Mott Transition in Degenerate Hubbard Models: Application to Doped Fullerenes

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(April 22, 1996)

The Mott-Hubbard transition is studied for a Hubbard model with orbital degeneracy $N$, using a diffusion Monte Carlo method. Based on general arguments, we conjecture that the Mott-Hubbard transition takes place for $U/W \sim \sqrt{N}$, where $U$ is the Coulomb interaction and $W$ is the bandwidth. This is supported by exact diagonalization and Monte Carlo calculations. Realistic parameters for the doped fullerenes lead to the conclusions that stoichiometric $A_3C_{60}$ $(A=K, Rb)$ are near the Mott-Hubbard transition, in a correlated metallic state.

The fullerenes have attracted much interest, not least because of the superconductivity of $A_3C_{60}$ $(A=K, Rb)$ [1]. Much work has been performed to explain this phenomenon [2]–[5], starting from the assumption that the systems are metallic. The metallicity is an experimental fact [6], but surprising from a theoretical point of view. The Coulomb interaction $U$ between two electrons on the same $C_{60}$ molecule may be a factor 1.5–2.5 larger than the width $W$ of the (partly occupied) $t_{1u}$ band [7]–[9]. Since systems with $U/W$ exceeding a critical value a bit larger than unity ($\sim 1.5$) are believed to be Mott-Hubbard insulators [10], one would expect this to apply to doped $C_{60}$ compounds.

The Mott-Hubbard transition is studied for a Hubbard model with orbital degeneracy $N$, where no electron can hop without an extra energy cost $U$. We thus consider the states $\langle \psi^{\dagger}_{\alpha} \rangle$ which is a Mott insulator with a band gap of $E_g$, and that experimental samples are metallic only if the critical value of $U/W$ is enhanced by a factor $\sqrt{N}$. Since systems with $U/W$ exceeding a critical value a bit larger than unity ($\sim 1.5$) are believed to be Mott-Hubbard insulators [10], one would expect this to apply to doped $C_{60}$ compounds. It has therefore been suggested that stoichiometric K$_3C_{60}$ is a Mott insulator with a band gap of $0.7$ eV, and that experimental samples are metallic only because they are nonstoichiometric [11]. Alternatively, the critical value $U_c/W$ could be larger than commonly believed. Which one of these alternatives apply, could have important implications for the properties of nonstoichiometric $A_3C_{60}$ as well.

In a treatment using the Gutzwiller Ansatz and the Gutzwiller approximation [12]–[14] for the Hubbard model, Lu found the critical value $U/W$ to vary as $(N + 1)$ at half-filling [15]. Here we provide qualitative arguments showing that the degeneracy is important, but that the critical value is substantially smaller and has a weaker $(\sqrt{N})$ dependence than in the work of Lu. Our arguments are supported by exact diagonalization and Quantum Monte-Carlo calculations.

To discuss the Mott-Hubbard gap for a model with the orbital degeneracy $N$, we first consider a (bipartite) lattice with $M$ sites and a hopping integral $t_{\alpha m,jm'} = t_{\delta mn}$ between orbitals with the same quantum numbers $m$ on neighboring sites $i$ and $j$. For half-filling the energy gap is then

$$E_g = E(NM + 1) + E(NM - 1) - 2E(NM),$$

where $E(L)$ is the ground-state energy for $L$ electrons. For $U \gg t$ we have

$$E(NM) = \frac{1}{2}N(N-1)MU + O(t^2/U),$$

since no electron can hop without an extra energy cost $U$. For instance, this energy is obtained for a Neel state $|0\rangle$, with the moment $N$. In the system with $NM + 1$ electrons, the extra electron can hop without an extra energy cost $U$. We thus consider the states

$$|i\rangle = \frac{1}{\sqrt{N}} \psi^{\dagger}_{\alpha} \sum_m \psi^{\dagger}_{jm} \psi_{1m} |0\rangle,$$

where $\psi^{\dagger}_{jm}$ creates a spin up electron on site $j$ in orbital $m$. The sites $i$ are nearest neighbors of site 1, which we have assumed to have spin down electrons in the state $|0\rangle$. We then have

$$\langle i|H|1\rangle = \sqrt{N}t,$$

i.e., an electron hops from site 1 to site $i$ with a matrix element which is a factor $\sqrt{N}$ larger than in the one-particle case [16]. This is due to the fact that any of the transitions for $U/W$ inferred from experiment and encourages theoretical calculation.

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$N$ spin up electrons can hop from site 1 to $i$. We next construct states $|ij\rangle$ ($j \neq 1$) where a nearest neighbor $j$ of $i$ has an extra electron. The corresponding matrix element is $\sqrt{N}t$. However, the states $|ij\rangle$ depend on which site $i$ had an extra electron in the intermediate state. We use the analogy with the one-electron case, although it is not rigorous, since in the many-body case there is a string of reduced spins along the path of the moving additional occupancy. In the one-electron case, the hopping of an electron lowers the energy by $e_b$, where $e_b$ is the bottom of the band. The close analogy between the one- and many-particle problems then suggests

$$E(NM + 1) \approx E(NM) + NU + \sqrt{N}e_b,$$

with an extra factor $\sqrt{N}$ in front of $e_b$. Using a similar result for $E(NM - 1)$ we obtain

$$E_g = U - \sqrt{N}(e_t - e_b) \equiv U - \sqrt{NW},$$

where $e_t (= -e_b$ in this model) is the top of the one-particle band. This can be generalized to the case where all the hopping integrals $t_{im,jm'} \equiv t$ for $i$ and $j$ nearest neighbor sites. For $N = 1$ we obtain $E_g = U - W$. If this result is extrapolated to smaller $U$, it predicts a Mott-Hubbard transition for $U/W \sim 1$, close to previous results. Eq. (6) suggests, however, that for a degenerate system the transition takes place for a larger ratio $\sim \sqrt{N}$.

To test this, we have performed exact diagonalization calculations for a Hubbard model with a six site ($3 \times 2$) lattice with $(N = 2)$ and without $(N = 1)$ orbital degeneracy. Table I compares the exact band gap with the all the hopping integrals of two orientations in accordance with experiment [23], and the hopping integrals are chosen so that this orientational disorder is included [24]. The band width of the infinite system is $W = 0.63$ eV. The model neglects multiplet effects. The inclusion of these effects may favor antiferromagnetism, which could reduce the critical value $U_c/W$ for a Mott-Hubbard transition.

We first consider a cluster of four $C_{60}$ molecules, for which the Hamiltonian (7) can be diagonalized exactly. The results are shown in Table I for the cases of three ($A_2C_{60}$) and four $C_{60}$ molecules. $W=0.6$ for the six atom cluster and 0.58 for the $C_{60}$ cluster. $E_g(n)$ is the band gap for $n$ electrons per site. All energies are in eV.

| $U$ | $N = 1$ (6-site) | $N = 2$ (6-site) | $N = 3$ (4C$_{60}$) |
|-----|-----------------|-----------------|-----------------|
| $E_g(1)$ | $U - W$ | $E_g(2)$ | $U - \sqrt{2}W$ | $E_g(3)$ | $U - \sqrt{3}W$ |
| 10  | 9.35 | 9.40 | 9.06 | 9.15 | 8.39 | 9.00 |
| 5   | 4.39 | 4.40 | 4.12 | 4.15 | 3.48 | 4.00 |
| 3   | 2.44 | 2.40 | 2.18 | 2.15 | 1.64 | 2.00 |
| 2   | 1.48 | 1.40 | 1.24 | 1.15 | 0.90 | 1.00 |
| 1   | 0.54 | 0.40 | 0.35 | 0.15 | 0.46 | 0.00 |

To study the Mott-Hubbard transition, we consider larger systems. We use a diffusion Monte Carlo method, which we have developed along the lines of ten Haaf et al. [25]. Starting from a trial function $|\Psi_T\rangle$, we calculate

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

where the sum $<ij>$ is over nearest neighbor sites. We have used a fcc lattice. The hopping integrals $t_{im,jm'}$ have been obtained from a tight-binding parametrization [21][22]. The molecules are allowed to randomly take one of two orientations in accordance with experiment [23], and the hopping integrals are chosen so that this orientational disorder is included [24]. The band width of

| $M$ | g | VM | DMC | Exact |
|-----|---|---|-----|------|
| 11  | 0.45 | 8.4970 | 8.4677 | 8.4649 |
| 11  | 0.50 | 8.4842 | 8.4777 | 8.4684 |
| 12  | 0.45 | 10.7364 | 10.7014 | 10.6994 |
| 12  | 0.50 | 10.7226 | 10.7009 | 10.6994 |
| 13  | 0.45 | 13.4363 | 13.3990 | 13.3973 |
| 13  | 0.50 | 13.4211 | 13.3988 | 13.3973 |
| 13  | 0.55 | 13.4233 | 13.3991 | 13.3973 |
| $E_g$ | 0.45 | 0.4605 | 0.4639 | 0.4634 |
| $E_g$ | 0.50 | 0.4601 | 0.4647 | 0.4634 |
| $E_g$ | 0.51 | 0.4608 | 0.4651 | 0.4651 |
where $w$ is an estimate of the ground-state energy. If $\tau$ is sufficiently small and $|\Psi_T\rangle$ is not orthogonal to the ground-state, $|\Psi^{(n)}\rangle$ converges to the ground-state as $n \to \infty$. $|\Psi^{(n)}\rangle$ is calculated in a Monte Carlo approach. Although this approach in principle is exact, it suffers from the usual sign problem. We therefore use the lattice equivalent of a fixed node approximation [24], and introduce an effective Hamiltonian for which the nondiagonal terms are zero if

$$
\langle \Psi_T | R \rangle \langle R | F \rangle \langle F | \Psi_T \rangle < 0,
$$

(9)

where $R$ represents the coordinates of all the electrons. A term is added to the diagonal part of the effective Hamiltonian, so that its energy is an upper bound to the exact energy, with the upper bound agreeing with the exact energy if $|\Psi_T\rangle$ is the exact wave function [23].

For the trial function we make the Gutzwiller Ansatz

$$
|\Psi_T\rangle = g^{n_d} |\Psi_0\rangle
$$

(10)

where $g$ is a Gutzwiller parameter and the power $n_d$ is the number of double occupations $n_d = \sum_m \sum_{\sigma < \sigma'} n_{m\sigma} n_{m\sigma'}$ in the Slater determinant $|\Psi_0\rangle$. To construct $|\Psi_0\rangle$ we solve the Hamiltonian [9] in the Hartree-Fock approximation, replacing $U$ by a variational parameter $U_0$. Depending on $U_0$ the trial function is paramagnetic or antiferromagnetic.

As a test, we study a cluster of four C$_{60}$ molecules. We calculate the expectation value of $H$ for $|\Psi_T\rangle$ in a variational Monte Carlo (VMC) approach and perform a diffusion calculation (DMC). The results are compared with the exact results in Table I. The agreement is very good, with an error of 0.003 eV or less in the DMC calculation for the parameters considered.

To obtain an efficient extrapolation to infinite systems, we correct for finite size effects [24]. For the present problem, there should be a gap for a finite system even for a small $U$. We can see this by distributing the charge uniformly over all the levels and calculate the electrostatic energy. This gives a contribution $U/M$ to the gap [24], where $M$ is the number of molecules. We then introduce

$$
\tilde{E}_g \equiv E_g - \frac{U}{M} - E_g(U = 0),
$$

(11)

where $E_g(U = 0)$ is the gap in the one-particle spectrum. We may then expect $\tilde{E}_g$ to be rather independent of $M$ for itinerant systems. Both $U/M$ and $E_g(U = 0)$ go to zero for $M \to \infty$, so the subtracted quantities improve the convergence but do not change the $M \to \infty$ result.

In Fig. 1 we show results for $\tilde{E}_g$ that suggest a Mott-Hubbard transition for $U$ between 1.5 and 1.75 eV. This corresponds to a critical ratio $U_c/W \sim 2.5$. This is substantially smaller than the ratio 4 found by Lu [19]. For a fully frustrated system with infinite dimension but without orbital degeneracy $U_c/W = 1.5$ was obtained [18].

Multiplying by the degeneracy factor $\sqrt{3}$ leads to the ratio $\sqrt{3} \times 1.5 = 2.6$ in good agreement with our results. It is interesting to note that for $U=1.75$, which gives an insulator, an antiferromagnetic trial function results in the lowest energy for the larger systems.

The average Coulomb $U$ has been estimated to be 1.6 eV [1] and 1.4 $\pm$ 0.2 eV [10] from Auger experiments for the occupied orbitals. A slightly smaller (0.2 eV) value was found for the highest occupied orbital ($h_u$) [9], and $U$ may be somewhat further reduced for the higher-lying $t_{1u}$ orbital. The reduced screening in the surface layer is estimated to increase $U$ in this layer by 0.3 eV [1]. The surface sensitivity of Auger may therefore slightly overestimate $U$. Theoretically, $U$ has been estimated to be in the range 0.8-1.3 eV [14]. Band structure calculations have found the band width 0.41 eV [13], 0.6 eV [12] and 0.65 eV [14] for K$_3$C$_{60}$. Many-body effects were found to increase the band width by about 30% in the GW approximation for undoped C$_{60}$ [7]. The many-body effects treated in the Hubbard model, due to the
interactions in the $t_{1u}$ band, are not included in the GW calculation, since the $t_{1u}$ band was empty in the GW calculation. Using the GW enhancement of the band width is therefore not a double-counting. For Rb$_3$C$_60$ the band width may be reduced by about 15% [22], compared with K$_3$C$_60$. This leads to a likely ratio $U/W$ in the range 1.5-2.5. In view of our QMC results, this is probably too small to cause a Mott-Hubbard transition for A$_3$C$_60$.

One could ask what are the effects of $U > W$ in a metal. The system can remain a metal in spite of the large value of $U/W$ thanks to the hopping via several channels (Eq. (3)). As in the impurity problem [20], this may favor the formation of a singlet state. In A$_3$C$_60$, which has an odd number of electrons per site, the singlet is consistent with a correlated non-magnetic state, which must be metallic if it obeys the Luttinger theorem [28]. It is suggestive that such singlet correlations could tend to promote superconductivity in these systems.

While A$_3$C$_60$ are metals, A$_4$C$_60$ are insulators [28], although band structure calculations predict that they should be metals [30]. A$_3$C$_60$ is therefore not a band insulator, and this raises interesting questions about the difference between A$_3$C$_60$ and A$_4$C$_60$. The presence of four electrons per molecule in A$_4$C$_60$ favors the formation of a static Jahn-Teller effect, which may open up a gap [31], in particular if electron correlation effects are also included. The electron-phonon coupling should reduce the effective hopping for both A$_3$C$_60$ and A$_4$C$_60$. One may also speculate that the gap in A$_4$C$_60$ is a consequence of the interactions in a case with an even number of electrons per site. This could be a correlation induced gap with no development of magnetic moments, i.e., a different type of order than in other correlated Mott insulators such as NiO. Besides A$_4$C$_60$ is bipartite while A$_3$C$_60$ is not, which may favor the development of ordered phases (anti-ferromagnetic or other types of order) and the opening of a gap in A$_4$C$_60$. Finally, the Fermi surface of A$_4$C$_60$ has almost perfect nesting, which may favor a charge density wave and the opening of a gap [32].

To summarize, we have shown that the orbital degeneracy increases the value of $U/W$ where the Mott-Hubbard transition takes place, due to the more efficient hopping. This puts the critical ratio for A$_3$C$_60$ at the upper range of ratios $U/W$ estimated for doped C$_60$ compounds and makes it likely that A$_3$C$_60$ (A=K, Rb) is on the metallic side. Although experimental samples of A$_3$C$_60$ may be nonstoichiometric, it is therefore not necessary to assume so to explain the metallicity. The large value of $U/W$ may nevertheless lead to substantial correlation effects, which may have a large influence on certain properties. Most systems of interest have orbital degeneracy [4]. Therefore our results should be relevant also for many other systems close to a Mott-Hubbard transition.

We would like to thank D.F.B. ten Haaf, H.J.M. van Bemmel, J.M.J. van Leeuwen, and W. van Saarloos for helpful conversations in the early stages of this work. A. Burkhardt and A. Schulmacher provided invaluable help in adapting the programs for parallel computation. This work was supported in part by the the NSF under grants DMR-94-22496 and DMR-89-20538.

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