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Metal-insulator transitions in degenerate Hubbard models and A_xC_{60}

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(Received 12 November 1993)

Analytic results for Mott-Hubbard metal-insulator transitions in N-fold degenerate Hubbard models are obtained using the Gutzwiller approximation. It is found that for any commensurate filling with integer (x) electrons per site, there exists a metal-insulator transition at the critical correlation energy $U_c(N,x)=\{[\sqrt{x(2N-x+1)}+\sqrt{(x+1)(2N-x)}]^2/(2N-x)\}|\bar{\epsilon}(x)|$, where $\bar{\epsilon}$ is the energy per particle in the absence of correlation. U_c increases with x reaching the maximum at the half filling $x=N$. Therefore, it is possible for a system to be metallic at half filling and insulating away from half filling. This provides an explanation for the unusual metal-insulator transitions observed in fullerides A_xC_{60}.

The discovery of superconductivity in A_3C_{60} (Ref. 1) has given rise to great interest in alkali-metal-doped fullerides A_xC_{60}.[2] One of the most puzzling phenomena is the unusual metal-insulator transitions observed in these materials: only A_3C_{60} is metallic, all other phases, A_1C_{60}, A_2C_{60}, and A_4C_{60} being insulating.[3] This is in contradiction with band-structure calculations,[4] which predict all of them to be metallic due to the threefold degeneracy of the conduction band. This suggests that the intramolecular electron-electron interaction is important. The existence of strong correlation in fullerides is supported by spectroscopy experiments. The estimated correlation energy $U\sim 1-2$ eV (Refs. 3, 5, and 6) is much larger than the conduction-band width $W\sim 0.2-0.4$ eV.[4,7] Based on this fact, a suggestion has been made that A_3C_{60} ($x=3$ corresponds to the half filling of the conduction band) is a Mott-Hubbard insulator and the superconducting phase is not stoichiometric.[5] However, structural, transport, and spectroscopic measurements show that the superconducting phase is stoichiometric and there is no evidence of insulating behavior in A_3C_{60}.[2] Therefore a simple nondegenerate Hubbard model, which is known to be insulating at half filling when $U\gg W$, cannot explain the unusual metal-insulator transitions observed. The threefold degeneracy of the conduction band must be taken into account.

In this paper we report results of a study on the general N-fold degenerate Hubbard model using the Gutzwiller approximation.[8] It is found that metal-insulator transitions exist for all commensurate fillings (integer numbers of electrons per site). The critical correlation energy $U_c(x,N)$ is found to depend strongly on both the number of electrons per site x and the degeneracy N. The maximum U_c occurs at the half filling $x=N$. This demonstrates the possibility that for a given fixed ratio, U/W, a system can be metallic at half filling and insulating at other rational fillings. Our results provide a plausible explanation for the unusual metal-insulator transitions observed in A_xC_{60}.

We consider the tight binding N-fold degenerate Hubbard model with an on-site Hubbard U independent of orbitals and spins,

$$H=\sum_{i,j,\alpha,\beta} t_{i,j}^{\alpha,\beta} c_{j,\beta}^{\dagger} c_{i,\alpha}+\frac{U}{2}\sum_{i,\alpha\neq\beta} n_{i,\alpha}n_{i,\beta}\,. \tag{1}$$

Here $\alpha=(r,\sigma)$ includes both the spin (σ) and the orbital (r) indices; $n_{i,\alpha}=c_{i,\alpha}^{\dagger}c_{i,\alpha}$ is the number operator. The $N=1$ case, which is generally referred to as the Hubbard model, has been extensively studied in the last three decades. In particular, the pioneer work of Hubbard[9] and Gutzwiller[8] has lead to significant progress in understanding the metal-insulator transitions in strongly correlated systems. In contrast, the degenerate Hubbard model has received little attention since the early work,[10] in part due to the great difficulty of the problem and the lack of analytic results.

Let L be the size of the lattice and $m=xL/2N$ the number of electrons per orbital (a complete symmetry between orbitals is assumed). By commensurate filling we mean that the average number of electrons per site x is an integer. If U is sufficiently large, one expects an insulating ground state where x electrons are localized at every site and hopping is forbidden. As U decreases, the metal-insulator transition sets in at a critical U_c. In general, the insulating ground state of the degenerate Hubbard model can be magnetically ordered. Here we will consider only the nonmagnetic (or disordered) insulating state. This makes the analytical calculations tractable. In addition, for applications to A_xC_{60} this is sufficient, as the insulating state in these materials is known to be nonmagnetic. The absence of magnetic order in A_xC_{60} is likely due to the nonbipartite nature of the lattice struc-

tures (fcc or close approximates), which causes frustration, and to the intrinsic orientational and displacement disorder existing in these materials.[7,11] Though we believe that the qualitative results described below are likely to be valid for a magnetically ordered state, it is clear that further work is required to address this issue.

The simple Hubbard model has been extensively studied in the past, particularly in recent years as a model of high-T_c superconductors. At half filling it is known that (1) in one dimension (1D), exact solution by Bethe ansatz gives an insulating ground state for any U.[12] (2) In 2D, numerical calculations on a square lattice suggest an antiferromagnetic insulator ground state for large and moderate U.[13] It is not clear whether a finite U_c exists for the square lattice. However, for an extended Hubbard model (the so-called Kievelson-Schriffer-Su-Heeger model)[14] it has been shown exactly that the Mott-Hubbard transition exists at a finite U_c, and the U_c found in the exact solution coincides with that found for the Hubbard model using the Gutzwiller approximation.[8] (3) In 3D or higher it is generally believed that a finite U_c exists for the Mott-Hubbard transition. (4) In the infinite dimension the Gutzwiller approximation is exact. (5) The Gutzwiller approximation has been shown to be the mean-field solution of the slave-boson theory, which is a systematic expansion in $1/N$ and becomes exact as N goes to infinity. From these facts, we conclude that the Gutzwiller approximation should provide a reasonable estimate of the Mott-Hubbard transition in 3D degenerate systems, assuming a nonmagnetic insulating state.

In a nondegenerate Hubbard model each site can be described as empty, singly occupied or doubly occupied. Because doubly occupied sites cost energy, the idea of the Gutzwiller variational approach is to introduce a variational function in which the weight of doubly occupied sites is reduced. To accomplish this one starts from the uncorrelated Fermi sea $|\phi_0\rangle=|\{k_1,\alpha_1,\ldots,k_n,\alpha_n\}\rangle$, and partially projects the doubly occupied site by the variational factor η. This leads to the Gutzwiller projected wave function

$$|\phi_G\rangle=\prod_{i,\alpha\neq\beta}[1-(1-\eta)c^{\dagger}_{i,\alpha}c^{\dagger}_{i,\beta}]|\phi_0\rangle \ . \tag{2}$$

For large U, $\eta\rightarrow 0$, and doubly occupied sites are forbidden. To determine η, one calculates the expectation of the Hamiltonian in $|\phi_G\rangle$,

$$E=\frac{\langle\phi_G|H|\phi_G\rangle}{\langle\phi_G|\phi_G\rangle} \tag{3}$$

and minimizes it with respect to η. In general, this can be done only numerically. Gutzwiller introduced approximations which make analytical calculations possible. This approach is known as the Gutzwiller approximation.[8] The many-body wave function $|\phi_G\rangle$ can be written as superposition of states with different numbers of doubly occupied sites ν. It is assumed that (1) in the thermodynamic limit, the expectation $\langle\phi_G|\phi_G\rangle$ is dominated by the largest term which determines the optimal value of ν. (2) In evaluating $\langle\phi_G|H|\phi_G\rangle$ spatial correlations are neglected; this is equivalent to the mean-field approximation. Using these approximations E can be calculated analytically. The results of Gutzwiller were later elaborated by Brinkman and Rice[8] who obtained the result that the metal-insulator transition occurs at $U_c=8|\bar{\epsilon}|$, where $\bar{\epsilon}$ is the average energy per particle in the absence of correlation ($U=0$).

For the N-fold degenerate Hubbard model, each site can be occupied by $0-2N$ electrons, which can be far from the average number of electrons per site, x. However, very near the metal-insulator transition one expects the fluctuation of occupancy from x to be small. Thus, we make the additional approximation that each site can be only "empty" ($x-1$ electrons), "singly occupied" (x electrons), or "doubly occupied" ($x+1$ electrons). For a given site there are $C^{x+1}_{2N}=(2N)!/(x+1)!(2N-x-1)!$ possible distinct double-occupied configurations. Using this and the Gutzwiller approximation, we are able to calculate analytically the expectation Eq. (3). Elsewhere we will present details of the derivation.[15] Below we summarize the results obtained. Let $\nu\ll L$ be the total number of doubly occupied sites; by symmetry the number of empty sites is also ν. We find that the average energy per particle, in reference to the paramagnetic insulating state, can be written as

$$E(N,x)=Q(x,\nu,N)\bar{\epsilon}(x)+\frac{\nu}{2Nm}U \ , \tag{4}$$

where $\bar{\epsilon}(x)$ is the energy per particle in the absence of correlations ($U=0$). The band is assumed to be symmetric, $\bar{\epsilon}(x=2N)=0$. The quotient Q, which reflects the reduction of hopping due to correlation,[8,15] is given by

$$Q(x,\nu,N)=\frac{\nu\left[m-\frac{x\nu}{N}\right]x(2N-x+1)}{2m^2N(2N-x)}\times\left[1+\eta\frac{m-\frac{x\nu}{N}}{\nu}\frac{2N(2N-x)}{x(2N-x+1)}\right]^2 , \tag{5}$$

with the optimal projection parameter

$$\eta=\frac{\nu}{m-\frac{x\nu}{N}}\left[\frac{x(x+1)(2N-x+1)}{4N^2(2N-x)}\right]^{1/2} . \tag{6}$$

Substituting Eqs. (5) and (6) into (4) and minimizing the energy with respect to $\bar{\nu}=\nu/2Nm$, one obtains

$$\bar{\nu}=\frac{1}{4x}\left[1-\frac{U}{U_c}\right] , \tag{7}$$

with

$$U_c(N,x)=\frac{[\sqrt{x(2N-x+1)}+\sqrt{(x+1)(2N-x)}]^2}{2N-x}|\bar{\epsilon}(x)| \ , \tag{8}$$

and

$$E=-\frac{U_c(x,N)}{8x}\left[1-\frac{U}{U_c(x,N)}\right]^2 . \tag{9}$$

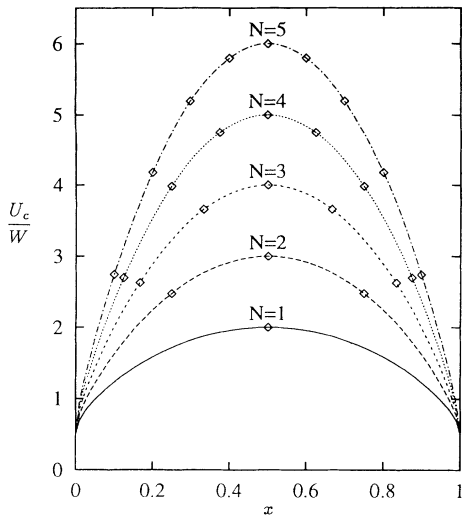

FIG. 1. Phase diagrams for Mott-Hubbard metal-insulator transitions in N-fold degenerate Hubbard models. Critical correlation energy U_c/W, above which the system is insulating, is plotted against filling $x/2N$. A flat band with bandwidth W is assumed. Shown are results for $N=1,2,3,4,5$. Note that only the points corresponding to integer (x) number of electrons per site, are meaningful. Lines are drawn using Eq. (8).

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

Equation 8 is our main result (Fig. 1). Qualitatively, it can be understood in the following way. Imagine approaching the transition from the insulating state, where there are exactly x particles localized on every site. Then a single particle-hole excitation costs the correlation energy U, but the gain in kinetic energy due to the mobile excitation is of the order $\sim x|\bar{\epsilon}(x)|$. Therefore, one expects $U_c \sim x|\bar{\epsilon}(x)|$, similar to the value given by Eq. (8) for $x \ll N$. The difference reflects the Pauli exclusion principle of fermions. As examples, in Fig. 1 we show the results for the first several N using a simple flat band of bandwidth W, $\bar{\epsilon}(x)=[(x-2N)/4N]W$. Clearly one sees that U_c depends sensitively on N and x. Several limits of Eq. (8) are worth discussion. (1) The particle-hole symmetry is preserved if $|\bar{\epsilon}(x)|=[x/(2N-x)]|\bar{\epsilon}(2N-x)|$; this is expected because the starting Hamiltonian Eq. (1) contains particle-hole symmetry. (2) For $N=1$, the only commensurate filling is the half filling $x=1$, and the Brinkman-Rice result $U_c=8|\bar{\epsilon}|$ is recovered. (3) For $N=2$, $x=1$, we obtain $U_c=[(10+4\sqrt{6})/3]|\bar{\epsilon}|$, in agreement with the result obtained by Chao.[10] (4) In the limit of $N\rightarrow\infty$ and finite x, the fermion problem is equivalent to the boson problem which has been widely studied in recent years.[16-18] Our result, $U_c=(\sqrt{x}+\sqrt{x+1})^2|\bar{\epsilon}(x)|$, is identical to that obtained for the boson Hubbard model using the Gutzwiller approximation,[17] and is very close to that of path-integral quantum Monte Carlo calculations[18] and the mean-field results.[16]

The most important conclusions indicated by Eq. (8) are (a) U_c depends sensitively on both the degeneracy N and the number of electrons per site. (b) U_c monotonically increases with x reaching a maximum at half filling, $U_c(N,N)=4(N+1)|\bar{\epsilon}|\sim(N+1)W$. Thus the higher the degeneracy the more difficult for a system to become a Mott insulator. For a given degeneracy the closer to half filling the more difficult it is to be insulating. We believe that these qualitative conclusions will hold for more accurate calculations of U_c. Our results clearly show the necessity of further quantitative studies on degenerate Hubbard models.

Now let us turn to the specific application of the above results to the metal-insulator transitions in A_xC_{60}. In this system it is known that each alkali metal donates one electron and that the conduction band is formed by overlap of the threefold degenerate t_{1u} molecular orbitals. For $x=1,3,4$, structures are known to be rhombohedral, face-centered-cubic, and body-centered-tetragonal, respectively.[2] For these structures local-density-approximations (LDA) calculations suggest that all of them are metals.[4] Experimentally, except $x=3$, all phases with integer x are found to be insulating. It has been shown that the band structure can be accurately represented by a tight-binding model; the density of states is approximately flat due to the intrinsic orientational disorder.[7] The bandwidth W determined from both experiments[19] and calculations[4,7] is very small, $W\sim 0.2-0.4$ eV. On the other hand, spectroscopic studies[3,5] and theoretical calculations[6] suggest that the intramolecular electron correlation energy is around $U\sim 1-2$ eV. The value of U is expected to remain unchanged with doping because the screening is provided by the large number of molecular orbitals above t_{1u}, which are not affected by doping. From Eq. (8) and assuming a flat band one obtains $U_c(x,N=3)/W=2.62,3.65,4$, respectively, for $x=1,2,3$. Thus, there exists a window of parameters (U,W) in which it is possible that the family of materials A_xC_{60} with $x=1,2,4,5$ are Mott-Hubbard insulators, while $x=3$ is metallic. If this picture is correct then one expects that A_3C_{60} is a strongly correlated metal. Palstra *et al.*[20] have observed that magnetic susceptibility in Rb_3C_{60} is strongly enhanced over that of K_3C_{60} (Ref. 20) in comparison with that expected from estimates of density of states. Recently a large T^2 term in resistivity at low temperature has also been observed.[21] These characteristics are signatures of a strongly correlated metal, in agreement with our results. Our theory also predicts that both A_2C_{60} and A_3C_{60} are very close to the metal-insulator transition, so their conducting properties should be very sensitive to the lattice constant. Finally, we caution that there are large uncertainties in our calculation of U_c using the Gutzwiller approximation, and in experimental estimates of U and W; thus only qualitative conclusions are expected to hold.

In conclusion we present analytical results of Mott-Hubbard transitions in the N-fold degenerate Hubbard model within the Gutzwiller approximation. It is found that for any commensurate filling there exists a critical correlation energy U_c above which the system is a Mott-Hubbard insulator. U_c is found to depend sensitively on both the degeneracy and the filling; it is maximum at half filling. It is more difficult for a degenerate system to be-

come a Mott-Hubbard insulator near half filling. Our results give a plausible explanation for the unusual metal-insulator transitions observed in the fullerides A_xC_{60} and suggest that A_3C_{60} is a strongly correlated metal.

I am grateful to M. P. Gelfand for many discussions, and collaborations on related projects. I thank A. Hebard, J. Fisher, and J. Weaver for providing experimental results prior to publication. Discussions with Q. Si are acknowledged. This work was supported by The University Research Council of the University of North Carolina at Chapel Hill.

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