Metal-Insulator transitions in generalized Hubbard models

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Abstract

We study the Mott transition in Hubbard models with a degenerate band on different 3-dimensional lattices. While for a non-degenerate band only the half-filled system may exhibit a Mott transition, with degeneracy there can be a transition for any integer filling. We analyze the filling dependence of the Mott transition and find that $U_c$ (the Hubbard interaction $U$ at which the transition takes place) decreases away from half-filling. In addition we can change the lattice-structure of the model. This allows us to study the influence of frustration on the Mott transition. We find that frustration increases $U_c$, compared to bipartite systems. The results were obtained from fixed-node diffusion Monte Carlo calculations using trial functions which allow us to systematically vary the magnetic character of the system. To gain a qualitative understanding of the results, we have developed simple hopping arguments that help to rationalize the doping dependence and the influence of frustration on the Mott transition. Choosing the model parameters to describe the doped Fullerides, we can make contact with experiment and understand why some of the Fullerides are metals, while others, which according to density functional theory should also be metallic, actually are insulators.

Key words: Mott transition, Hubbard model, degenerate, filling, bipartite, frustration, Fullerenes, quantum Monte Carlo

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1 Introduction

The Hubbard model is an elementary model to study strongly interacting systems. In particular it can be used to understand the Mott metal-insulator transition. The original Hubbard model describes $s$ electrons in a narrow band. With one electron per site, the half-filled system will become insulating for large enough correlation strength. To describe more realistic situations one has to generalize the Hubbard model to systems with degenerate (or near-degenerate) orbitals. Such degenerate orbitals can arise for example in molecular solids or transition metal compounds. For such a degenerate Hubbard model there will be a Mott transition not only at half-filling, but for all integer fillings. It is then a natural question how the location of the Mott transition depends, for an otherwise unchanged Hamiltonian, on the filling. An other issue is the problem of how the Mott transition depends, for the same filling, on the lattice-structure of the system. To address these questions we have determined the Mott transition for degenerate Hubbard models with various integer fillings and different lattice-structures. We have used Hamiltonians that describe the alkali doped Fullerenes, since these materials have been synthesized in various integer dopings and crystal structures.

2 Model and Method

The inter-molecular interaction in solid $C_{60}$ is very weak. Therefore the energy levels of the molecule merely broaden into narrow, well separated bands [1]. The conduction band originates from the lowest unoccupied molecular orbital, the 3-fold degenerate $t_{1u}$ orbital. To get a realistic, yet simple description of the electrons in the $t_{1u}$ band, we use a Hubbard-like model that describes the interplay between the hopping of the electrons and their mutual Coulomb repulsion [2]:

$$H = \sum_{\langle ij \rangle} \sum_{mm'\sigma} t_{im,jm'} c_{im\sigma}^\dagger c_{jm'\sigma} + U \sum_i \sum_{\langle m\sigma\rangle < \langle m'\sigma'\rangle} n_{ima} n_{ima'}.$$

The sum $\langle ij \rangle$ is over nearest-neighbor sites. The hopping matrix elements $t_{im,jm'}$ between orbital $m$ on molecule $i$ and orbital $m'$ on molecule $j$ are obtained from a tight-binding parameterization [3,4]. The molecules are orientationally disordered [5], and the hopping integrals are chosen such that this orientational disorder is included [6]. The band-width for the infinite system is $W = 0.63 \, \text{eV}$. The on-site Coulomb interaction is $U \approx 1.2 \, \text{eV}$. The model neglects multiplet effects, but we remark that these tend to be counteracted by the Jahn-Teller effect, which is also not included in the model.
To identify the Mott transition we calculate the energy gap

\[ E_g = E(N + 1) - 2E(N) + E(N - 1), \quad (2) \]

where \( E(N) \) is the energy of a cluster of \( N_{mol} \) molecules with \( N = n N_{mol} \) electrons (integer filling \( n \)). We determine these energies using fixed-node diffusion Monte Carlo \[7\]. Starting from a trial function \( |\Psi_T\rangle \) we calculate

\[ |\Psi^{(n)}\rangle = (1 - \tau(H - w))^n |\Psi_T\rangle, \quad (3) \]

where \( w \) is an estimate of the ground-state energy. The \( |\Psi^{(n)}\rangle \) are guaranteed to converge to the ground state \( |\Psi_0\rangle \) of \( H \), if \( \tau \) is sufficiently small and \( |\Psi_T\rangle \) is not orthogonal to \( |\Psi_0\rangle \). Since we are dealing with Fermions, the Monte Carlo realization of the projection (3) suffers from the sign-problem. To avoid the exponential decay of the signal-to-noise ratio we use the fixed-node approximation \[7\]. For lattice models this involves defining an effective Hamiltonian \( H_{eff} \) by deleting from \( H \) all nondiagonal terms that would introduce a sign-flip. Thus, by construction, \( H_{eff} \) is free of the sign-problem. To ensure that the ground-state energy of \( H_{eff} \) is an upper bound of \( E_0 \), for each deleted hopping term an on-site energy is added in the diagonal of \( H_{eff} \). Since \( |\Psi_T\rangle \) is used for importance sampling, \( H_{eff} \) will depend on the trial function. Thus, in a fixed-node diffusion Monte Carlo calculation for a lattice Hamiltonian we choose a trial function and construct the corresponding effective Hamiltonian, for which the ground-state energy \( E_{FNDMC} \) can then be determined without sign-problem by diffusion Monte Carlo.

For the trial function we make the Gutzwiller Ansatz

\[ |\Psi(U_0, g)\rangle = gD |\Phi(U_0)\rangle, \quad (4) \]

where the Gutzwiller factor reflects the Coulomb term \( U D = U \sum n_{i\sigma} n_{i\sigma'} \) in the Hamiltonian (1). \( |\Phi(U_0)\rangle \) is a Slater determinant that is constructed by solving the Hamiltonian in the Hartree-Fock approximation, replacing \( U \) by a variational parameter \( U_0 \). Increasing \( U_0 \) will change the character of the trial function from paramagnetic to antiferromagnetic. This transition is also reflected in the variational energies obtained in quantum Monte Carlo, as shown in Fig. 1. Clearly, for small \( U \) the paramagnetic state is more favorable, while for large \( U \) the antiferromagnetic state gives a lower variational energy. Details on the character of the trial function and the optimization of the parameters can be found in Ref. \[8\].
Fig. 1. Dependence of variational (VMC) and fixed-node diffusion Monte Carlo (FN-DMC) on the trial function. $U_0$ is the Hubbard interaction that was used for the Slater determinant in the Gutzwiller wavefunction $\Psi_T(R) = g^{D(R)} \Phi(U_0)$. The Gutzwiller parameter $g$ has always been optimized. The results shown here are the energies (relative to the atomic limit) for a Hamiltonian that describes $K_3C_{60}$ (32 sites), with $U$ being varied from 1.25 (lowest curve) to 2.00 eV (highest curve).

3 Results

We now turn to the problem of the Mott transition in degenerate Hubbard models for different integer dopings and for different lattice-structures. The examples will be for integer-doped Fullerides $A_nC_{60}$, where $A$ stands for an alkali metal like K, Rb, or Cs. Density functional calculations predict that all the doped Fullerides $A_nC_{60}$ with $n = 1 \ldots 5$ are metals [1]. Only $C_{60}$ and $A_6C_{60}$ are insulators with a completely empty/filled $t_{1u}$ band. On the other hand, Hartree-Fock calculations for the Hamiltonian (1) predict a Mott transition already for $U$ smaller than the band-width, and hardly any doping dependence. General arguments also suggest that the alkali doped Fullerenes should be Mott insulators, since the Coulomb repulsion $U$ between two electrons on the same $C_{60}$ molecule ($U \approx 1.2 \text{ eV}$) is substantially larger than the width of the $t_{1u}$ band ($W \approx 0.6 \text{ eV}$). It has therefore even been suggested that experimental samples of, say, the superconductor $K_3C_{60}$ are metallic only because they are non-stoichiometric, i.e. that they actually are $K_{3-\delta}C_{60}$ [9].

3.1 $K_3C_{60}$

In a first step we investigate what consequences the degeneracy of the $t_{1u}$-band has for the Mott transition in $K_3C_{60}$. The analysis is motivated by the following simple argument [2,10]. In the limit of very large $U$ we can estimate the energies needed to calculate the gap (2). For half-filling, all molecules will have three electrons in the $t_{1u}$ orbital (Fig. 2 a). Hopping is strongly suppressed since it would increase the energy by $U$. Therefore, to leading order in $t^2/U$, there will be no kinetic contribution to the total energy $E(N)$. In contrast,
Fig. 2. Degeneracy argument: a) In the large-$U$ limit hopping is suppressed for an integer-filled system. b) An additional charge can hop without extra Coulomb energy. For degenerate orbitals and an antiferromagnetic background there are several different ways the extra charge can hop to a neighboring molecule.

the systems with $N \pm 1$ electrons have an extra electron/hole that can hop without additional cost in Coulomb energy. To estimate the kinetic energy we calculate the matrix element for the hopping of the extra charge against an antiferromagnetic background. Denoting the initial state with extra charge on molecule $i$ by $|1\rangle$, we find that the second moment $\langle 1|H^2|1\rangle$ is given by the number of different possibilities for a next-neighbor hop times the single electron hopping matrix element $t$ squared. By inserting $\sum_j |j\rangle\langle j|$, where $|j\rangle$ denotes the state with the extra charge hopped from site $i$ to site $j$, we find $\langle 1|H|j\rangle = \sqrt{3} t$, since, with an antiferromagnetic background and degeneracy 3, there are three different ways an extra charge can hop to a neighboring molecule (Fig. 2, b). Thus, due to the 3-fold degeneracy, the hopping matrix element is enhanced by a factor $\sqrt{3}$ compared to the single electron hopping matrix element $t$. In the single-electron problem the kinetic energy is of the order of half the band-width $W/2$. The enhancement of the hopping matrix element in the many-body case therefore suggests that the kinetic energy for the extra charge is correspondingly enhanced. Inserting the energies into (2) we find that for the 3-fold degenerate system our simple argument predicts a gap

$$E_g = U - \sqrt{3} W,$$

instead of $E_g = U - W$ in the non-degenerate case. Extrapolating to intermediate $U$, it appears that the degeneracy shifts the Mott transition towards larger $U$.

The above argument is, of course, not rigorous. First, it is not clear whether the result for $E_g$ that was obtained in the limit of large $U$ can be extrapolated to intermediate $U$, where the Mott transition actually takes place. Also the analogy of the hopping in the many-body case with the hopping of a single electron is not rigorous, since the hopping of an extra charge against an antiferromagnetic background creates a string of flipped spins [11]. Nevertheless the argument suggests that orbital degeneracy should play an important role for the Mott transition.
Fig. 3. Finite-size corrected gap $\tilde{E}_g = E_g - U/M - E_g(U = 0)$ for increasing Coulomb interaction $U$ as a function of $1/M$, where $M$ is the number of molecules. The calculations are for a Hubbard model with hopping matrix elements appropriate for K$_3$C$_{60}$. The band-width varies between $W = 0.58\, eV$ for $M = 4$ and $W = 0.63\, eV$ in the infinite-size limit.

To check this proposition, we look at the results of the quantum Monte Carlo calculations for the model Hamiltonian (1) [2]. The Coulomb interaction $U$ has been varied from $U = 0 \ldots 1.75\, eV$ to study the opening of the gap. Since the Monte Carlo calculations are for finite systems, we have to extrapolate to infinite system size. To improve the extrapolation we correct for finite-size effects: First, there could be a gap $E_g(U = 0)$ already in the spectrum of the non-interacting system. Further, even for a metallic system of $M$ molecules, there will be a finite-size contribution of $U/M$ to the gap. It comes from the electrostatic energy of the extra charge, uniformly distributed over all sites. Both corrections vanish in the limit $M \to \infty$, as they should. The finite-size corrected gap $\tilde{E}_g = E_g - U/M - E_g(U = 0)$ for systems with $M = 4, 8, 16, 32$, and $64$ molecules is shown in Fig. 3. We find that the gap opens for $U$ between $1.50\, eV$ and $1.75\, eV$. Since for the real system $U = 1.2 \ldots 1.4\, eV$, K$_3$C$_{60}$ is thus close to a Mott transition, but still on the metallic side — even though $U$ is considerably larger than the band-width $W$. This is in contrast to simpler theories that neglect orbital degeneracy.

### 3.2 Doping dependence

The degeneracy argument described above for K$_3$C$_{60}$ can be generalized to integer fillings. Away from half-filling the enhancement of the hopping matrix elements for an extra electron is different from that for an extra hole. The effective enhancement for different fillings are given in Table 1. We find that the enhancement decreases as we move away from half-filling. Therefore we expect that away from half-filling correlations become more important, putting the system closer to the Mott transition, or maybe even pushing it
filling enhancement

| n = 3 | $\sqrt{3} \approx 1.73$ |
| n = 2, 4 | $\frac{\sqrt{3} + \sqrt{2}}{2} \approx 1.57$ |
| n = 1, 5 | $\frac{\sqrt{2} + 1}{2} \approx 1.21$ |

Table 1
Degeneracy enhancement for different integer fillings.

Fig. 4. Doping dependence of the Mott transition. The error bars indicate the estimate of the critical ratio $U/W$ for different integer fillings of the $t_{1u}$ band. The calculations are for Fm$\bar{3}$m Fullerides with fcc lattice-structure and orientational disorder. The shaded region shows the range of $U/W$ in which the doped Fullerenes are falling.

across the transition, making it an insulator. We have analyzed the doping dependence of the Mott transition for the same Hamiltonian as used for K$_3$C$_{60}$, changing the filling of the $t_{1u}$ band from $n = 1$ to 5. This model describes the Fm$\bar{3}$m-Fullerides $A_n$C$_{60}$ with fcc lattice and orientational disorder [12]. The critical Coulomb interaction $U_c$, at which, for the different integer fillings, the transition from a metal (for $U < U_c$) to an insulator ($U > U_c$) takes place, is shown in Fig. 4. As expected from the degeneracy argument, $U_c$ decreases away from $n = 3$. We note, however, that $U_c$ is asymmetric around half-filling. This asymmetry is not present in the simple degeneracy argument, where we implicitly assumed that the lattice is bipartite. In such a situation we have electron-hole symmetry, which implies symmetry around half-filling. For frustrated lattices, like the fcc lattice, electron-hole symmetry is broken, leading to an asymmetry in $U_c$ that is seen in Fig. 4.

3.3 Dependence on lattice-structure

To understand the effect of frustration in terms of the hopping arguments that we have made so far, we have to consider more than just one next-neighbor
Fig. 5. Basis states for four electrons on a triangle in the limit of large Hubbard interaction $U$. They are generated e.g. by hopping the extra charge clockwise around the triangle. After three hops the extra charge has returned to the original site. It takes, however, an extra lap to restore the spins to the original configuration.

The simplest system where we encounter frustration is a triangle with hopping matrix elements $-t$ between neighboring sites. In the single-electron case we can form a bonding state with energy $E_{\text{min}} = -2t$, but because of frustration we cannot form an anti-bonding state. Instead the maximum eigenenergy is $E_{\text{max}} = t$. Hence frustration leads to an asymmetric 'band' of width $W = 3t$.

In the many-body case the situation is different. Like in the degeneracy argument, we look at the hopping of an extra electron against a (frustrated) antiferromagnetic background in the large-$U$ limit. For simplicity we assume a non-degenerate system, i.e. there is one electron per site on the triangle, plus the extra electron. In this case we have to move the extra charge twice around the triangle to come back to the many-body state we started from (cf. Fig. 5). Thus in the large-$U$ limit the many-body problem is an eigenvalue problem of a $6 \times 6$ matrix with extreme eigenvalues $\pm 2t$. In the degeneracy argument we have assumed that the kinetic energy of the extra charge is given by $W/2$. On the triangle, we find, however, that the hopping energy is by a factor of $4/3$ larger than that. This suggests that for frustrated systems the single electron band-width $W$ in (5) should be multiplied by a prefactor larger than one. We therefore expect that frustration alone, already without degeneracy, shifts the Mott transition to larger $U$.

To analyze the effect of frustration on the Mott transition we have determined the critical $U$ for a hypothetical doped Fullerene $A_4C_{60}$ with body centered tetragonal (bct) structure, a lattice without frustration, having the same band-width ($W = 0.6 \text{eV}$) as the fcc-Fullerides, shown in Fig. 4. For $U = 1.3 \text{eV}$, we find a gap $E_g \approx 0.6 \text{eV}$ for the Fulleride with bct structure, while the frustrated fcc compound still is metallic $E_g = 0$. This difference is entirely due to the lattice-structure. Using realistic parameters for $K_4C_{60}$ [4] that crystallizes in a bct structure we find a Mott insulator with gap $E_g \approx 0.7 \text{eV}$, which is in line with experimental findings: $E_g = 0.5 \pm 0.1 \text{eV}$ [13].
4 Conclusion

We have seen that, due to more efficient hopping, orbital degeneracy increases the critical $U$ at which the Mott transition takes place. This puts the integer-doped Fullerenes close to a Mott transition. Whether they are on the metallic or insulating side depends on the filling of the band and the lattice-structure: Since the degeneracy enhancement is most efficient for a half-filled band, systems doped away from half-filling tend to be more insulating. The effect of frustration, on the other hand, is to make the system more metallic.

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