)$ and $h_{ab}^r$ is defined according to Eq. 10 with a straightforward extension for three site states.

III. THE MOTT INSULATOR

In the strong coupling limit, Eq. 10 of this model the system is an insulator at any integer filling with a gap to charge carrying excitations of order $U$. At odd integer filling the ground state is the highly degenerate $|GS, 1/3, 1⟩ = \prod_r |n = 1/3, L = 1, S = 1⟩_r$ and the hopping $t$ will introduce strong correlations in analogy with the half-filled single band Hubbard model. We will return to this problem briefly in discussing the fact that $A_3C_{60}$ is generally on the metallic side of the Mott transition.

However, at even integer filling, $n = 2$ or 4, the ground state is non-degenerate, $|GS, 2/4⟩ = \prod_r |n = 2/4, L = 0, S = 0⟩_r$. Here, we will find that much of the physics can be understood in terms of a simple non-interacting single particle picture. This will be the focus of the subsequent discussion and the main issue of the paper. We will discuss $n = 4$ to compare with experiments on $\text{K}_3C_{60}$ and $\text{Rb}_3C_{60}$ but the treatment of $n = 2$ is completely analogous.

At filling $n = 4$ there are three types of excitations of the ground state that can be readily identified and which are indicated in figure 1. We can excite a single site into a higher energy multiplet, creating states $|4, 2, 0, L^z⟩_r \prod_{r' \neq r} |4, 0, 0⟩_r$ or $|4, 1, 1, L^z⟩_r \prod_{r' \neq r} |4, 0, 0⟩_r$ with energy $\Delta = E(4, 2, 0) - E(4, 0, 0) = 6J_L$ and $\Delta = E(4, 1, 1) - E(4, 0, 0) = 2J_L + 2J_S$ respectively. There is also “particle-hole” excitations in different multiplets, the one with lowest energy being $|3, 1, L^z⟩_r \prod_{r' \neq r} |5, 1, \frac{1}{2}, L^{z'}⟩_r \prod_{r'' \neq r'} |4, 0, 0⟩_r$ with energy $\Delta_0 = U + 4J_L + \frac{1}{2}J_S$. The energy $\Delta_0$ is the Mott gap to the ground state.

The degeneracy of the excited states will be lifted by the hopping $h$ and using the effective Hamiltonian Eq. 17 we can study the spectrum perturbatively in $t$.

A. Spin gap, spin and orbital modes

The spin and orbital excitations $|4, 1, 1, L^z⟩_r \prod_{r' \neq r} |4, 0, 0⟩_r$ and $|4, 2, 0, L^z⟩_r \prod_{r' \neq r} |4, 0, 0⟩_r$ are degenerate in $L^z$ and $S^z$ as well as position $r$. Acting with the effective Hamiltonian Eq. 17 will split the degeneracy in space (as
\( (n=3, L=1, S=1/2) + (n=5, L=1, S=1/2) \)

\( (n=4, L=1, S=1) \)

\( (n=4, L=2, S=0) \)

\( (n=4, L=0, S=0) \)

**FIG. 1:** Spectrum at \( t = 0 \) and doping \( n = 4 \) showing the lowest energy excitations of the three distinct kinds discussed in the text.

well as the orbital degeneracy) leading to a band description of these states. Clearly to first order in \( h (t) \), the effective Hamiltonian will not affect these states as it necessarily creates a high energy particle-hole state. For the same reason the second order three site interaction will not contribute. However, the second order nearest neighbor term can hop the excited state at \( r \) to a nearest neighbor \( r' \) or to the same site \( r \) through an intermediate particle-hole state.

Focusing on the spinless excitations we define the "bosonic" operator

\[
b_{r,m}^{\dagger} = \langle 4, 2, 0, m | r \rangle \langle 4, 0, 0 | r \rangle
\]

in terms of which we can write an excited orbital state as \( b_{r,m}^{\dagger} | GS, 4 \rangle \). These operators do not obey proper commutation relations but if we consider only single particle physics this is irrelevant. With these operators we can write the following single particle Hamiltonian describing the dynamics of such excitations

\[
H = \sum_{\langle r, r' \rangle} \tilde{t}_{mm'}^{r'r'} b_{r,m}^{\dagger} b_{r',m'} + \sum_r \tilde{t}_{mm'} b_{r,m}^{\dagger} b_{r,m'},
\]

where

\[
\tilde{t}_{mm'}^{r'r'} = \frac{1}{U + 3/2 J_S - 2 J_L} \sum \langle 4, 2, 0, m | r \rangle \langle 4, 0, 0 | r \rangle \langle c_{r,0}^{\dagger} c_{r',s} + h.c. | ph \rangle \times \langle ph | t_{jj'}^{r'r'} (c_{r,0}^{\dagger} c_{r',s} + h.c.) | 4, 0, 0 | r \rangle \langle 4, 2, 0, m' | r' \rangle,
\]

and similarly for \( \tilde{t}_{mm'} \). Here |ph\rangle are particle-hole states \( | 5, 1, \frac{1}{2}, I, s \rangle_r | 3, 1, \frac{1}{2}, I', s \rangle_{r'} \) (or with reversed positions) and the sum is over all indices except \( m, m' \) and \( r, r' \). Similar contributions but with larger denominators from intermediate particle hole excitations in higher energy multiplets have been ignored in Eq. 21.

Deriving the Hamiltonian Eq. 20 is thus a straightforward problem. The Hamiltonian is non-interacting and can in principle be diagonalized in momentum space. In general the five orbital components will be mixed with a complicated band structure. The same calculation can be carried out for the spinful \( (n = 4, L = 1, S = 1) \) states, where there are nine coupled states per site. Although the band width of these spin and orbital modes are naively order \( t^2 / U \) the high degeneracy of these states is expected to give a significant broadening of band width, perhaps by a factor of the spin and orbital degeneracy of these states. The spinful excitations should be readily detectable experimentally as a band of magnons with some gap \( \Delta_s \), a spin gap. We will return to the issue of the spin modes in discussing NMR on \( A_2C_{60} \) and \( A_4C_{60} \).
B. Charge Excitations

At filling \( n = 4 \) the lowest energy charge carrying excitations are the “particle-hole” states \( |3, 1, \frac{1}{2}, l, s\rangle_r \prod_{r'' \neq r} |4, 0, 0\rangle_{r''} \) with an energy \( \Delta_0 = U + 4J_L + \frac{3}{2}J_S \). Acting with the effective Hamiltonian Eq. (11) on such a state will translate either the particle \((n = 5)\) or the hole \((n = 3)\) to a nearest neighbor site through the linear term in \( \hbar \) \((t)\). To second order, there is next nearest neighbor hopping through an intermediate state in a higher energy multiplet. Since it is higher order, \( O(t^2/\Delta E) \), we will ignore this contribution. However, it should be noted that the denominator \( \Delta E \) for this process is proportional to \( J_S \) and/or \( J_L \) not \( U \), implying of course that we should consider the higher energy particle and hole multiplets if the strong coupling limit Eq. (7) is not strictly valid. Note that due to the energy constraint in the effective Hamiltonian the particle and hole are not allowed to annihilate by hopping to the same site. We will ignore the constraint which in three dimensions is expected to give a vanishing contribution to the spectrum at low densities.

1. Charged single particle excitations

In order to understand charge transport, we need to consider the single particle and single hole states \( |5, l, s\rangle_r \prod_{r'' \neq r} |4, r''\rangle \) and \( |3, l, s\rangle_r \prod_{r'' \neq r} |4, r''\rangle \). Here we have dropped the multiplet indices \((L, S) = (1, \frac{1}{2})\) or \((0, 0)\). When acted on by \( \hat{H}_{eff} \) these excitations are translated to a nearest neighbor through \( \hbar \) with a matrix element

\[
\langle 4|_{r'} \langle 5, l', s'|r| \sum_{j',\sigma} t_{j,j'} c_{r',j',\sigma} c_{r,j,\sigma} |5, l, s\rangle_r |4\rangle_{r'} = \frac{1}{3} \delta_{s's} t_{j,j'}^{s'} \]

and similarly with a factor \(-1/3\) for holes and \(2/3\) for particles with respect to the \( n = 2 \) ground state. The matrix elements in Eq. (22) follow from the explicit expressions for the states

\[
|5, 1, \frac{1}{2}, l, s\rangle = \sqrt{3}sls|4, 0, 0\rangle
\]

\[
|3, 1, \frac{1}{2}, l, s\rangle = \sqrt{3} cls|2, 0, 0\rangle = \sqrt{3}(2s)^{2|l|} c_{-l-s}|4, 0, 0\rangle
\]

\[
|1, 1, \frac{1}{2}, l, s\rangle = c_{ls}|0\rangle = \sqrt{3}(2s)^{2|l|} c_{-l-s}|2, 0, 0\rangle
\]

which is a simple exercise in elementary quantum mechanics to derive.

We note the reduced magnitude of the matrix elements compared to the single particle particle hopping on empty sites

\[
\langle 0|_{r'} \langle 1, l', s'|r| \sum_{j',\sigma} t_{j,j'} c_{r',j',\sigma} c_{r,j,\sigma} |1, l, s\rangle_r |0\rangle_{r'} = \delta_{s's} t_{j,j'}^{s'} .
\]

This is a general result of the reduced Hilbert space due to constraining the \( n \) particle states to the lowest energy multiplet.

Let us define the particle and hole creation operators

\[
c_{5,r|ls}^\dagger = |5, l, s\rangle_r \langle 4|_r
\]

\[
c_{3,r|ls}^\dagger = |3, l, s\rangle_r \langle 4|_r
\]

through which the particle and hole states can be written as \( c_{5,r|ls}|GS, 4\rangle \) and \( c_{3,r|ls}|GS, 4\rangle \) with \( |GS, 4\rangle = \prod_{r} |4, 0, 0\rangle \). Note that these operators do not obey on-site anticommutation relations, we can only use them with confidence in describing non-interacting single-particle physics.

In terms of these particle and hole operators we now straightforwardly arrive at the following single particle Hamiltonians for the particle and hole states

\[
H_5 = \sum_{\langle rr'\rangle, ll'|ss'} \frac{1}{3} t_{ll'} r' c_{5,r|ls}^\dagger c_{5, r'|ls} + \sum_{r,l,s} (9/2U + 3/4J_S + 2J_L - \mu) c_{5,r|ls}^\dagger c_{5, r|ls}
\]

\[
H_3 = -\sum_{\langle rr'\rangle, ll'|ss'} \frac{2}{3} t_{ll'} r' c_{3,r|ls}^\dagger c_{3, r'|ls} + \sum_{r,l,s} (-7/2U + 3/4J_S + 2J_L + \mu) c_{3,r|ls}^\dagger c_{3, r|ls}
\]
where the on-site energy is defined with respect to the \(E(4, 0, 0) = 8U - 4\mu\) and where we have introduced the chemical potential \(\mu\).

These are just simple tight binding Hamiltonians which we can diagonalize in momentum space in terms of states

\[
|5, k, l_s\rangle = c_{5,kl_s}^\dagger|GS, 4\rangle = \frac{1}{\sqrt{V}} \sum_r e^{i\vec{k} \cdot \vec{r}} c_{5,rll_s}^\dagger|GS, 4\rangle
\]

\[
|3, k, l_s\rangle = c_{3,kl_s}^\dagger|GS, 4\rangle = \frac{1}{\sqrt{V}} \sum_r e^{-i\vec{k} \cdot \vec{r}} c_{3,rll_s}^\dagger|GS\rangle.
\] (28)

In general these are not eigenstates due to the fact that the hopping is not diagonal in \(l\) and we would get three (or more if there are inequivalent sites) non-degenerate bands depending on the precise nature of the hopping integrals which depend on the crystal symmetry. Quite intriguingly, as seen from Equations 26 and 27 the band structure for these particle and hole excitations from the Mott insulating ground state is precisely the noninteracting band structure up to a rescaling factor. The reason for this remarkably simple behavior is that the ground state at even integer filling is in the trivial \((L = 0, S = 0)\) representations of spin and angular momentum and as such is basically equivalent to the zero-particle vacuum.

2. Mott gap

The Mott gap is defined as the gap between the ground state and the lowest energy charge carrying excitation of the insulator. What is often measured however is the optical gap as defined by optical conductivity or reflectivity measurements and we will be interested in calculating this too.

The Kubo formula for the optical conductivity which is the short wavelength limit of the electrical conductivity is at zero temperature

\[
\sigma_{aa}(\omega, q = 0, T = 0) = \frac{2\hbar^2 e^2}{m^2 V} \sum_m \omega_m \frac{|\langle m | j^a(q = 0) | GS \rangle|^2}{\omega(\omega + i\eta) - \omega_m^2}
\] (29)

where \(|m\rangle\) are excited states with \(\hbar \omega_m = E_m - E_{GS}\). The current operator can be derived from the continuity equation \(i\hbar^{-1}[n(r), H] + \nabla \cdot \vec{j}(r)\). For the Hamiltonian Eq. 1 considered here only the tight binding part contributes and we get

\[
\vec{j}(\vec{q}) = \sum_{\vec{p},ll's} \left( \frac{\partial}{\hbar \partial \vec{p}} \sum_\delta e^{-i\vec{p} \cdot \vec{\delta}} \delta_{ll'}^{\delta} c_{p,ll's} \right) c_{p+q,ls} c_{p',l's}.
\] (30)

where \(\delta\) is the set of nearest neighbor lattice vectors. For a cubic or orthorhombic lattice this simplifies to

\[
\vec{j}(\vec{q}) = -\frac{1}{\hbar} \sum_{\vec{p},ll's,\delta} \delta^a \sin(\vec{p} \cdot \vec{\delta}) \delta_{ll'}^{\delta} t_{ll'}^{0\delta} c_{p+q,ls} c_{p',l's}.
\] (31)

The current operator creates particle-hole pairs when acting on the ground state \(|GS, 4\rangle\) and we expect to get non-zero matrix elements with states

\[
|kl's, k'l's'\rangle_{p-h} = c_{5,kl's}^\dagger c_{3,k'l's'}^\dagger|GS, 4\rangle
\] (32)

defined according to Eq. 28 and 27

With this we can calculate the matrix element

\[
\langle kl's, k'l's'|_{p-h} j^a(q = 0) |GS\rangle = -\sqrt{2} \frac{\sqrt{3}}{2^{|\delta|}} (2s')^{2|\delta|-1} \sum_\delta \delta^a \sin(\vec{k} \cdot \vec{\delta}) t_{ll'}^{0\delta} \delta_{kl,k'l's,s'}. (33)
\]

Introducing an explicit band structure, i.e. defining \(t_{ll'}^{rr'}\), we can in principle calculate the optical conductivity due to the particle hole excitations. A lower bound to the support of the sum in Eq. 29 will tell us the optical gap, below which \(\omega, \sigma(\omega)\) will decay. We simply maximize the kinetic energy of the particle and hole under the zero momentum constraint in the usual manner to obtain this. We will ignore the possible complications due to the dispersion and
angular momentum part \( \sum_\delta \delta^a \sin(\vec{k} \cdot \vec{\delta}) t^a_{\delta - \delta} \) which may kill the matrix elements at some high symmetry points. Moving slightly away from such symmetry points will give a finite contribution to the response.

The optical gap is thus given by

\[
\Delta_{\text{optical}} \geq U + 4J_L + \frac{3}{2} J_S + \left( \frac{1}{3} \varepsilon^t_{i}(\vec{k}) - \frac{2}{3} \varepsilon^t_{j}(\vec{k}) \right)_{\min(\vec{k}, i, j)},
\]

(34)

where \( \varepsilon^t_{j}(\vec{k}) \) is the kinetic energy of the \( j \)'th band at momentum \( \vec{k} \) and \( \min(\vec{k}, i, j) \) means minimizing with respect to the momentum and the band indices.

To get the Mott gap we just need to find the lowest energy particle-hole state, which will in general be smaller than the optical gap. This corresponds to putting the particle at the bottom of the single particle band and the hole at the top

\[
\Delta_{\text{Mott}} = U + 4J_L + \frac{3}{2} J_S + \left( \frac{1}{3} \varepsilon^t_{i}(\vec{k}) - \frac{2}{3} \varepsilon^t_{j}(\vec{k}'') \right)_{\min(\vec{k}, \vec{k}'', i, j)}.
\]

(35)

In Figure 2 we present a caricature of the band structure around \( n = 4 \) based on an explicit non-interacting band structure calculated for \( K_4C_{60} \) by Gunnarsson et al.\(^{23}\) which is rescaled by a factor 1/3 for the particle band and 2/3 for the hole band. For this band structure, and any other where the max and min are not at the same \( \vec{k} \)-vector, we find an indirect gap where the optical gap is larger than the Mott gap and that the lowest energy particle-hole excitations have non-zero momentum.\(^{24}\)

A word of caution may be appropriate in considering this figure, namely that the single particle states in the bands are only well defined within our theory for a small density of such states. We depict the lower "band" as filled with
single particle states, but the real entities are only the holes in this band. This is a strongly interacting system and the analogy with a weakly interacting semiconductor has limitations. For instance it is quite obviously nonsensical to fill up the particle band with a density of more than two particles because that would correspond to a total electron density of more than six. We will return to issue of doping away from the Mott insulator in section III.

For comparison with other models of the Mott transition on degenerate Hubbard models it is useful to write down a more general expression for the Mott gap. If we make the reasonable assumption that the top and bottom of the band structure are roughly the same magnitude \( W/2 \), where \( W \) is the bandwidth of the tight binding Hamiltonian \( h \), we can write

\[
\Delta_{\text{Mott}} \approx U_{\text{eff}}(4) - \frac{1}{2} W,
\]

where \( U_{\text{eff}}(4) = U + 4J_L + \frac{4}{3}J_S \). This expression is in sharp contrast to calculations on \( N \)-band Hubbard models without the multiplet splitting terms, \( \vec{S}^2 \) and \( \vec{L}^2 \), where forms such as \( \Delta_{\text{Mott}} \approx U - NW \) or \( \Delta_{\text{Mott}} \approx U - \sqrt{NW} \) has been suggested. The intuitive motivation for the \( N \) dependence is an increase in the kinetic energy of the particle hole state due to the additional hopping channels. In this model we see a different behavior since the number of hopping channels are limited by the strong spin dependent on-site interactions.

\[\]

C. Why is \( A_3C_{60} \) metallic?

One of the most striking facts about the fullerides is that the \( A_3C_{60} \) materials are generally metallic given that the even integer filling materials are likely large \( U \) insulators. The problem of odd-integer filling is significantly more complicated than that of even integer filling as presented above. The reason for this is that even in the strong coupling limit, Eq. 7, the ground state consists of states \( (n = 3, L = 1, S = \frac{1}{2}) \) with spin and orbital degeneracies. This problem resembles the half-filled single band Hubbard model with a highly degenerate ground state which will be split to order \( t^2/U \). The ground state may then have magnetic and/or orbital order.

However, if we assume that the putative insulating ground state is not ordered so that the hopping of particles, \( (n = 4, L = 0, S = 0) \), and holes, \( (n = 2, L = 0, S = 0) \), is not frustrated by the spin interactions we can derive a Mott gap in analogous fashion to that for \( n = 4 \) above which reads

\[
\Delta_{\text{Mott}}(n = 3) \gtrsim U - 4J_L - \frac{3}{2}J_S + (\frac{2}{3}j_i^\dagger(\vec{k}) - \frac{2}{3}j_i(\vec{k}))_{\text{min}(\vec{k}^2, i, j)} \approx U_{\text{eff}}(3) - \frac{2}{3} W,
\]

where \( W \) again is the non-interacting bandwidth of \( h \). If the ground state has significant magnetic or orbital correlations we expect the gap to be bigger because of a lower ground state energy and frustration of the motion of the particle and hole.

Compared to the expression 30 for the Mott gap at \( n = 4 \) we note an increase from \( W/2 \) to \( 2W/3 \) in the kinetic energy of the particle and hole due to the larger phase space allowed for hopping. In \( A_2C_{60} \) where the bandwidth is around \( 5eV \) it appears that this difference will not be large enough to close the \( 5eV \) Mott gap seen in \( A_2C_{60} \).

However, in addition there is in this model also a more distinct difference between even and odd integer filling, namely the sign change of the \( J_S \) and \( J_L \) terms between the effective Hubbard repulsion \( U_{\text{eff}}(4) = U + 4J_L + \frac{4}{3}J_S \) and \( U_{\text{eff}}(3) = U - 4J_L - \frac{4}{3}J_S \). This difference comes from the fact that the lowest energy particle and hole excitations are \( (L = 0, S = 0) \) at odd integer filling while they are \( (L = 1, S = \frac{1}{2}) \) at even integer. If the multiplet splitting interactions are large enough they could certainly destabilize the Mott insulating ground state at odd integer filling. For instance, if \( J_S \) and \( J_L \) are very large such that \( U_{\text{eff}}(3) < 0 \) and \( |U_{\text{eff}}(3)| \gg t \) we would have a spinless Bose liquid consisting of an equal number of two and four particle singlets which could only propagate to second order in \( t \). At intermediate coupling \( U_{\text{eff}}(3) \sim t \) we would expect some correlated metallic state with most of the spectral weight in low spin configurations of the two, three and four particle states, allowing for hopping to first order in \( t \). Evidence for the formation of singlet configurations on short time scales in the metallic fullerides \( Na_3CsC_{60} \), \( RB_3C_{60} \) and the quenched cubic \( CsC_{60} \) \( (n = 1) \) have been presented from NMR spin-lattice relaxation measurements.

In addition, we know that \( A_3C_{60} \) is quite close to a metal insulator transition. It has been found that intercalating ammonia into the crystal can cause a transition into an insulating magnetically ordered phase. The main effect here is presumably the expansion of the lattice and corresponding decrease in the bandwidth, although the crystal symmetry is also reduced which may be important in facilitating a magnetically ordered ground state. An important consequence of these findings if interpreted through our model is that for \( A_3C_{60} \) \( U_{\text{eff}}(3) > 0 \) because the ground state for small \( t \) is magnetic and that \( |U_{\text{eff}}(3)| \sim t \) because changes in the magnitude of \( t \) can induce a metal insulator transition.
D. Experiment

A basic observation from experiments is that there appears to be two distinct energy scales in these materials. Probes that are sensitive to spin, in particular NMR, are consistent with a spin gap of around 50-100meV while optical conductivity sees a larger charge gap of around 500meV. Here we will look at the consistency of the model with these observations and make a fit to estimate our microscopic parameters \( U, J_L \) and \( J_S \).

1. Optical Gap

The charge gap is seen in optical conductivity as a depletion of the low energy weight in K\(_4\) and Rb\(_4\)C\(_60\) below roughly 500meV\(^2\). By inspection of Figure 2 together with the expression \( \text{opt} \) for the optical gap we get the following estimate

\[
\Delta_{\text{opt}}(K_4C_{60}) \approx U_{\text{eff}}(4) - 200\text{meV} \approx 500\text{meV},
\]

where again \( U_{\text{eff}}(4) = U + 4J_L + \frac{3}{2}J_S \). Solving Eq. \( 38 \) gives \( U_{\text{eff}}(4) \approx 700\text{meV} \).

We can compare this to \( A_3C_{60} \) where we expect the charge gap to close. Using expression \( 39 \) for the charge gap at \( n = 3 \) together with a bare bandwidth of 600meV gives

\[
\Delta_{\text{Mott}}(A_3C_{60}) \approx U_{\text{eff}}(3) - 400\text{meV} \leq 0,
\]

with \( U_{\text{eff}}(3) = U - 4J_L - \frac{3}{2}J_S \). Together with the estimate \( U_{\text{eff}}(3) > 0 \) as discussed in Sec. IIIIC we thus find the rough estimate of \( 0 < U_{\text{eff}}(3) \lesssim 400\text{meV} \).

Combining the values for \( U_{\text{eff}}(4) \) and \( U_{\text{eff}}(3) \) we can now estimate the microscopic parameters of the model. We find \( U \lesssim 550\text{meV} \) and 150meV \( \lesssim \frac{3}{2}J_S + 4J_L < 350\text{meV} \).

2. NMR, 1/T\(_1\)

Various probes\(^{55}\) have detected a thermally activated magnetic susceptibility in K\(_4\)C\(_60\) and Rb\(_4\)C\(_60\) and more recently also in Na\(_2\)C\(_60\). This has been interpreted as evidence for a singlet-triplet gap of Jahn-Teller distorted molecules where a a molecule is thermally excited from the JT ground state singlet to the triplet which then acts as a local moment. In the model presented here it is natural to assign such experimental signatures of gapped spin excitations to the spin modes or magnons which are a necessary part of the spectrum of the non-magnetic Mott insulator.

We will be focusing on measurements of 1/T\(_1\), the spin lattice relaxation rate, deriving the temperature dependence of the relaxation by the magnons in the limit \( T \ll \Delta_s \).

The probability of a transition between nuclear spin states with z-component \( m' = m \pm 1 \) due to a two magnon process which scatters a magnon with \( i = (L^z, S^z) \) and momentum \( k \) to \( i' = (L'^z, S'^z) \) and \( k' \) is given by Fermi’s golden rule as

\[
W_{m,m'} = \sum_{i,k,k'} \frac{2\pi}{\hbar} |\langle m, n_{ik}, n'_{ik'}|V|m', n_{ik} - 1, n'_{ik'} + 1 \rangle|^2 \delta(E_{ik} - E_{ik'}),
\]

Here \( n_{ik} \) is the magnon number operator, the interaction \( V = A\vec{I} \cdot \vec{S}_0 \) with hyperfine coupling \( A \), nuclear spin \( \vec{I} \) and electron spin at the nuclear site \( \vec{S}_0 \). We have dropped the tiny, typically \( \sim 10^{-6}eV \), Zeeman splitting of the nuclear spin.

The electron spin operator will act as \( b^{\dagger}_{r,L^zS^z}(m-m')b_{r,L^zS^z} \) with some small prefactor given by the overlap of these states with the single atom, where \( b^{\dagger}_{r,L^zS^z} \) creates a triplet excitation. Ignoring the details of the matrix element between the different triplet states one finds that the general magnon matrix element is given by \( \langle n_{ik} + 1 | n_{ik} \rangle \), where \( \langle n_{ik} \rangle = (e^{\frac{\Delta_s}{2}} - 1)^{-1} \) is just the Bose occupation of the magnons. Finally the relaxation rate is given by

\[
\frac{1}{2} \sum_{m,m'} \frac{W_{mm'}(E_m - E_{m'})^2}{E_m} = \frac{N^2(\epsilon)}{\sinh^2(\beta\epsilon/2)}
\]

where the magnon part of \( W_{mm'} \) clearly is independent of \( m \) and \( m' \). We thus arrive at the final expression

\[
1/T_1 \sim \int_{\Delta_s} d\epsilon \frac{N^2(\epsilon)}{\sinh^2(\beta\epsilon/2)}
\]
where we have converted the sums to integrals by introducing the density of magnon states \(N(\epsilon)\). Here \(\Delta_s\) is the spin gap, i.e. the lower edge of the magnon band, and \(W_{\text{mag}}\) is the magnon bandwidth.

For \(T \ll \Delta_s\) we can replace the \(1/\sinh^2(\beta\epsilon/2)\) by \(4e^{-\beta\epsilon}\) and the integral is dominated by \(\epsilon \sim \Delta_s\). Assuming a quadratic dispersion at the band edge we get \(N(\epsilon) \sim \sqrt{\epsilon - \Delta_s}\) for \(\epsilon \gtrsim \Delta_s\). By change of integration variable we arrive at the temperature dependence

\[
1/T_1 \sim T^2 e^{-\Delta_s/\epsilon}, \quad T \ll \Delta_s
\]

(42)

Figure 3 shows a fit of this model to \(^{13}\text{C}\) \(1/T_1\) data on \(\text{K}_4\text{C}_6\text{O}_6\) and \(\text{Na}_2\text{C}_6\text{O}_6\).\(^{30}\)

![FIG. 3: Fit to \(^{13}\text{C}\) NMR data by Brouet et al.\(^{30}\) The thick lines are fits to \(1/T_1 \sim T^2 e^{-\Delta_s/\epsilon}\) with \(\Delta_s = 240K\) for \(\text{K}_4\text{C}_6\text{O}_6\) and \(\Delta_s = 710K\) for \(\text{Na}_2\text{C}_6\text{O}_6\). The thin lines are fits to \(1/T_1 \sim e^{-\Delta_s/\epsilon}\) with corresponding \(\Delta_s = 660K\) and \(1260K\). (The bump around 180K for \(\text{Na}_2\text{C}_6\text{O}_6\) is a presumably a molecular motion peak.)](image)

We get an excellent fit to the below room temperature activated behavior with a value \(\Delta_s = 240K \approx 25\text{meV}\) for \(\text{K}_4\text{C}_6\text{O}_6\). For comparison we also show fits to a model of localized triplet states corresponding to \(W_{\text{mag}} = 0\) and \(1/T_1 \sim e^{-\Delta_s/\epsilon}\). This is the fit used in the the experimental work\(^{5,6,30}\) which is based on a model of a static uniform Jahn-Teller singlet-triplet gap. In this intermediate temperature regime it is difficult to tell which fit is best, in particular considering the fact that both models clearly fail at higher temperatures where the relaxation rapidly saturates, and we conclude that the NMR data cannot resolve the two scenarios.

Nevertheless, using the value \(\Delta_s = 25\text{meV}\) for the spin gap we may estimate the microscopic parameters. Given a bandwidth \(W_{\text{mag}}\) which we assume to be symmetric around the center we get

\[
\Delta_s = \bar{\Delta} - W_{\text{mag}}/2, \quad (43)
\]

where \(\bar{\Delta} = 2J_L + 2J_S\) is the \(t = 0\) spin gap. (There is an additional corrections to the spin gap of order \(t^2/U\) which is a shift of the ground state energy which should be included in a more rigorous treatment.) A very rough estimate of the bandwidth may be given by the degeneracy of the spin modes \(W_{\text{mag}} = 9t^2/U\). With \(U \approx 500\text{meV}\) as derived from charge gap and taking \(t \approx 100\text{meV}\) form band structure calculations gives \(W_{\text{mag}} \approx 200\text{meV}\). Collecting into Equation (43) for the spin gap gives \(\bar{\Delta} = 2J_L + 2J_S \approx 125\text{meV}\) which seems in reasonable agreement with the estimate \(150\text{meV} \lesssim 2J_S + 4J_L < 350\text{meV}\) from the charge gap. This order of magnitude agreement for the coupling constants \(J_S\) and \(J_L\) is certainly encouraging in that it comes from experiments on two apparently separate physical quantities.

A fit to \(1/T_1\) for \(\text{Na}_2\text{C}_6\text{O}_6\) gives a larger gap of around 700K. Within our model the \(t = 0\) spin gap \(\bar{\Delta}\) is the same for \(n = 2\) and \(n = 4\) so the differing spin gaps are somewhat unexpected. However, since the crystal structure is different, the tight binding Hamiltonians of these materials may be very different and consequently the bandwidth of the spin modes. In fact, \(\text{Na}_2\text{C}_6\text{O}_6\) is fcc while \(\text{K}_4\) and \(\text{Rb}_4\) are body centered tetragonal. The natural interpretation for the variations within this model is thus variations of the magnon bandwidth. Along the same lines we note the behavior of \(1/T_1\) in \(\text{Rb}_4\text{C}_6\text{O}_6\) under pressure where it is found that the activated behavior is replaced or coexists with a non-activated component related to gapless excitations.\(^{34}\) It has been suggested that this is related to a closing of the Mott gap due to the expected pressure induced increase of the bare bandwidth. Within our model we find a possible alternative interpretation in terms of a closing of the spin gap.

Above room temperature the activated behavior stops and the the relaxation rate saturates. Within our simple non-interacting model for the spin modes we cannot expect to be able to address the high-temperature behavior when a significant number of modes are excited. A more sophisticated treatment requires us to properly account for the interactions between the spin modes as well as the exclusion statistics that are ignored in the single particle picture.
The saturation could also be related to molecular degrees of freedom at higher temperatures which are completely neglected in our model.\textsuperscript{39} However, we note that this rapid saturation is very reminiscent of the behavior of $1/T_1$ in spin ladder materials with gapped magnons\textsuperscript{32}, where it is believed to have a purely electronic origin.\textsuperscript{33}

IV. THE DOPED MOTT INSULATOR

We will now look at the problem of an incommensurate particle density away from the Mott insulators at even integer filling $n = 2$ and $n = 4$. This is obviously a much more difficult task because in the strong coupling limit the ground state will be highly degenerate. As a concrete example, at a doping $n = 2 + x$ ($x < 1$) the ground state at $t = 0$ is the set of states with $x$ 3-particle states $(3, 1, \frac{1}{3})$ and $(1 - x)$ 2-particle states $(2, 0, 0)$ at arbitrary positions in space. Introducing $t$ by means of the the effective Hamiltonian\textsuperscript{17} we find to first order in $t$ nearest neighbor interchange of the 2- and 3-particle states and to second order in $t$ spin and orbital exchange terms between nearest neighbor 3-particle states. This can be described by a generalized $t-J$-model including a no double occupancy constraint because only 2 and 3 particle states are allowed.

At first glance this may appear to be an even more difficult problem than that of a doped antiferromagnet because of the additional orbital degrees of freedom. However, in the low density limit, $x << 1$, it is in fact considerably simpler than the doped antiferromagnet because only the doped particles (or holes) have internal spin and orbital degrees of freedom. In the doped antiferromagnet the scenario is just the opposite with a large number $1 - x$ of spinful particles and a small number $x$ of spinless holes. This of course gives rise to the very complex behavior in such systems where the spin interactions $J$ can compete with the hopping $t$ even in the limit $J \sim t^2/U << t$ because the important energetics is given roughly by $xt$ and $(1 - x)J$. Here for the doped non-magnetic Mott insulator a similar consideration would lead us to compare $xJ$ with $xt$ because it is the dopant particles or holes that carry both the spin and momentum. Effectively we are thus looking at the low density (heavily doped) limit of a t-J model.

We will completely neglect the nearest neighbor exchange interactions as well as the no double occupancy constraint and only consider the single particle physics. Certainly, for the problem of a single particle or hole doped into the non-magnetic Mott insulator this is completely rigorous and again in sharp contrast to the problem of a single hole in an antiferromagnet where interactions obviously cannot be neglected. Even this simple particle physics has some interesting implications for the doping dependence in the metallic fullerides.

A. Small Fermi surface

The problem of a single particle or hole was addressed already in Section\textsuperscript{11,12,17} in connection with particle-hole excitation. There we showed that the single particle or hole spectra are equivalent to the non-interacting $H_I = 0$ spectrum up to a rescaling by a factor $1/3$ or $2/3$. At least in the very low density limit, $n = 2 + x$ or $n = 4 + x$ with $|x| << 1$, we expect these single particle states to give a qualitatively accurate picture by filling $x$ such states.

In particular this implies a “small Fermi surface” where the number of delocalized charge carriers is proportional to the number of doped holes or particles $x$ and not the total filling $n$. The remaining degrees of freedom are frozen below the Mott gap. One important consequence is that the density of states at the Fermi surface for small doping $x$ will be given by the density of states at the band edges of the of non-interacting problem by the simple relation

\begin{align*}
DOS_{\text{strong coupling}}(n = 2 - x) &\approx 3 \times DOS_{\text{non-interacting}}(n = 6 - x) \\
DOS_{\text{strong coupling}}(n = 2 + x) &\approx 3/2 \times DOS_{\text{non-interacting}}(n = x) \\
DOS_{\text{strong coupling}}(n = 4 - x) &\approx 3/2 \times DOS_{\text{non-interacting}}(n = 6 - x) \\
DOS_{\text{strong coupling}}(n = 4 + x) &\approx 3 \times DOS_{\text{non-interacting}}(n = x), \quad x << 1.
\end{align*}

A detailed picture of what happens at larger doping $x \to 1$ as we approach odd integer filling is beyond our methods. However, a naive extrapolation of the results valid for small $x$ all the way to $x = 1$ gives a density of states as shown in Figure\textsuperscript{11} where the density of states is generally peaked at odd integer filling as a consequence of the rapid decay toward the effective band edges at even integer filling. For reasons discussed in Section\textsuperscript{13} we have to be in an intermediate coupling regime where the system is metallic at odd integer filling for this extrapolation to have any credibility.

There is an interesting experiment that corroborates the small Fermi surface picture in Cs\textsubscript{60} which is the variation of density of states in Na\textsubscript{2}Cs\textsubscript{3}Cs\textsubscript{60} ($0 < x < 1$) corresponding to a doping range $2 < n < 3\frac{2}{3}$. It was estimated from the Pauli susceptibility that for samples with $n = 2.25, 2.5, 2.75, 3$ the density of states varies as $5, 7, 11, 15$ $eV^{-1}$ (both spins). Correspondingly, $T_c$ drops rapidly from 12K at $n = 3$ to 7K at $n = 2.75$ and to $< 0.5K$ at $n = 2.5$. Certainly,
this behavior seems consistent with the scenario sketched in figure 4 where the density of states drops rapidly as the effective Hubbard band edges are approached at even integer filling.

The failure of naive band theory in the presence of strong local repulsion is a consequence of the large inherent charge fluctuations of such an uncorrelated state of delocalized electrons. It may be illuminating to recall some of Hubbard’s original work on the topic of narrow band systems. For an $m$-fold degenerate band at filling $n$ the probability $P_N(m,n)$ of having $N$ electrons on a particular atom (molecule) is given by

$$P_N(m,n) = \binom{m}{N} \left( \frac{n}{m} \right)^N \left( 1 - \frac{n}{m} \right)^{m-N},$$

where $\binom{m}{N}$ is the multiplicity of atomic states with $N$ particles. The rms fluctuation is given by $(\Delta_N)_{\text{RMS}} = \sqrt{n(1-n/m)}$ which has a maximum $(\Delta_N)_{\text{RMS}} = \sqrt{m/2}$ at half filling $n = m/2$. Clearly, at finite doping there are significant charge fluctuations of order one which cost an energy of order $U$ per site in an uncorrelated state and which grows with the degeneracy. We can get an estimate of the energy cost of the charge fluctuations for our model by comparing the potential energy $E = \langle H_I \rangle$ in an uncorrelated state which is the ground state of the kinetic energy $h$ with that given by the small Fermi surface state which is the ground state of the potential energy $H_I$. The latter is at filling $n$ given by $p_N N$-particle states and $p_{N+1} N+1$-particle states in the lowest energy multiplet where $N \leq n < N+1$ and $p_N N + p_{N+1} (N+1) = n$. The potential energy of this state is given by

$$\langle H_I \rangle_{\text{corr}} = p_N E_0(N) + p_{N+1} E_0(N+1),$$

where $E_0(N)$ is the energy of the ground state multiplet with $N$ particles. The expression turns into

$$P_{N,L,S}(n) = (2L+1)(2S+1)\left( \frac{n}{m} \right)^N \left( 1 - \frac{n}{m} \right)^{6-N},$$

for this model where the $N$-particle multiplets are split according to $L$ and $S$ and the corresponding potential energy for the uncorrelated state is

$$\langle H_I \rangle_{\text{uncorr}} = \sum_{N,L,S} P_{N,L,S}(n) E(N,L,S).$$

Figure 5 shows $\Delta E = \langle H_I \rangle_{\text{uncorr}} - \langle H_I \rangle_{\text{corr}}$ as a function of doping and in units of $U_{\text{eff}}(2) = U_{\text{eff}}(4) = U + 4J_L + 3/2J_S$ for two cases $J_L = J_S = 0$ and $J_L = .1U$, $J_S = .2U$. 

![Figure 4: Density of states (both spins) as function of filling $n$ given the non-interacting DOS inset. The dashed lines are extrapolations of Eqn. (44) toward odd integer filling. The non-interacting DOS is calculated from the band structure of unidirectional $A_3C_{60}$.](image)
We see that in a wide doping range around half filling there is a significant energy cost due to charge fluctuations in an uncorrelated state. Given that this leads to the Mott insulating behavior at even integer filling we would also expect significant correlation effects in the metallic regions 2 < n < 4, consistent with the small Fermi surface scenario.

Hubbard’s treatment of narrow band systems used a real space Greens function method which is exact in the zero bandwidth t = 0 case but which depend critically on neglecting correlations between electrons on different atoms in the finite bandwidth case. He found that in the narrow bandwidth limit the original non-interacting band splits into a large number of bands which correspond to transitions between states with particle number differing by one. In addition these Hubbard bands reflect the non-interacting band with density of states which are some functional of the non-interacting density of states. Our result for the doped Mott insulator is essentially a special case of Hubbard’s results for which we can solve for the quasi particle spectrum exactly in the low density limit where we can neglect interactions between the doped particles or holes.

B. High Temperatures

In the previous section we discussed the ground state properties of the doped Mott insulator close to even integer filling. We found a band of single particle states which up to a rescaled hopping are equivalent to the states of the non-interacting problem. At low temperatures we thus expect a simple metallic behavior with band like charge transport. Here we will speculate on some of the interesting physics which could emerge from the model at higher temperatures.

The derivation of the single particle Hamiltonians, Eq. 26 and 27 for the particle and hole states depend crucially on the fact the Mott insulating ground state is of the simple non-degenerate form |GS, 4/2⟩ = \prod_r |n = 4/2, L = 0, S = 0 > r, and that we can ignore the higher orbital and spin multiplets in the 2 and 4 particle molecular spectra. At elevated temperatures of order the spin gap \( \Delta_s \), this assumption is no longer justified as the the spin and angular momentum modes discussed in Section III A are thermally occupied and we should consider their effect on the quasiparticle states. (The activated behavior discussed in Sec. III D 2 which has been linked to gapped triplet excitations is seen in NMR (1/T) also in the metallic Na\(_2\)CsC\(_6\)\(_0\) and Rb\(_3\)C\(_6\)\(_0\)\(_2\).) These, in fact, interact very strongly with the quasiparticles in a quite non-trivial fashion. In the presence of such an excited spin or orbital state the nearest neighbor hopping integrals described by Equation 22 turn into some more complicated expression given by for instance

\[
\langle 4, 1, 1, L^{\sigma z}, S^{\sigma z} | r, 3, l', s' \rangle | r, \sum_{j,j',\sigma} t_{j,j'}^{r} c_{j,\sigma}^\dagger c_{j',\sigma} | 3, l, s \rangle | 4, 1, 1, L^{\sigma z}, S^{\sigma z} \rangle_{r},
\]

(49)
in the case of a hole hopping to a site occupied by a spin triplet. Depending on the configurations of the spin triplet states the hopping of the hole \([3, l, s]\) may be completely suppressed or it may require a spin flip. Certainly the nearest-neighbor hopping integrals would be completely altered from the simple form of Equation 22.

It is not obvious how to model this problem but the most naive scenario might be to ignore the hopping of the spin and orbital states and replace them by thermally excited impurities causing disorder in the hopping of the particles or holes. Such a model would be similar to that suggested by Varma to explain the paramagnetic insulator to ferromagnetic metal transition in lanthanum manganites (giant magnetoresistive compounds)\[26\].

One may speculate that this temperature activated off-diagonal disorder could destroy the band like motion of the charge carriers and possibly be related to anomalous properties of A\(_3\)C\(_6\)\(_0\) at elevated temperatures such as the...
evidence for localization from NMR\textsuperscript{\textbf{27}}, the disappearance of the Fermi edge\textsuperscript{\textbf{26}} and the non-saturation of resistivity and the correspondingly extremely short mean free path\textsuperscript{\textbf{27}}.

V. CONCLUSIONS

We have studied an orbitally degenerate 3-band Hubbard model with additional multiplet splitting on-site interactions $J_S \hat{S}^2$ and $J_L \hat{L}^2$ which favor low spin and low orbital angular momentum. We use the effective Hamiltonian method in the strong coupling limit $U >> JS >> JL >> t$ perturbatively to second order in $t$. At even integer filling, $n = 2$ or $n = 4$, this model is a insulator with a non-degenerate ground state where the electrons at each site occupy the $L = 0$ and $S = 0$ configurations and with distinct spin and charge gaps. The trivial ground state allows for a simple single particle description of spin and charge excitations. The lowest energy spinful excitations is a band of magnons with a bandwidth $W_{\text{mag}} \sim t^2/U$ and a gap $\Delta_s = 2J_L + 2JS - O(t^2/U)$. A single particle or hole doped into the Mott insulator are described by the non-interacting tight-binding Hamiltonian but with an overall rescaling by a factor $1/3$ or $2/3$ of the hopping integrals and corresponding bandwidth. The latter allows for a detailed description of the particle-hole excitations and the corresponding charge gap is given by $\Delta_{\text{Mott}} \approx U + 4J_L + 3/2JS - W/2$ in terms of the band width $W$ of the non-interacting Hamiltonian.

Close to the Mott insulator, at filling $2 + x$ or $4 + x$ with $|x| << 1$, we find a metallic state with a “small Fermi surface” where the density of charge carriers is given by $|x|$ and a density of states which is simply a renormalization by a factor 3 or 3/2 of the density of states at the band edges of the non-interacting band structure. Consequently, in three dimensions the density of states will in general increase rapidly with the the doping $x$.

In this model there is also a distinct difference between even and odd integer filling which follows from the simple fact that an odd number of electrons cannot form a spin singlet. From this follows that the effective on-site repulsion is given by $U_{\text{eff}}(n = 2/4) = U + 4J_L + 3/2JS$ at even integer filling and by $U_{\text{eff}}(n = 1/3/5) = U - 4J_L - 3/2JS$ at odd. Consequently, depending on the magnitude of $J$ and $JS$, the Mott gap may be significantly reduced or vanish at odd integer filling.

The properties of this model are strikingly similar to the phenomenology of the fullerides $A_nC_{60}$ with $2 \leq n \leq 4$. The non-magnetic Mott insulator at even integer filling with a small spin gap and a larger charge gap, the even/odd effect at integer doping where $A_3C_{60}$ is generally metallic, as well as the rapid suppression of the DOS and the corresponding superconducting transition temperatures as the filling approaches even integer. We do a fit of the model to the charge gap from optical conductivity and the spin gap from NMR $1/T_1$ in $K_4C_{60}$ which appear consistent with values of $\Delta_s$ and $J_L$ of around $50 - 100meV$.

There is a number of interesting open questions about the model and the possible implications to alkali doped $C_{60}$. In particular we need a better understanding of the physics at odd integer filling on the metallic side of the Mott transition. Can this state have a superconducting ground state even though, as evidence suggest, $U_{\text{eff}}(3) > 0$ such that there is no bareattraction in the way envisioned by Chakravarty and coworkers as an electronic mechanism of superconductivity? In fact, also at even integer filling there have been intriguing suggestions of an intermediate superconducting state in the metal-insulator transition\textsuperscript{\textbf{16,17}}. Another issue is the properties of the model at elevated temperatures approaching the spin gap where we have found that the spin and orbital modes interact strongly with the charge carries and may significantly effect the simple band like charge transport.

APPENDIX: SECOND ORDER CANONICAL TRANSFORMATION.

Here we derive the expressions for the second order terms in the effective Hamiltonian Eq. 17. Starting with Eq. 16

\[ H_{\text{eff}} = H_I + h^0 + i[S_1, h^0] + \frac{i}{2}[S_1, h^1] + i[S_2, H_I], \]

where $S_1$ is given by

\[ S_1 = \sum_{(r,r')} \frac{i h_{ab}^{1,rr'} E(b) - E(a)}{E(b) - E(a)} |a\rangle_{rr'} \langle b|_{rr'} \] (A.1)

Our purpose is to construct $S_2$ such that it cancels terms which connect different energy subsectors from the
commutators \([S_1, h^{0/1}]\). We have

\[
i[S_1, h^{0/1}] = - \sum_{(r,r'),(r'',r''')} \frac{h_{ab}^{1,rr'} h_{cd}^{1,rr''} h^{0/1,rr''}}{E(b) - E(a)} \langle [a]_{rr'} | b_{rr''}, c_{rr''} \rangle \langle d_{rr''} | \rangle
\]

\[
= - \sum_{(r,r')} \frac{h_{ab}^{1,rr'} h^{0/1,rr'}}{E(b) - E(a)} \langle [a]_{rr'} | b_{rr''} \rangle \langle c_{rr''} | d_{rr''} \rangle
\]

\[
- \sum_{(r,r'',r''')} \frac{h_{ab}^{1,rr'} h^{0/1,rr''}}{E(b) - E(a)} \langle [a]_{rr'} | b_{rr''} \rangle \langle c_{rr''} | d_{rr''} \rangle,
\]

where we have used the fact the operators commute if there is no overlap between sites. Using the complete set of three site states \(1 = \prod_{a} |a_{rr''},c_{rr''} \rangle \) for the three site interaction we arrive at

\[
i[S_1, h^{0/1}] = - \sum_{(r,r'),c} \left( \frac{h_{ac}^{1,rr'} h^{0/1,rr''}}{E(c) - E(a)} + \frac{h_{ac}^{1,rr'} h^{0/1,rr'} h_{cb}^{1,rr''}}{E(c) - E(b)} \right) |a_{rr'} \rangle \langle b_{rr''} | \rangle
\]

\[
- \sum_{(r,r'',r'''),c} \left( \frac{h_{ac}^{1,rr'} h^{0/1,rr''}}{E(c) - E(a)} + \frac{h_{ac}^{1,rr'} h^{0/1,rr''} h_{cb}^{1,rr''}}{E(c) - E(b)} \right) |a_{rr',rr''} \rangle \langle b_{rr''} | \rangle,
\]

(A.2)

We now split this into a part \(\delta E(a)E(b)\) which is diagonal in energy and \((1 - \delta E(a)E(b))\) which connects different energy sectors. The latter part we can cancel by solving for \(S_2\), schematically

\[
[S_2, H_I] = -(|S_1, h^0| + \frac{1}{2} |S_1, h^1|) \text{ off-diagonal}. \quad (A.4)
\]

Using an ansatz \(S_2 = \sum_{(r,r')} S_{2,rr'}^{rr''} |a_{rr'}, b_{rr''} \rangle + \sum_{(r,r'',r''')} S_{2,rr''}^{rr''} |a_{rr',rr''}, b_{rr''} \rangle + \sum_{(r,r',r''')} S_{2,rr''}^{rr''} |a_{rr',rr''}, b_{rr''} \rangle \) and using the fact that \(|a_{rr',rr''}, b_{rr''}, H_I = (E(b) - E(a)) |a_{rr',rr''}, b_{rr''} \rangle\), we can solve for \(S_2 \sim O(t^2/\Delta E)\). Apart from the cancellation, \(S_2\) will only contribute to higher orders.

Having done the cancellation we are left with terms that are diagonal in energy. Clearly \([S_1, h^0]\) does not contribute to this because \(h^0\) is diagonal in energy and \(S \sim h^1\) is strictly off-diagonal. The result for the remaining second order terms is

\[
i \frac{1}{2} [S_1, h^1]_{\text{diagonal}} = \frac{1}{2} \sum_{(r,r'),c} \frac{h_{ac}^{1,rr'} h_{cb}^{1,rr''} + h_{ac}^{1,rr'} h_{cb}^{1,rr'} h_{cb}^{1,rr''}}{E(c) - E(a)} \delta E(a)E(b) |a_{rr'} \rangle \langle b_{rr''} | \rangle
\]

\[
- \frac{1}{2} \sum_{(r,r',r'''),c} \frac{h_{ac}^{1,rr'} h_{cb}^{1,rr''} + h_{ac}^{1,rr'} h_{cb}^{1,rr''} h_{cb}^{1,rr''}}{E(c) - E(a)} \delta E(a)E(b) |a_{rr',rr''} \rangle \langle b_{rr''} | \rangle,
\]

(A.5)

which simplifies to the final expression given in 17.
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