ABSTRACT

The one-band Hubbard model at half-filling on a truncated tetrahedron (C$_{12}$), and on the C$_{60}$ molecule is studied. Within the Hartree-Fock approximation, we find a magnetic-like instability of the “Fermi sea” towards a spin-ordered phase for an intermediate value of the coupling (U/t)$_c$ $\approx$ 2.6. The ordered phase presents a spin arrangement similar to that of the classical Heisenberg model defined on the same clusters. We study the linear excitations around the Hartree-Fock ground states using the random-phase approximation. On a finite cluster, we expect that these results signal the presence of a rapid crossover between a paramagnetic region and a regime where spin correlations are important. The relationship with the Heisenberg limit (large U/t) is discussed. Finally, we comment on implications of our results for purely repulsive models of superconductivity in alkali-metal-doped fullerenes.
The recent discovery\textsuperscript{1} of superconductivity in alkali-metal-doped fullerenes, $K_3C_{60}$ and $Rb_3C_{60}$, has led to considerable interest in the electronic structure and superconductivity mechanism of this new class of organic solids. The remarkable structure of $C_{60}$ leads to one active p-orbital per carbon atom, and it has been suggested that a one-band Hubbard model will capture at least some of the physics of the $\pi$-electrons of the fullerenes.\textsuperscript{2,3} The theoretical analysis of this simplified model can lead to an understanding of correlation effects that are beyond the range of one-electron approximations. The same model is currently widely used in the study of the cuprate high-$T_c$ superconductors. We have recently begun an investigation of the Hubbard model on fullerene clusters, concentrating in this paper on the Hartree-Fock and the Random Phase approximations. Results obtained using the Quantum Monte Carlo method and the spin-wave approximation in the Heisenberg limit were previously reported in Ref. 4.

In this paper we study the one-band Hubbard model at half-filling (one electron per site) for two particular clusters: the truncated tetrahedron $C_{12}$, and the truncated icosahedron $C_{60}$. Our main result is the appearance of a magnetic-like instability beyond a critical value of the Hubbard coupling $(U/t)_c \approx 2.6$. For larger values of $U/t$ we observe that a generalized spin-density wave state (SDW), i.e. a state with “classical” spin order on the cluster, has an energy lower than the Fermi sea constructed from the tight-binding eigenstates. This new spin-density wave state reduces, in the $U = \infty$ limit, to the classical spin configuration which minimizes the antiferromagnetic Heisenberg Hamiltonian on the cluster.\textsuperscript{5,4} This configuration is highly non-trivial as was shown in Ref.5. Physical consequences of this instability are discussed at the end of the paper.

Certainly, for a finite cluster we do not expect that the exact ground state will present a sharp singularity at some value of $U/t$ (unless a level crossing occurs). This is an artifact
of our approximation. There is no phase transition leading to magnetic ordering on a finite system such as C\textsubscript{60}. In the case of C\textsubscript{12} it has been shown\textsuperscript{3} by exact diagonalization of the Hubbard Hamiltonian that the ground state of the neutral molecule is a singlet for all values of U/t. We also expect this to be true in the case of C\textsubscript{60}. However it may very well be that the physics of these finite systems is captured by a broken symmetry state. For example, this is known to happen in the case of the square lattice Heisenberg antiferromagnet: in the thermodynamic limit the quantum ground state is Néel ordered (according to the general belief) and nevertheless the ground state of any finite piece of square lattice is a singlet as demonstrated long ago. But antiferromagnetic correlations indicative of Néel order are present in these finite systems as clearly shown by numerical studies.\textsuperscript{6} The ground state degeneracy that we expect due to broken symmetry appears only in the thermodynamic limit. For any finite system vector order parameters will be zero (such as the staggered magnetization of the square lattice magnet) but correlations can be properly studied through the use of singlet correlation function such as
\[ < \mathbf{S}_i \cdot \mathbf{S}_j >. \]

Thus, we expect that the exact ground state of C\textsubscript{60} or C\textsubscript{12} will show indications of the magnetic instability discussed in this paper by presenting a rapid crossover at \((U/t)\textsubscript{c}\) from nonmagnetic to magnetic dominated correlations. The ground state will always remain a singlet, but after the crossover a state of spin one will reduce its energy approaching the ground state when the size of the clusters grow.

The Hamiltonian of the Hubbard model is
\[
H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + \frac{U}{2} \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} c_{i-\sigma}^\dagger c_{i-\sigma}. \tag{1}
\]

The indexes \(i, j\) label sites of the cluster (\(i, j = 1, ..., 60\) for C\textsubscript{60}), \(c_{i\sigma}^\dagger\) is the creation operator for an electron on site \(i\) with spin \(\sigma\), \(t\) is the hopping integral that we assume to
be the same for all bonds, U is the on-site repulsion energy, and the first sum runs over all neighbouring sites. It is worth recalling that a simple tight-binding Hamiltonian for π orbitals reproduces extremely well the order and degeneracies of electronic levels near the Fermi energy as obtained in more sophisticated molecular orbital calculations.\textsuperscript{7} At half-filling the only parameter of the model is the ratio U/t. Its precise value is unknown, but the intermediate regime U/t \approx 3-5 may be realistic.\textsuperscript{2,3,8} Recently, in the framework of a two-band Hubbard-like model, R. Lof \textit{et al.}\textsuperscript{2} claimed that doped C\textsubscript{60} should be considered as a highly correlated system with U/W comparable to that in high-T\textsubscript{c} superconductors (W being the one hole bandwidth). Then, it is clearly interesting to study strongly correlated electrons defined on fullerene clusters for all values of U/t.

The HF method searches for the Slater determinant \textket{HF} which minimizes the energy. This determinant is built from the lowest eigenstates of the following one-particle Hamiltonian:

\begin{equation}
\hat{h} = -t \sum_{\langle i, j \rangle, \sigma} (c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.}) + U \sum_{i, \sigma} \left\{ n_{i-\sigma} c^\dagger_{i\sigma} c_{i\sigma} - \rho_{i\sigma, i-\sigma} c^\dagger_{i\sigma} c_{i-\sigma} \right\}.
\end{equation}

In this equation, \rho_{i\sigma, j\sigma'} = \langle HF | c^\dagger_{j\sigma'} c_{i\sigma} | HF \rangle is the one-body density matrix, and \( n_{i\sigma} \equiv \rho_{i\sigma, i\sigma} \). One possible Ansatz for the density matrix, which always provides a self-consistent solution, is \( n_{i\uparrow} = n_{i\downarrow} = 1/2 \) and \( \rho_{i-\sigma, i\sigma} = 0 \). The interaction term in \( \hat{h} \), Eq.(2), is then proportional to the particle number operator and the eigenstates of \( \hat{h} \) are those of the tight-binding Hamiltonian. We refer to this solution as to the trivial or “non-magnetic” state. Its energy grows linearly with U, starting from the ground state energy of the tight-binding Hamiltonian. Its energy per site is, in units of t, \(-1.5+0.25(U/t)\) for C\textsubscript{12} and \(-1.5527+0.25(U/t)\) for C\textsubscript{60}. Of course, the energy of this non-magnetic state is
overestimated by the Hartree-Fock approximation. As U increases, one expects the doubly occupied states to be depleted. The resulting correlations could be taken into account by using a better variational state, e.g. the Gutzwiller projection of this Slater determinant. However, when U becomes large enough, it is possible to find a better Slater determinant which takes into account some of the correlations induced by the on site repulsion. We turn now to the description of this new solution.

In the strong coupling regime \((U/t \gg 1)\) the half-filled Hubbard model reduces at leading order in perturbation theory to the antiferromagnetic Heisenberg model \((HAF)\):

\[
H_{HAF} = \frac{4t^2}{U} \sum_{(i,j)} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}),
\]

where \(\mathbf{S}_i\) are spin-1/2 operators. To study this quantum model on finite clusters, one can search for the ground state of the corresponding classical model and perform the spin-wave expansion around this state. This non-trivial ground state classical spin configuration has been recently discussed.\(^5\)\(^,\)\(^4\) For the quantum problem, a spin wave analysis has been performed,\(^4\) leading to a critical spin value (below which spin order is washed out by quantum fluctuations) rather close to 1/2. This result was in rough agreement with more sophisticated QMC simulations.\(^4\) Here, we construct a Hartree-Fock solution based on the classical spin configuration obtained by minimizing the Hamiltonian Eq.(3). For this purpose, we define a new basis \(|i\sigma\rangle\) where the quantization axes are site-dependent, and lie in the directions of the classical spins. These directions are specified by polar angles \(\theta_i\) and \(\phi_i\). In this new basis the Hamiltonian reads

\[
H = -t \sum_{\langle i,j \rangle, \sigma, \sigma'} ((R_i^\dagger R_j)_{\sigma\sigma'} c_{i\sigma}^\dagger c_{j\sigma'} + \text{h.c.}) + \frac{U}{2} \sum_{i,\sigma} c_{i\sigma}^\dagger c_{i\sigma} c_{i-\sigma}^\dagger c_{i-\sigma},
\]
where \( R_i \) is an \( SU(2) \) matrix which rotates the original quantization axis at site \( i \) into the direction of polar angles \( \theta_i, \phi_i \). Next, and after the HF approximation is made in Eq.(4), we try an Ansatz for which \( \rho_{i\sigma,i-\sigma} = 0 \) and \( n_i^{\uparrow} - n_i^{\downarrow} \) is site-independent. This solution, when it exists, will be called the “magnetic” solution. The corresponding state may be viewed as a generalized spin-density wave defined on clusters with the topology of a sphere.

The calculation of the classical ground state of the HAF has been carried out for \( C_{12} \) and \( C_{60} \). Using these results, our HF calculations indicate that there is a magnetic solution beyond a critical value \( (U/t)_c \sim 2.6 \) for \( C_{60} \), and \( \sim 2.7 \) for \( C_{12} \) for which the order parameter \( n_i^{\uparrow} - n_i^{\downarrow} \) becomes non-zero. For larger values of \( U/t \), the magnetic solution is always lower in energy than the nonmagnetic one. Figure 1 shows the value of \( n_i^{\uparrow} \) for \( C_{60} \) as a function of \( U/t \). The curve for \( C_{12} \) has a similar shape. In the limit of large \( U/t \), \( n_i^{\uparrow} \to 1 \), and thus the spins align in the directions of the classical order \( (\theta_i, \phi_i) \). In the same limit, the HF energy, which behaves as \( t^2/U \), tends towards the energy of the ground state of the equivalent classical HAF. Figure 2 shows the energy per site for the \( C_{60} \) cluster, in units of \( t \), as a function of \( U/t \), for both the magnetic and the non-magnetic solutions. The energies per site of the classical ground states are \( -2.5(t^2/U) \) for \( C_{12} \), and \( -2.809(t^2/U) \) for \( C_{60} \), to be compared against the energy per site of the magnetic HF solution calculated for \( (U/t) = 5 \) and \( 100 \) which are, respectively, \( -2.395(t^2/U) \) and \( -2.499(t^2/U) \) for \( C_{12} \), and \( -2.64(t^2/U) \) and \( -2.808(t^2/U) \) for \( C_{60} \). Finally, the gap between the highest occupied and the lowest unoccupied orbitals approaches \( U \) for increasing values of \( (U/t) \) since the excitations in the Hartree-Fock approximation correspond to flipping one spin against the mean field. Of course, the interaction among these elementary spin flip excitations strongly alters this picture, as revealed by the spin wave analysis or the RPA calculation to be presented below. They clearly show that spin-wave-like states appear in the HF gap.
The magnetic instability that we have found is qualitatively similar to that observed for the Hubbard model on a lattice without nesting of the Fermi surface, where antiferromagnetism appears only above a critical (non vanishing) value of the on-site repulsion. This is to be contrasted with the case of the square lattice where an antiferromagnetic instability develops as soon as $U$ is nonzero due to perfect nesting of the Fermi surface: there, the non-magnetic solution is always unstable against the antiferromagnetic spin-density wave.

The HF magnetic solution breaks rotational symmetry. This is an artifact of the mean-field approximation and, of course, the true ground state of a finite system, such as the $C_{60}$ cluster, is an eigenstate of the total spin, presumably a singlet. However, the spin correlations present in the Hartree-Fock state may be relevant to the physics of the cluster. They may be found by the use of singlet observables.

Further insight on the spin correlations and the associated instability of the non-magnetic Hartree-Fock solution may be obtained from the Random Phase Approximation (RPA). For $C_{12}$, we have performed a complete RPA calculation in the space of the 144 particle-hole configurations, for both the magnetic and the non-magnetic states. In the case of $C_{60}$ we have only determined the lowest spin excited states from a study of the spin susceptibility $\chi_{ij} = -i\langle TS_i^z(t)S_j^z(0)\rangle$, in real (lattice) space, and this only for the non-magnetic solution. We find, in both cases of $C_{12}$ and $C_{60}$, that the non-magnetic solution is stable against particle-hole excitations as long as $(U/t) < (U/t)_c$. As $(U/t)$ crosses the critical value, the lowest RPA excitations energies, which are degenerate (at least 3 times; for $C_{12}$ the total degeneracy is 9), do vanish and become imaginary. This is illustrated in Fig. 3. This behaviour of the RPA eigenvalues reflects the fact that the non-magnetic HF solution is unstable for couplings $(U/t) > (U/t)_c$. 
We have checked explicitly, in the case of C\textsubscript{12}, that the HF magnetic solution is stable against small amplitude oscillations as given by the RPA. Note that, in this case, the RPA spectrum contains 3 zero energy modes reflecting the breaking of global spin rotational symmetry. We have calculated, again for C\textsubscript{12}, the corrections to the total energy coming from including RPA correlations in the ground state. In the strong coupling limit, we find that the resulting energy approaches, as expected,\textsuperscript{10,11} the linear spin-wave result for the limiting Heisenberg Hamiltonian, i.e. \(-3.313(t^2/U)\) for C\textsubscript{12}, and \(-3.503(t^2/U)\) for C\textsubscript{60}. The values obtained in RPA for U/t=5 and U/t=100 are \(-3.203(t^2/U)\) and \(-3.3127(t^2/U)\), respectively. Note that the RPA correlations, or equivalently the spin waves, provide a substantial correction to the Hartree-Fock or classical energies. In the strong coupling limit, the 144 RPA excitation energies of C\textsubscript{12} separate into a group of 12 lowest lying ones whose values coincide with the spin-wave energies of the equivalent HAF, including the 3 zero energy states, and another group of 132, starting at an energy of order U, which correspond to charge excitations.

Finally, the nature of the instability, as well as the structure of the non trivial Hartree-Fock state, may be obtained from the RPA calculation in the non-magnetic sector. To understand this, note that within RPA an instability manifests itself by the divergence of some static susceptibility. In the present case, \(\chi = \chi^0(1 + U\chi^0)^{-1}\), where \(\chi^0\) denotes the unperturbed spin susceptibility, and the instability occurs when Det\((1 + U\chi^0(\omega = 0)) = 0\). The particular mode along which the instability develops is found by the response of the system to a magnetizing field \(h_i\) pointing locally in the directions \((\theta_i, \phi_i)\) of the classical spins. The corresponding response function \(\propto \chi_{ij} h_i \cdot h_j\) diverges at \(U=U_c\). There are indeed three degenerate eigenvectors of the matrix \(\delta_{ij} + U\chi^0_{ij}(\omega = 0)\) that vanish right at
whose components can be identified with the vectors \( \mathbf{h}_i \). More precisely, if \( X_i, Y_i, Z_i \) denote the components of these three eigenvectors, we identify \( h^x_i = X_i, h^y_i = Y_i, h^z_i = Z_i \), while the norm of the vector \( \mathbf{h}_i \), i.e. \( X_i^2 + Y_i^2 + Z_i^2 \), is site independent. The relative angles between the orientations of the magnetizing field at sites \( i \) and \( j \) are then given by \( \cos \theta_{ij} = (\mathbf{h}_i \cdot \mathbf{h}_j)/h^2 \), where \( h \) is the strength of the magnetizing field, common to all sites.

Thus, we recover precisely the configuration that is found in the Heisenberg limit and in the HF calculation. We should emphasize that we have done this construction only for the magnetic instability. The possibility of other types of instabilities cannot be excluded. Actually, we observed in the case of \( C_{12} \), for which a complete RPA calculation has been performed, the presence of nine RPA eigenvalues which vanish as \( U \) approaches \( U_c \). We still do not have a simple physical interpretation to offer for these extra soft modes and the possible associated instabilities.

To summarize, we have found and studied a generalized spin-density wave state for the Hubbard model on the clusters \( C_{12} \) and \( C_{60} \). This state is lower in energy than the normal Fermi sea constructed from tight binding orbitals when \( U/t \gtrsim 2.6 \). Qualitatively, it resembles the spin order found by minimizing the energy of the classical Heisenberg model defined on these clusters. We expect that our approximate broken symmetry solution leads to a smooth crossover towards spin correlations on the finite system as already advocated in ref. 5 on general grounds. This magnetic instability may have an important effect on the effective interaction between valence electrons. We note in this respect that the perturbative calculations presented in Ref. 2 indicate that an attraction sets in for a value of the coupling \( U/t \sim 3 \). It has been argued that such an attraction could be the origin of superconductivity in doped \( C_{60} \). Exact studies\(^3\) of small clusters, including \( C_{12} \), have
confirmed the existence of an intermediate range of values of U/t where the pair-binding energy is positive (equivalent to an effective attractive interaction between electrons). It is interesting to note that this pairing tendency appears in the range where spin correlations can be expected to appear smoothly in the finite system.

We have checked that the new Hartree-Fock ground state is stable against small fluctuations as calculated in the RPA. However, this concerns only local stability, and we cannot exclude the possible existence of other minima in the Hartree-Fock energy. An important question regarding the magnetic structure that we have found is whether the spin correlations extend over the whole molecule or if there is a finite spin correlation length smaller than the molecular diameter. This requires further studies. Let us just mention that for the C_{12} cluster in the Heisenberg limit, we have diagonalized the spin Hamiltonian in the S^z = 0 sector and computed the exact spin correlations \langle S_i \cdot S_j \rangle. For the maximal separation (3 sites), the correlation is reduced by a factor \approx 5 from the classical value but does not disappear. Thus it seems plausible that the SDW state is not washed out by quantum fluctuations on C_{12}. For the considerably larger C_{60} molecules, the same question has been addressed recently by \textit{ab initio} techniques such as Quantum Monte-Carlo. There is evidence\textsuperscript{4} that the fluctuations are stronger in C_{60}, leading perhaps to a spin liquid ground state\textsuperscript{12} that resembles the SDW here discussed only below the spin correlation length. However, the QMC simulations were performed at finite temperature and, as recently remarked in Ref.\textsuperscript{5}, it may occur that reducing further the temperature in those simulations, an ordered state may be reached. This and related issues will be addressed in the future.

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**FIGURE CAPTIONS:**

**Figure 1:** The value of $N_z \equiv n_{i\uparrow}$ as a function of $U/t$ for $C_{60}$. Below $(U/t)_c \approx 2.6$ the Hartree-Fock ground state is nonmagnetic, and $n_{i\uparrow} = n_{i\downarrow} = 1/2$. Above the critical value, the quantization axis points in the directions of the classical spins, and $n_{i\uparrow}$ approaches its fully saturated value $n_{i\uparrow} = 1$, as $U \to \infty$.

**Figure 2:** The energy per site in units of $t$ for the HF solutions on $C_{60}$. The nonmagnetic solution (upper curve) rises linearly with $U$. Beyond $(U/t)_c$, the magnetic solution (lower curve) has lower energy.

**Figure 3:** The energy, in units of the HF gap, of the three soft RPA modes which vanish at $(U/t)_c$, indicating the presence of the magnetic instability.
GENERALIZED SPIN DENSITY WAVE STATE
OF THE HUBBARD MODEL ON C_{12} AND C_{60} CLUSTERS.

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