Magnetic moments in the presence of topological defects in graphene

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We study the influence of pentagons and heptagons, dislocations, and other topological defects breaking the sublattice symmetry on the magnetic properties of a graphene lattice. It is known that vacancies and other defects involving uncoordinated atoms induce localized magnetic moments in the lattice. Within the Hubbard model the total spin of the nonfrustrated lattice is equal to the number of uncoordinated atoms for any value of the Coulomb repulsion U according to the Lieb theorem. With an unrestricted Hartree-Fock calculation of the Hubbard model we show that the presence of a single pentagonal ring in a large lattice is enough to alter the standard behavior and a critical value of U is needed to get the polarized ground state. Dislocations, Stone-Wales, and similar defects are also studied.

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I. INTRODUCTION

The recent synthesis of a single layer of graphite[1,2] and the expectations of future nanoelectronics applications have renewed the interest in graphitic materials. Among the possible exotic properties of graphene, magnetism is one of the least studied and most appealing given the interest of potential applications of organic magnets. Ferromagnetic order enhanced by proton irradiation has been observed in graphite samples[3] and demonstrated to be due to the carbon atoms by dichroism experiments.[4] Ferromagnetism has also been reported in carbon nanotubes induced by magnetic impurities[5] and in honeycomb lattice arranges of first row elements.[6] By now it is clear that the underlying mechanism leading to ferromagnetism in all carbon structures is the existence of unpaired spins at defects induced by a change in the coordination of the carbon atoms (vacancies, edges, or related defects)[7] although the mechanism for the occurrence of long-range magnetic order is still unknown.

The structure of disorder is crucial to explain the magnetism found in graphite samples. While local disorder has been thoroughly investigated in graphene (see Ref. 8 for a review and references therein) topological defects, where a hexagonal ring of the graphene honeycomb lattice is replaced by another polygon, have been less pursued. The theoretical description of these defects in the continuum limit is very old[9–11] and their influence on the electronic and transport properties of graphene has been studied recently in a number of papers[12–14] but their implications on the magnetic structure have not been fully explored. Recent observations of extraordinary mechanical stiffness coexisting with ripples in large graphene samples[15] point toward topological defects as the main source of curvature.[12,13] Nucleation of dislocations in the fabrication of the samples by mechanical cleavage of graphite is practically unavoidable. These types of defects have very recently been produced and observed with transmission electron microscopy in suspended graphene samples.[16]

Graphene is made of carbon atoms arranged in a two-dimensional hexagonal lattice that can be seen as two interpenetrating triangular lattices A and B. It is the peculiar geometric structure of the honeycomb lattice with two atoms per unit cell that determines the very interesting low energy properties of the system whose quasiparticles are massless Dirac fermions in two dimensions.[1] The graphene lattice is an example of a *bipartite* lattice: it is made of two sets of sites A and B and the coordination is such that atoms of either set are only connected to atoms belonging to the opposite subset. In a beautiful paper concerning the magnetic properties of the Hubbard model in bipartite lattices, Lieb[17] proved a theorem stating that for a repulsive value of the Hubbard interaction U the ground state of the half filled lattice is nondegenerate and has a total spin equal to half the number of unbalanced atoms: $2S=N_A-N_B$. This rule has been confirmed recently in a number of studies of graphene with vacancies, edges, or larger defects[18–25] and the Lieb theorem[17] has become a paradigm of magnetic studies in graphene clusters and in nanographite. What is more interesting, although the original theorem deals with the Hubbard interaction, the rule seems to survive when more complicated calculations such as *ab initio*, density functional, or molecular dynamics are performed.[26–28] The purpose of this work is to emphasize the fact that the crucial property that determines the magnetic behavior of the lattice is its bipartite nature as it was already established in the original paper.[17] Vacancies, islands, cracks, or whatever defects preserving this property will in most cases obey the Lieb rule[17] even if the interactions go beyond the Hubbard model. We will show that a slight frustration of the bipartite property is enough to alter the rule.

We show that the ground state of the honeycomb lattice in the presence of pentagonal, heptagonal rings or dislocations (pentagon-heptagon pairs) deviates from the predictions of Lieb's theorem.[17] In the classical configuration of a graphene lattice with several vacancies of the same sublattice the total spin of the ground state is half the number of unpaired sites for any arbitrarily small value of the Hubbard repulsion U. This behavior is due to the presence of zero energy states generated by the unpaired electrons in the bipartite lattice and their subsequent polarization when an electron-electron interaction U is added.

In the presence of the topological defects discussed in this work a finite critical value U_c is needed to reach the polarized ground state. For values of $U<U_c$ the total spin of the ground state remains zero. Above the critical value of U the

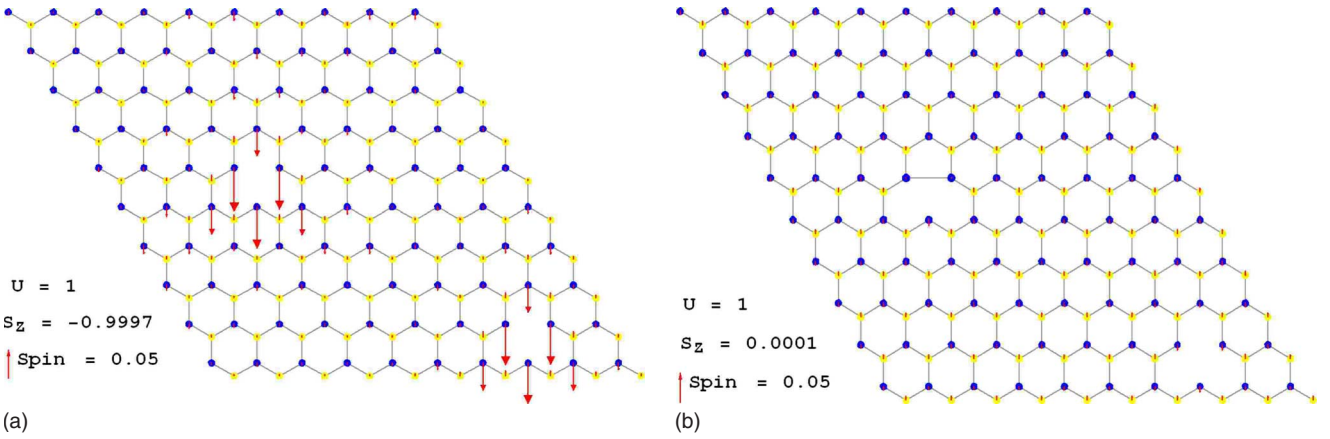

FIG. 1. (Color online) Left: Spin distribution in a lattice with two vacancies of the same sublattice with $U=1$. Right: Same configuration in the presence of a pentagon for the same value of U.

system is insensitive to the frustrating links and behaves as a normal bipartite lattice. In the simplest case considered in which we have a number of vacancies of the same sublattice in the system and any number of them develops a pentagonal ring, the critical value obtained to reach the polarized ground state is similar to the critical U at which the perfect system undergoes a phase transition from the semimetal to an antiferromagnetic (AF) insulator.[29,30]

II. MODEL

We use a single band model for the π electrons of graphene and perform a mean-field calculation of the Hubbard Hamiltonian,

$$H = -t \sum_{\langle ij \rangle, \sigma} c_i^+ c_j + U \sum_i n_{i\uparrow} n_{i\downarrow},$$

where $\langle ij \rangle$ stands for nearest neighbors of the honeycomb lattice and σ stands for the spin polarization. The tight-binding model for the π orbitals is the simplest approach that captures the electronic structure of graphene[31] and mean-field calculations of the Hubbard Hamiltonian are often in good agreement with those obtained by density-functional calculations in the honeycomb lattice.[32,33]

III. RESULTS I: PARTIALLY RECONSTRUCTED VACANCIES

We begin by studying configurations of two vacancies belonging to the same sublattice in a graphene sheet where in one of them, two unpaired electrons have been joined by a link forming a pentagon as shown in Fig. 1. This configuration has been suggested to form naturally as the first step of vacancy reconstruction[34,35] and has also been shown to lower the energy in density-functional studies of vacancies in irradiated graphite.[36] It is the simplest situation to exemplify the behavior that we want to emphasize.

Figure 1 shows the ground-state configurations for a value of the Hubbard repulsion $U=1$ (throughout the paper U will be measured in units of the hopping parameter t) for both the pentagonal defect and the vacancy. The total spin of the ground state in the standard configuration shown in the left side of the figure is $S_z=1$, which accounts for half the two impaired atoms of the same sublattice. The polarization for each site of the lattice is represented by an arrow (its scale in units of $\hbar$ is also shown adjacent to each figure). We see a relatively strong polarization localized at the atoms surrounding the vacancy as expected. In the right-hand side of Fig. 1 one of the vacancies has relaxed and formed a pentagonal link that we model with a hopping t of the same value as the rest of the lattice (this assumption is not important to the results that remain the same if reasonably different values of the pentagonal t are assumed). This little frustration of the sublattice order is enough to destroy the polarization around the two vacancies and the total spin of the ground state is zero. The structure presented in the figure corresponds to a density of defects, vacancies in this case, of 1%, which is large. We have performed the calculation with various defect densities from 0.1 to 10^{-3} and the results remain the same independent not only of the density of defects but also of the relative distances among them. We have also computed the case in which both vacancies have a pentagonal link and the results are the same: in the presence of at least a pentagonal ring there is a critical value of U of approximately $U\sim 2$ above which the spin of the ground state recovers the full value $S_z=1$. To better appreciate the effect of the pentagonal link we note that the critical U to polarize the ground state for vacancies in the bipartite lattice is zero if the density of vacancies is not too big. In the nonfrustrated case there is also a transition from an unpolarized semimetal with magnetic moments strongly localized at the positions of the uncoordinated atoms surrounding the vacancy to a perfectly ordered antiferromagnetic state with two frozen holes and with total spin determined by the unpaired electrons. The low U configuration has been described by Lieb[17] in the original paper as an example of itinerant ferromagnetism and the high U case as ferrimagnetism, where there is a perfect antiferromagnetic order in a system with a nonzero total spin. It is quite remarkable that the presence of a single link frustrating the sublattice symmetry in a cluster or up to 3200 atoms is enough to rise the critical U to the rather high value of $U=2$. As noted before, the critical value found in this case is similar to the one that sets the semimetal–AF insulator transition in the perfect system.

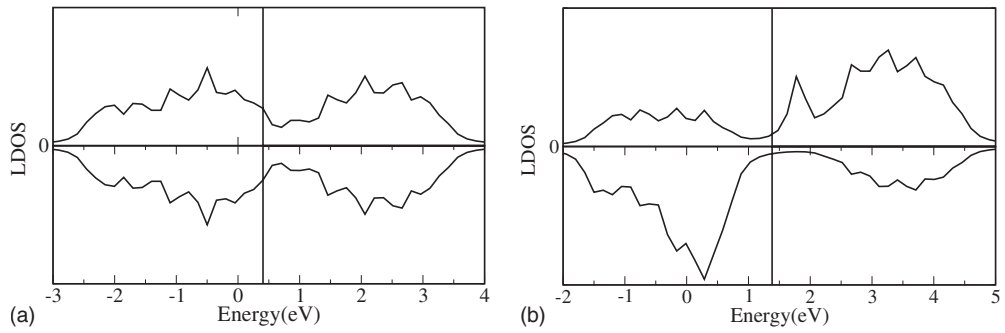

FIG. 2. Left: Local density of states at the vertex of the pentagon in the configuration given in Fig. 1, right for the spin up and down electrons with $U=1$. Right: Same for $U=3$. The vertical line shows the position of the Fermi energy.

In Fig. 2 we show the local density of states (DOS) for the lattice configuration shown at the right-hand side of Fig. 1 at a lattice site on the pentagonal defect. The upper (lower) curve represents the density of electrons with spin up (down). The left of the figure corresponds to the unpolarized ground state obtained for a value of $U=1$ and the right-hand side shows the fully polarized system obtained with $U=3$. The vertical line signals the position of the Fermi level which is shifted from zero by the interaction U. We can see that in the unpolarized situation the local DOS at the position of the dangling bond is higher than in the case of the polarized case.

IV. RESULTS II: DISLOCATIONS

Next we turn to the more interesting case of having dislocations in the lattice. Recent works on the elasticity in the flat honeycomb lattice[37] have demonstrated that two types of dislocations are stable configurations: shuffle dislocations—an octagon with a dangling bond—and the more usual glide dislocations—made of a pentagon-heptagon pair. These defects were described in Ref. 38 and experimental observations were reported in Ref. 39; dislocations have also been observed very recently in graphene grown on Ir in Ref. 40. The presence of dislocations can affect the magnetic properties of the graphene samples in two ways: shuffle dislocations can nucleate local magnetic moments similar to the ones induced by vacancies, while the structure of the glide dislocations frustrates the bipartite nature of the lattice. Dislocations of either type (glide or shuffle) add—or suppress—a row of atoms to the lattice. In order to eliminate the influence of the edges and perform the calculation with periodic boundary conditions we introduce a pair of dislocations such that the extra row begins in one and ends in the other one. Figure 3 shows the basic structure discussed in this work. The shuffle dislocation is made of an octagon with an unpaired atom of a given sublattice. The dislocation line ends in a glide dislocation made of a pentagon-heptagon pair. This basic block does not alter the edges of the sample and should behave like a single vacancy. We have checked that indeed the total spin of the lattice for this configuration is $S=1/2$ for a critical value of $U\sim 0$ showing that the dangling bond of the shuffle dislocation behaves as a vacancy of the other sublattice, that of its missing nearest neighbor. If a vacancy of the same sublattice as the dangling bond atom is added, the total spin of the system is zero in agreement with Lieb's theorem.[17] When the additional vacancy belongs to the opposite sublattice, a critical value of the interaction U_c is needed to obtain the total spin $S=1$. For $U<U_c$ the total spin is zero. The situation is similar to the one discussed previously with pentagons but in the case of the dislocations there is a critical region in the parameter space U, $0.2<U<1$, where the fully polarized and the unpolarized ground states are almost degenerate in energy and we find a coexistence of both cases. In Fig. 3 we show the two spin configurations obtained at a value of $U=0.3$ for two defects located at the same relative distances on the lattice with total spin

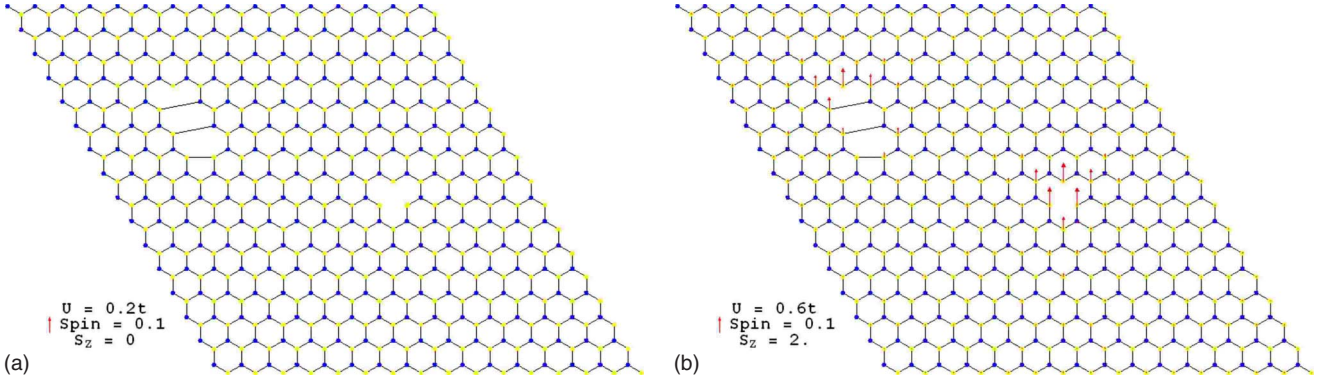

FIG. 3. (Color online) Spin structure for two different configurations of dislocations and a vacancy with $U=0.3$ with total spin polarizations $S=0$ (left) and $S=1$ (right).

$S_z=0$ (left) and $S_z=1$ (right). The critical region depends on the density and on the relative positions of the defects and a full phase diagram will be presented elsewhere. This situation points toward a first-order magnetic transition in the presence of dislocations but this issue cannot be explored with the techniques of the present work and will be studied in the future with density-functional theory.

V. SUMMARY AND DISCUSSION

We end by a summary of the findings and some remarks. We have shown that the nucleation of magnetic moments in the graphene honeycomb lattice is severely modified by the slightest frustration of the bipartite character of the lattice. The most dramatic effect appears when considering standard vacancies of the same sublattice. It is known that for values of the defect density not exceeding a certain value of about 1%, the ground state of the system at half filling has maximal spin given by the sublattice unbalance for any value of the Hubbard U. This result has been proven to be quite robust and to apply for interactions beyond the Hubbard model. We have shown that the presence of a single link frustrating the sublattice symmetry in a cluster of up to 3200 atoms is enough to rise the critical U to a rather high value of $U=2$. This critical value is similar to the one that induces an antiferromagnetic instability in the perfect lattice estimated to be in the mean field of the order of $U\sim 1.8$ although the value increases up to $U\sim 4.5$ when more refined calculations are done.[29]

We have explored a complete variety of situations with several vacancies or with several shuffle dislocations acting as sources of unpaired electrons and found the same results. The presence of a single link joining two atoms of the same sublattice (not necessarily forming a pentagon) is enough to induce a finite critical value of U_c. In the case of more complicated distributions of 5-7 rings like the ones discussed in Fig. 3, the critical U state depends on the density and relative position of the defects.

As was explicitly mentioned in the original paper by Lieb[17] the ferromagnetic properties of bipartite lattices such as graphene are determined by the appearance of midgap states associated to defects and to the electron-electron interactions (U) within them. The perfect degeneracy of the zero energy states induced by vacancies or voids belonging to the same sublattice is broken by the inclusion of a frustrating link and the interplay of kinetic energy and Coulomb repulsion becomes more subtle. The importance of the present work relies on the fact that the frustrating topological defects that we discuss have been observed in suspended graphene samples[16] and have to be taken into account when designing prospective magnetic graphene devices. The role of these defects in graphite should be similar and will be studied in the future. The findings of this work are somehow negative for the expectations to get magnetic graphene since the presence of 5-7 rings will always increase the critical value of U needed to get a fully polarized ground state.

Stone-Wales (SW) defects made of two pentagon-heptagon pairs (two glide disclinations with opposite Burgers vectors) that are known to play a very important role in the physics of fullerenes and carbon nanotubes have been shown to be unstable in the flat lattice[41] where they evolve to the perfect lattice. Although they have almost no effect on the electronic structure,[37] their presence does alter the magnetic structure of the unperturbed lattice in the way described in this work due to the presence of odd-membered rings. Their effect is similar to the pair of dislocations discussed in Sec. IV: in a lattice configuration with a number of dangling bonds of the same sublattice and in the presence of a SW defect a finite critical value of U is needed to reach a fully polarized ground state. This result agrees with the effect studied in Ref. 42 where Stone-Wales defects were assumed to be responsible for the destruction of the magnetization of graphene with atomic hydrogen adsorbed. After the study done in this work, we can anticipate that the same results will be obtained if the SW defect is replaced by a single pentagon, heptagon, or 5-7 configuration. Our results can also be of importance in relation to the recent finding that any edge defect spoils the metallicity of graphene nanoribbons[43] since dislocations always affect the edges of the ribbons.

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