PHYSICAL REVIEW B VOLUME 54, NUMBER 16 15 OCTOBER 1996-II

Mott transition in degenerate Hubbard models: Application to doped fullerenes

Olle Gunnarsson
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

Erik Koch and Richard M. Martin
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany
and Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 5 August 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. [S0163-1829(96)51940-5]

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[2–7] starting from the assumption that the systems are metallic. The metallicity is an experimental fact,[8] 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.[9–15] Since systems with U/W exceeding a critical value a bit larger than unity (~ 1.5) are believed to be Mott-Hubbard insulators,[16] 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.[9] 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. We here study the Hubbard model, which has become the standard model for describing correlated systems. In spite of the extensive studies of this model, U_c/W is known accurately only for infinite dimension in the absence of orbital degeneracy.[16] Since, however, almost all systems of physical interest have orbital degeneracy,[17] we here focus on the effects of such a degeneracy, considering a three-dimensional fcc lattice.

First, we provide qualitative arguments suggesting that for a half-filled system with orbital degeneracy N, the critical value of U/W is enhanced by a factor $\sqrt{N}$. These arguments are supported by exact diagonalization calculations for small systems and by diffusion Monte Carlo calculations for larger systems. The reason for the enhancement is that in the many-body treatment, the degeneracy increases the hopping rate of an extra electron or hole in these systems relative to the one-particle bandwidth. The degeneracy can thus stabilize a metallic state which may be highly correlated. This puts the doped fullerenes A_nC_{60} (n=3, 4) (N=3) close to a Mott-Hubbard transition, so that a correlated metallic state of stoichiometric A_3C_{60} is consistent with the large values of U/W inferred from experimental and theoretical information.

In a treatment using the Gutzwiller ansatz and the Gutzwiller approximation[18] for the Hubbard model, Lu found the critical value U/W to vary as $(N+1)$ at half-filling.[19] 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 $t_{im,jm'} = t\delta_{mm'}$ between orbitals with the same quantum numbers m on neighboring sites i and j. For half-filling the energy gap is then

$$E_g = E(NM+1) + E(NM-1) - 2E(NM), \tag{1}$$

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

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

since no electron can hop without an extra energy cost U. For instance, this energy is obtained for a Néel 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

$$|1\rangle = \psi^\dagger_{11\downarrow}|0\rangle$$

$$|i\rangle = \frac{1}{\sqrt{N}} \psi^\dagger_{11\downarrow} \sum_m \psi^\dagger_{im\uparrow}\psi_{1m\uparrow}|0\rangle, \tag{3}$$

where $\psi^\dagger_{jm\uparrow}$ 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

$$\langle i|H|1\rangle = \sqrt{N}t, \tag{4}$$

TABLE I. Band gap as a function of U and N compared with $U-\sqrt{N}W$ for a six-site model ($N=1$ and $N=2$) and a cluster of 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 in eV.

U	$N=1$ (six-site)		$N=2$ (six-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

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.[20] This is due to the fact that any of the 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 ε_b, where ε_b is the bottom of the band. The close analogy between the one- and many-particle problems then suggests

$$E(NM+1)\approx E(NM)+NU+\sqrt{N}\varepsilon_b, \tag{5}$$

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

$$E_g=U-\sqrt{N}(\varepsilon_t-\varepsilon_b)\equiv U-\sqrt{N}W, \tag{6}$$

where ε_t ($=-\varepsilon_b$ 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. Equation (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 ($3*2$) lattice with ($N=2$) and without ($N=1$) orbital degeneracy. Table I compares the exact band gap with the estimate $U-\sqrt{N}W$. The exact results agree very well with the simple estimate for large U, confirming the estimate in the limit it was made. For intermediate U the agreement is less good. The reason could be that the gap is finite for a finite system or that the extrapolation of the estimate to intermediate U is invalid. To check this, we consider larger systems.

To study A_3C_{60} we have considered a model which includes the threefold degenerate, partly occupied t_{1u} level. We include the on-site Coulomb interaction U and the hopping integrals $t_{im,jm'}$ between the molecules. This leads to the Hubbard-like model

$$H=\sum_{i\sigma}\sum_{m=1}^{3}\varepsilon_{t_{1u}}n_{i\sigma m}+\sum_{\langle ij\rangle\sigma mm'}t_{ijmm'}\psi^{\dagger}_{i\sigma m}\psi_{j\sigma m'}$$
$$+U\sum_{i}\sum_{\sigma m<\sigma' m'}n_{i\sigma m}n_{i\sigma' m'}, \tag{7}$$

where the sum $\langle ij\rangle$ is over nearest-neighbor sites. We have used a fcc lattice. The hopping integrals $t_{imjm'}$ 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 bandwidth 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_3C_{60}) electrons per site. Except for small values of U, the gap E_g is actually *smaller* than $U-\sqrt{3}W$, which may be due to the nonbipartite character of the fcc lattice or the hopping being more complicated than discussed above. The importance of the degeneracy is, however, clear.

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

$$|\Psi^{(n)}\rangle=[1-\tau(H-w)]^n|\Psi_T\rangle\equiv F^n|\Psi_T\rangle, \tag{8}$$

where w is an estimate of the ground-state energy. If τ is sufficiently small and $|\Psi_T\rangle$ is not orthogonal to the ground state, $|\Psi^{(n)}\rangle$ converges to the ground state as $n\rightarrow\infty$. $|\Psi^{(n)}\rangle$ 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,[25] and introduce an effective Hamiltonian for which the nondiagonal terms are zero if

$$\langle\Psi_T|R\rangle\langle R|F|R'\rangle\langle R'|\Psi_T\rangle<0, \tag{9}$$

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.[25]

For the trial function we make the Gutzwiller ansatz

$$|\Psi_T\rangle=g^{n_d}|\Psi_0\rangle, \tag{10}$$

where g is a Gutzwiller parameter and the power n_d is the number of double occupations $n_d=\Sigma_i\Sigma_{\sigma m<\sigma' m'}n_{i\sigma m}n_{i\sigma' m'}$ in the Slater determinant $|\Psi_0\rangle$. To construct $|\Psi_0\rangle$ we solve the Hamiltonian (7) 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

TABLE II. The total energy for four C_{60} molecules with M electrons and $U=1$ according to the variational (VMC) and diffusion (DMC) Monte Carlo calculations compared with the exact results. The Gutzwiller parameter is given by g. The statistical error is estimated to be two units in the last digit.

M	g	VMC	DMC	Exact
11	0.45	8.4970	8.4677	
11	0.50	8.4842	8.4677	8.4649
11	0.55	8.4873	8.4684	
12	0.45	10.7364	10.7014	
12	0.50	10.7226	10.7009	10.6994
12	0.55	10.7249	10.7012	
13	0.45	13.4363	13.3990	
13	0.50	13.4211	13.3988	13.3973
13	0.55	13.4233	13.3991	
E_g	0.45	0.4605	0.4639	
E_g	0.50	0.4601	0.4647	0.4634
E_g	0.51	0.4608	0.4651	

results in Table II. 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.[26] 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,[27] where M is the number of atoms. We then introduce

$$\widetilde{E}_g \equiv E_g - \frac{U}{M} - E_g(U=0), \tag{11}$$

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

In Fig. 1 we show results for $\widetilde{E}_g$ 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.[16] 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.

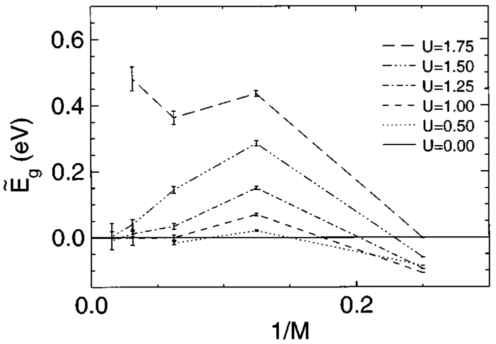

FIG. 1. $\widetilde{E}_g$ [Eq. (11)] for different U and as a function of $1/M$, where M is the number of molecules. The bandwidth varies between 0.58 eV ($M=4$) and 0.63 eV ($M=\infty$).

The inclusion of higher subbands may increase U_c/W further. In the large U, half-filled case, the hopping to a higher subband costs an extra "diagonal" energy $U+\Delta\varepsilon$, where $\Delta\varepsilon$ is the energy separation of the bands. The corresponding energy cost in the states with one extra electron or hole is only $\Delta\varepsilon$. The hopping to higher subbands should therefore lower the energy more in the latter two states, which decreases the gap. Simultaneously, the one-particle width of the t_{1u} band due to hopping into higher levels on neighboring molecules is *reduced* by a few per cent.[22] Only bands with $\Delta\varepsilon \lesssim U$ contribute to the reduction of the band gap. A simple model suggests that this could increase U_c/W by 0.1–0.2 for A_3C_{60}. For $3d$, $4f$, or $5f$ compounds ($N=5$ or 7), a crystal-field splitting may lower the degeneracy. The higher crystal-field split states cannot, however, be neglected when determining U_c/W, unless the crystal-field splitting is much larger than the Coulomb interaction.

The average Coulomb U has been estimated to be 1.6 eV (Ref. 9) and 1.4±0.2 eV (Ref. 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.[5] 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.[11] Band structure calculations have found the bandwidth 0.41 eV,[13] 0.6 eV (Ref. 12) and 0.65 eV (Ref. 14) for K_3C_{60}. Many-body effects were found to increase the bandwidth by about 30% in the GW approximation for undoped C_{60}.[15] 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 bandwidth is therefore not a double counting. For Rb_3C_{60} the bandwidth may be reduced by about 15%,[22] compared with K_3C_{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_3C_{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 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_3C_{60}, which has an odd number of electrons per site, the singlet is consistent with a correlated nonmagnetic 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_3C_{60} are metals, A_4C_{60} are insulators,[29] although band-structure calculations predict that they should be metals.[30] A_4C_{60} is therefore not a band insulator, and this raises interesting questions about the difference between

A_3C_{60} and A_4C_{60}. The presence of four electrons per molecule in A_4C_{60} favors the formation of a static Jahn-Teller effect, which may open up a gap,[31] particularly if electron correlation effects are also included. The electron-phonon coupling should reduce the effective hopping for both A_3C_{60} and A_4C_{60}. One may also speculate that the gap in A_4C_{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_4C_{60} is bipartite while A_3C_{60} is not, which may favor the development of ordered phases (antiferromagnetic or other types of order) and the opening of a gap in A_4C_{60}. Finally, the Fermi surface of A_4C_{60} has almost perfect nesting, which may favor a charge- density wave and the opening of a gap.[30]

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_3C_{60} at the upper range of ratios U/W estimated for doped C_{60} compounds and makes it likely that A_3C_{60} (A=K,Rb) is on the metallic side. Although experimental samples of A_3C_{60} may be nonstoichiometric, it is therefore not necessary to assume so to explain the metalicity. 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.[17] 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. Schuhmacher provided invaluable help in adapting the programs for parallel computation. This work was supported in part by the the NSF under Grants Nos. DMR-94-22496 and DMR-89-20538.

---

[1] A.F. Hebard *et al.*, Nature **350**, 600 (1991); K. Holczer *et al.*, *ibid.* **352**, 787 (1991).

[2] C.M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).

[3] M. Schlüter *et al.*, Phys. Rev. Lett. **68**, 526 (1992).

[4] I.I. Mazin *et al.*, Phys. Rev. B **45**, 5114 (1992).

[5] V.P. Antropov, O. Gunnarsson, and A.I. Liechtenstein, Phys. Rev. B **48**, 7551 (1993).

[6] O. Gunnarsson and G. Zwicknagl, Phys. Rev. Lett. **69**, 957 (1992); O. Gunnarsson, D. Rainer, and G. Zwicknagl, Int. J. Mod. Phys. B **6**, 3993 (1992).

[7] O. Gunnarsson *et al.*, Phys. Rev. Lett. **74**, 1875 (1995).

[8] R.C. Haddon *et al.*, Nature **350**, 320 (1991).

[9] R.W. Lof *et al.*, Phys. Rev. Lett. **68**, 3924 (1992).

[10] P.A. Brühwiler *et al.*, Phys. Rev. B **48**, 18 296 (1993).

[11] V.P. Antropov, O. Gunnarsson, and O. Jepsen, Phys. Rev. B **46**, 13 647 (1992).

[12] S.C. Erwin and W.E. Pickett, Science **254**, 842 (1991).

[13] N. Troullier and J.L. Martins, Phys. Rev. B **46**, 1766 (1992).

[14] V.P. Antropov *et al.* (unpublished).

[15] E.L. Shirley and S.G. Louie, Phys. Rev. Lett. **71**, 133 (1993).

[16] See A. Georges *et al.*, Rev. Mod. Phys. **68**, 13 (1996).

[17] N.E. Bickers, Rev. Mod. Phys. **59**, 845 (1987).

[18] M.C. Gutzwiller *et al.*, Phys. Rev. **137**, A1726 (1965).

[19] J.P. Lu, Phys. Rev. B **49**, 5687 (1994).

[20] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983); Phys. Rev. B **28**, 4315 (1983).

[21] O. Gunnarsson *et al.*, Phys. Rev. Lett. **67**, 3002 (1991).

[22] S. Satpathy *et al.*, Phys. Rev. B **46**, 1773 (1992).

[23] P.W. Stephens *et al.*, Nature **350**, 600 (1991).

[24] I.I. Mazin *et al.*, Phys. Rev. Lett. **26**, 4142 (1993).

[25] D.F.B. ten Haaf *et al.*, Phys. Rev. B **51**, 353 (1995); H.J.M. van Bemmel *et al.*, Phys. Rev. Lett. **72**, 2442 (1994).

[26] D.M. Ceperley and B.J. Alder, Phys. Rev. B **36**, 2092 (1987).

[27] Performing a Hartree-Fock-like calculation for this uniform system, would give a contribution $5U/(6M)$.

[28] R.M. Martin, Phys. Rev. Lett. **48**, 362 (1982).

[29] D.W. Murphy *et al.*, J. Phys. Chem. Solids **53**, 1321 (1992); R.F. Kiefl *et al.*, Phys. Rev. Lett. **69**, 2005 (1992).

[30] S.C. Erwin, in *Buckminsterfullerenes*, edited by W.E. Billups and M.A. Ciufolini (VCH-Publishing, Cambridge, 1993) p. 217.

[31] A. Auerbach, N. Manini, and E. Tosatti, Phys. Rev. B **49**, 12 998 (1994).