Magnetic Properties of Undoped C_{60}

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The Heisenberg antiferromagnet, which arises from the large-U Hubbard model, is investigated on the C_{60} molecule and other fullerenes. The connectivity of C_{60} leads to an exotic classical ground state with nontrivial topology. We argue that there is no phase transition in the Hubbard model as a function of U/t, and thus the large-U solution is relevant for the physical case of intermediate coupling. The system undergoes a first-order metamagnetic phase transition. We also consider the $S = \frac{1}{2}$ case using perturbation theory. Experimental tests are suggested.

The C_{60} molecule (buckminsterfullerene) has carbon atoms arranged like the vertices of a soccer ball [1]. We consider a neutral molecule. The active orbitals are one radial p orbital for each carbon atom. When the long-range Coulomb or on-site Hubbard repulsion is large compared with the nearest-neighbor hopping t, the molecule has essentially one electron in each orbital. There is an antiferromagnetic Heisenberg spin-spin interaction between nearest neighbors, caused by superexchange. The exchange constant $J = t^2/\Delta$, where Δ is the energy difference between a state with one electron in each orbital, and a state with two electrons in one orbital and none in a neighboring orbital. Including on-site U and nearest-neighbor V interactions, $\Delta = U - V$. The derivation is similar to that of the t-J model used in connection with the superconducting cuprates.

Estimates for real C_{60} are that U is approximately 9 eV and t is 2 to 3 eV [2,3]. The real molecule is thus in the intermediate U regime, and not in the large-U limit for which we calculate. The C_{60} molecule is too large to numerically solve for the intermediate U ground state. There is evidence, however, that there is no phase transition for the Hubbard model in the C_{60} geometry as a function of U/t. The spin correlations for intermediate U/t are then expected to be qualitatively similar, but smaller in magnitude, to those for large U/t. The evidence for a lack of a phase transition is as follows: For a finite quantum system at zero temperature, a phase transition as a function of the parameters occurs only if the quantum numbers of the ground state change. The only quantum numbers for this problem are spin S and angular momentum L (technically, what remains of L under the symmetry group of the icosahedron). $S = 0$ and $L = 0$ in the limit $U/t = 0$, and probably also in the limit $U/t \to \infty$ [4]. The simplest (and we believe correct) hypothesis is that there is no phase transition as a function of U/t. It may be useful in this regard to consider the simple example of the two-site Hubbard model with two electrons. Mean-field theory gives a phase transition with sublattice magnetization developing at finite U/t, which suggests that the large-U limit is not continuously connected to the small-U limit. The trivial exact solution, however, makes it clear that there is in fact no phase

transition, that local moments develop continuously, and that the spin correlations of the large-U limit develop continuously as U increases.

All carbon atoms on the C_{60} molecule are equivalent, but there are two slightly different bond lengths, 1.45 Å for the pentagon bonds and 1.40 Å for the nonpentagon bonds [5]. The magnetic exchange constant for two neighboring sites on the same pentagon is J_1. The constant connecting a site on one pentagon with a nearest neighbor on another pentagon is J_2. The Hamiltonian is

$$H = J_1 \sum_{\langle j,k \rangle}^{p} \sigma_j \cdot \sigma_k + J_2 \sum_{\langle j,k \rangle}^{np} \sigma_j \cdot \sigma_k , \qquad (1)$$

where the first sum is over the sixty pentagon bonds, and the second over the thirty nonpentagon bonds. J_2 is expected to be slightly larger than J_1, because the nonpentagon bonds are shorter. We first treat the Hamiltonian classically, so that σ is a classical unit vector. This is the $S \to \infty$ limit. (We consider the quantum $S = \frac{1}{2}$ case at the end of the paper.) The pentagons are frustrated, and cannot achieve a classical energy of $-J_1$ per bond. The ground state of an isolated pentagon (five spin system) has all spins coplanar and an energy of $J_1 \cos(4\pi/5) = -0.80902 J_1$ per bond. One immediately obtains a lower bound for the energy of the entire ball, which is $E_b = 60 J_1 \cos(4\pi/5) - 30 J_2$, where we have used the fact that nonpentagon bonds cannot have an energy lower than $-J_2$.

It would appear that the ground-state energy of Eq. (1) cannot achieve the lower bound E_b, because in simple trial states, connected pentagons interfere with each other and increase the energy. The classical ground-state configuration was found numerically by minimizing the energy over the spin variables $\{\theta_i, \phi_i\}$, $i = 1,60$. See Fig. 1. Surprisingly, the ground-state energy is equal to the lower bound E_b. The spin configuration is, however, nontrivial. The five spins in any given pentagon are coplanar, but the spins in a neighboring pentagon lie in a different plane. (A bond connects neighboring pentagons, but the spins on either end of the bond are precisely antiparallel, so that the spin planes need not be identical.) The ground-state configuration, which has zero net moment, is the same for all positive J_1 and J_2. In addition to the ob-
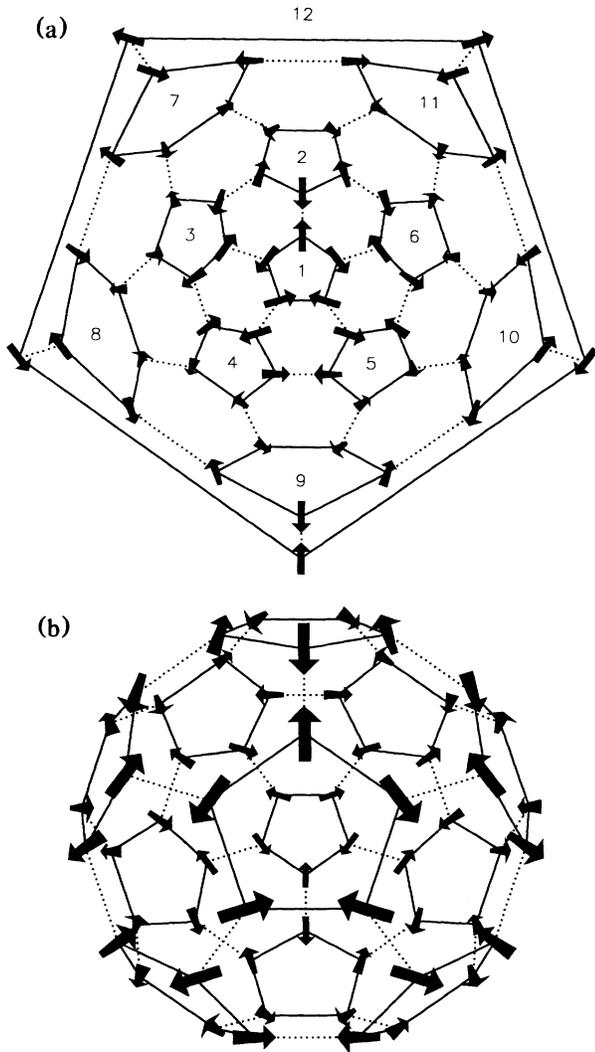
FIG. 1. (a) The C_{60} molecule is flattened into a plane by stretching the pentagon on the south pole. The spin directions are not changed. The spins in the center (north) pentagon are in the plane of the figure. A spin pointing up out of the plane of the figure is foreshortened, with an enlarged head. A spin pointing down into the plane has an enlarged tail. Nonpentagon bonds are dotted. (b) Perspective view of the spin arrangement on the ball.

vious global rotational symmetry of the ground state, there is a discrete parity symmetry whereby each spin $\sigma_i \rightarrow -\sigma_i$.

Since the spins in any given pentagon are coplanar, $\hat{n}$ for a pentagon can be defined to be the normal to the spin plane. Define a second vector $\hat{m}$ for the pentagon, which is normal to the physical plane of the pentagon (a unit vector pointing away from the center of the ball). For a particular global spin rotation, the set of normals to the spin planes for the twelve pentagons $\{\hat{n}_j\}$ is a nontrivial permutation of the set of physical normals $\{\hat{m}_j\}$. Let the global spin rotation be such that for the pentagon on the north pole, $\hat{n}_1 = \hat{m}_1$. The pentagon on the north pole is

surrounded by a first ring of five nearest-neighbor pentagons, a second ring of five second nearest neighbors, and one pentagon on the south pole. Any of the five pentagons in the first ring have an $\hat{n}$ equal to one of the $\hat{m}$ for a pentagon in the second ring. Using the pentagon numbering convention of Fig. 1, $\hat{n}_i = \hat{m}_{j(i)}$, with $(j(1), j(2), \ldots, j(12)) = (1,7,9,11,8,10,6,3,5,2,4,12)$. The solid angle subtended by the $\{\hat{n}_j\}$ for three pentagons that are mutual nearest neighbors is 7 times larger than the solid angle subtended by their $\{\hat{m}_j\}$. A topological Skyrmion number is the number of times one sphere covers another sphere, much as a vortex number is the number of times one circle covers another circle. The Skyrmion number for the field $\hat{n}$ is 7, for both of the parity-related ground states [6]. Given that the Hamiltonian is so simple, this exotic ground state arises because of the connectivity of the C_{60} [7].

The classical antiferromagnet on C_{12}, C_{20}, C_{70}, and C_{84} has also been solved numerically. The truncated tetrahedron C_{12} is a smaller system with properties similar to C_{60} [8]. It has four triangles and four hexagons. The classical lower bound for the truncated tetrahedron, $E_b^{(12)} = 12J_1 \cos(2\pi/3) - 6J_2$ is achieved by the ground state, which has a Skyrmion number 1.

A large number of C_n fullerenes have been isolated [9]. These compounds are closed (have the topology of a sphere), with twelve pentagons and a variable number of hexagons $n_h = (n/2) - 10$. The average frustration decreases as the number of hexagons increases. We have calculated the classical ground state for the smallest molecule in this series, the dodecahedron C_{20}, for the most stable D_{5h} isomer of C_{70}, and for the T_d isomer of C_{84} [10]. The C_{20} molecule has not been synthesized, while C_{70} and C_{84} are produced in carbon arcs.

The ground-state energy for the dodecahedron is $-22.360680J$, which does not reach the bound $E_b^{(20)} = 30J\cos(4\pi/5) = -24.270510J$. The pentagons interfere with each other, and prevent the system from reaching $E_b^{(20)}$. The Skyrmion number of the ground state is 7. Assuming that all C_{70} bonds have the same coupling J, the ground-state energy of C_{70} is $-93.346473J$, which is slightly higher than the lower bound $E_b^{(70)} = [60 \times \cos(4\pi/5) - 45]J = -93.541020J$. The Skyrmion number of the C_{70} ground state is undefined. There are pentagons neighboring across the equator whose spin plane normals are precisely antiparallel, resulting in an undefined solid angle. Many (but not all) states that differ infinitesimally from the ground state have Skyrmion number 7. The lowest-lying metastable configuration for C_{70} has a well-defined Skyrmion number 4. The T_d isomer of C_{84} has the symmetry of a tetrahedron. In contrast to the above systems, the ground-state spin configuration for C_{84} has a lower symmetry than that of the molecule. The ground-state energy is $-113.892689J$, which does not reach the lower bound $E_b^{(84)} = -114.541020J$. The ground state has Skyrmion number 1, which interestingly is the same Skyrmion num-

ber as the only other system investigated with T_d symmetry, the truncated tetrahedron C_{12}.

We do not yet understand the C_n problem well enough to predict the result for a general n isomer without doing the full calculation. The results on C_{20}, C_{60}, C_{70}, and C_{84} are consistent with the hypotheses that (1) C_{60} is the unique fullerene that reaches the energy lower bound, and (2) the ground state has a nonzero Skyrmion number when it can be defined.

We now calculate the response of C_{60} to a magnetic field by adding a term $-h\hat{z} \cdot \sum_i \sigma_i$ to the Hamiltonian. There is a first-order metamagnetic transition, which is surprising for an isotropic Heisenberg model. Usually magnetic anisotropy, arising from the spin-orbit interaction, is required for a metamagnetic transition. The symmetry of the ground state is different above and below the transition. Below h_c, sites i and j that are diametrically opposite each other have identical spins, $\sigma_i = \sigma_j$. Above h_c this symmetry is absent, but sites i and j that are mapped into each other by a rotation of π about the axis through the midpoint of one nonpentagon bond have spins related by $(\sigma_i^x, \sigma_i^y, \sigma_i^z) = (-\sigma_j^x, -\sigma_j^y, \sigma_j^z)$.

In nonzero field, the spins in a given pentagon are not coplanar. The pentagon spin plane normal $\hat{n}$ is generalized so that a variable $\hat{n}_{i,j}$ occupies each pentagon bond, with $\hat{n}_{i,j} \sim \sigma_i \times \sigma_j$. The Skyrmion number can be calculated for the field $\hat{n}_{i,j}$, and it is found that the Skyrmion number is 7 both above and below the transition.

The above results are for the lowest energy state at a given magnetic field. One can also obtain hysteresis loops by following metastable states while slowly changing the magnetic field, Fig. 2. A hysteresis loop can be complicated because of the large number of local minima, but it never encloses the origin.

We have also investigated the response of C_{12}, C_{20}, C_{70}, and C_{84} to an external magnetic field. Of these, only C_{20} has a metamagnetic transition at which the magnetic moment is discontinuous. The other members of this group have a transition at which the moment M is continuous, but dM/dh is discontinuous. We do not understand this
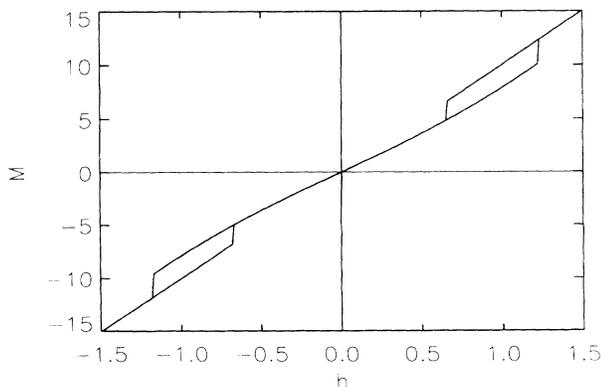

FIG. 2. Typical hysteresis loop, showing magnetic moment M as a function of applied field h, beginning and ending at $h = 0$. The couplings are $J_1 = 1$ and $J_2 = 1.2$.

difference in behavior.

The above $M(h)$ calculations for $S = \infty$ do not directly apply to C_{60}, which has $S = \frac{1}{2}$. Since S_z is a good quantum number for the $S = \frac{1}{2}$ system, it cannot have a magnetization that is linear in h for small h as shown in Fig. 2. The closest it can come to Fig. 2 is to follow in a staircase fashion, with a series of first-order transitions at which S increases from 0 to 1 to 2, etc., with a larger ΔS jump at the metamagnetic transition. Since the transition from $S = 0$ to 1 is at unobservably large fields (order of J or 1000 T), the spin susceptibility vanishes. For $U \gg t$, the orbital susceptibility falls as t^5/U^4 from the five-membered rings. Since the physical U is not very much larger than t, there is an orbital contribution to the measured susceptibility. Elser and Haddon have estimated that the orbital contribution nearly vanishes for C_{60} with $U = 0$ [11]. The effect of nonzero U is hard to estimate for C_{60}, but we note that for an isolated six-membered ring the orbital susceptibility for $U/t = 4$ is 0.49 that for $U = 0$. The orbital and spin susceptibility should thus be very small for C_{60}, which is consistent with measurements [12].

We now discuss the $S = \frac{1}{2}$ wave function. For $S = \frac{1}{2}$, σ in Eq. (1) is a 2×2 matrix. The simplest prescription to make an $S = \frac{1}{2}$ trial wave function is to form a coherent state $|\psi_0\rangle$ that is a product of spinors. The spinor on each site j is quantized in the local $+\hat{z}_j$ direction given by the classical spin direction. The expectation $\langle \psi_0 | H | \psi_0 \rangle$ is equal to the classical energy. Two modifications to this prescription are required. The first is to add zero-point spin fluctuations, which lower the energy and result in a wave function $|\psi_1\rangle$. The second is to make the wave function the sum over coherent states representing all of the classical ground states (including global rotations and parity). This results in a trial state of total spin $S = 0$.

The spin fluctuation energy is estimated in leading-(second-) order perturbation theory. This calculation gives an extremely accurate energy for the square lattice antiferromagnet [13]. The energy shift for C_{60} is

$$\Delta E = \sum_j \frac{|\langle j | H | \psi_0 \rangle|^2}{\epsilon_0 - \epsilon_j}, \qquad (2)$$

where each $|j\rangle$ has two adjacent spins flipped with respect to $|\psi_0\rangle$. For $J_1 = J_2 = 1$, the ground-state energy is shifted to $E_g = E_0 + \Delta E = -78.541 - 45.676 = -124.217$. The correction to the classical energy is somewhat larger than that for the $S = \frac{1}{2}$ Heisenberg model on a square lattice. The reason is that in this case each site is only threefold coordinated and the neighboring spins are not all exactly antialigned, so that the energy denominators are smaller. Another attractive variational trial state $|\psi_2\rangle$ is the product of singlets on each nonpentagon bond [14]. This state has an energy $E_2 = -90$, which is considerably higher than E_g. (The energy E_2 can also be reduced by adding fluctuations perturbatively.) We also

calculated the moment reduction in second-order perturbation theory on the coherent state. The local moment is reduced from 1 to 0.5590. This moment is smaller than that obtained for the square lattice [13].

Because of quantum fluctuations, a spin-$\frac{1}{2}$ wave function does not have a unique Skyrmion number. The wave functions $|\psi_0\rangle$ and $|\psi_1\rangle$ that we propose do, however, have unusual, nonvanishing spin-spin correlation functions even for widely separated spins on the molecule. Some of the correlation functions result from the fact that each pentagon tends to have a unique normal, which may be calculated from any of the five adjacent spin pairs in the pentagon, $\sigma_i \times \sigma_j$. Other nonzero correlation functions arise because the normals to *different* pentagons are related. We have calculated some correlation functions from exact diagonalizations of the smaller model system, the truncated tetrahedron. These calculations indicate that both short- and long-range classical spin correlations survive quantum fluctuations [15]. In contrast, the proposed local singlet state $|\psi_2\rangle$ and the resonating-valence-bond state [2] have only short-range antiferromagnetic correlations.

Motivated in part by the cuprate superconductors, there has been a large effort in calculating the properties of extra holes or electrons in a planar antiferromagnet using t-J and t-t'-J models [16]. An electron-doped crystal of C_{60} molecules is also a superconductor [17], and it may be useful to do similar calculations in its more complicated spin field.

In conclusion, we have investigated the low-energy magnetic properties of undoped C_{60}, the related fullerenes C_{20}, C_{70}, and C_{84}, and the truncated tetrahedron C_{12} in the strong interaction limit. We argue that there is no phase transition in C_{60} as a function of Hubbard U, and thus the spin-spin correlation functions at intermediate U are expected to be similar but smaller than those for large U. In the classical approximation, the connectivity of the ball leads to an exotic magnetic ground state with nontrivial topology even for the simplest antiferromagnetic Heisenberg Hamiltonian. C_{60} is the only fullerene investigated that reaches the energy lower bound, meaning that it has no frustration beyond that of an elementary pentagon. The spin correlations in C_{60} may be measurable by inelastic neutron scattering, by magnetic x-ray scattering, or by ^{13}C NMR.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, Nature (London) **318**, 162 (1985); W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).

[2] S. Chakravarty, M. Gelfand, and S. Kivelson, Science **254**, 970 (1991).

[3] G. Stollhoff, Phys. Rev. B **44**, 10998 (1991).

[4] The evidence for the large-U quantum numbers of the $S = \frac{1}{2}$ problem is that (1) we have exactly solved the qualitatively similar twelve-site truncated tetrahedron, which has $L = S = 0$ in the large-U limit, and (2) the classical ($S = \infty$) ground state for C_{60} has $S = 0$.

[5] C. S. Yannoni et al., J. Am. Chem. Soc. **113**, 3190 (1991).

[6] The Skyrmion number cannot be defined directly for the spin field σ, because many neighboring spins are antiparallel, which results in an undefined solid angle.

[7] The ground-state spin configuration can also be described in the language of polytopes. The vertices defined by the spin plane normals $\{\hat{n}_j\}$ form a star-polyhedron with Schläfli symbol $\{3, \frac{5}{2}\}$. This star-polyhedron has a *density* 7, equivalent to Skyrmion number 7, and is isomorphic to the icosahedron $\{3,5\}$ defined by the $\{\hat{m}_j\}$. See H. S. M. Coxeter, *Regular Polytopes* (Dover, New York, 1973), pp. 104 and 106.

[8] S. White, S. Chakravarty, M. Gelfand, and S. Kivelson, Phys. Rev. B **45**, 5062 (1992).

[9] R. F. Curl and R. E. Smalley, Sci. Am. **265**, No. 4, 32 (1991).

[10] K. Raghavachari and C. M. Rohlfing, J. Phys. Chem. **95**, 5768 (1991).

[11] V. Elser and R. C. Haddon, Nature (London) **325**, 792 (1987); Phys. Rev. B **36**, 4579 (1987).

[12] R. C. Haddon et al., Nature (London) **350**, 46 (1991); R. S. Ruoff et al., J. Phys. Chem. **95**, 3457 (1991); J. D. Thompson et al. (unpublished).

[13] E. Manousakis, Rev. Mod. Phys. **63**, 1 (1991).

[14] T. M. Rice (private communication).

[15] D. Coffey and S. A. Trugman, Report No. LA-UR-92-712 (to be published).

[16] See, for example, S. A. Trugman, Phys. Rev. B **37**, 1597 (1988); C. Kane, P. Lee, and N. Read, Phys. Rev. B **39**, 6880 (1989).

[17] A. F. Hebard et al., Nature (London) **350**, 600 (1991).