Exchange interactions and frustrated magnetism in single-side hydrogenated and fluorinated graphene

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(Dated: June 24, 2013)

Magnetism in single-side hydrogenated (C\textsubscript{2}H) and fluorinated (C\textsubscript{2}F) graphene is analyzed in terms of the Heisenberg model with parameters determined from first principles. We predict a frustrated ground state for both systems, which means the instability of collinear spin structures and sheds light on the absence of a conventional magnetic ordering in defective graphene demonstrated in recent experiments. Moreover, our findings suggest a highly correlated magnetic behavior at low temperatures offering the possibility of a spin-liquid state.

PACS numbers: 31.15.A-, 75.70.Ak, 75.30.Et, 75.10.Kt

Magnetism of \textit{sp} materials is an exotic phenomenon of a fundamental physical relevance and potential practical importance. In particular, one can expect much higher Curie temperatures for \textit{sp} magnets than for conventional magnetic semiconductors [1]. A discovery of graphene has revived an interest in this subject [2,3]. Recent studies provided persuasive experimental evidence for the existence of magnetism in graphene doped by hydrogen and fluorine atoms [4-6]. Although no magnetic ordering has been detected in defective graphene even at liquid helium temperatures [6,7], theoretical studies show that an ordered decoration of graphene with a composition of C:H(F)=2:1 (occasionally referred to as graphone) is unstable toward the formation of (anti-)ferromagnetism [8,9], offering perspectives of applications [10].

In contrast to single defects in graphene, whose magnetic properties are theoretically well understood [11,12], the magnetism in C\textsubscript{2}H and C\textsubscript{2}F lacks a consistent description. Although previous density functional (DF) studies point to the possibility of magnetic ordering in C\textsubscript{2}H and C\textsubscript{2}F [8,10], its origin and stability have not yet been analyzed in details. Moreover, the prediction of the magnetic ground state cannot be conclusive within the DF scheme due to symmetry constraints imposed by periodic boundary conditions. On the other hand, the possibility of a description in terms of spin models is not obvious due to the absence of a unique definition of local magnetic moments in \textit{sp} systems, which makes the parametrization of a model particularly challenging.

In this Letter, we construct an appropriate Heisenberg model to describe magnetic properties of C\textsubscript{2}H and C\textsubscript{2}F, and determine its parameters from first principles. For both systems, we find a frustrated ground state, which contradicts previous theoretical predictions. We show that the possibility of spontaneous magnetization in C\textsubscript{2}H and C\textsubscript{2}F is very unlikely, instead, an unconventional magnetic behavior is expected at low temperatures, such as non-collinear ordering or a spin liquid state.

We first analyze the electronic structure at the DF level and construct a tight-binding Hamiltonian by taking advantage of the Maximally-Localized Wannier Functions (MLWF) [13]. DF calculations were performed within the plane-wave pseudopotential method as implemented in the QUANTUM-ESPRESSO simulation package [14]. Exchange-correlation effects were taken into account by using the standard GGA-PBE functional [15]. To achieve high accuracy, we employed an energy cutoff of 50 Ry for the plane-wave basis and 400 Ry for the charge density, as well as a (64×64) \textit{k}-point mesh. The surface layers were separated by a vacuum region of

![FIG. 1. (Color online) Schematic representation of the atomic structure and Maximally-Localized Wannier Functions for (a) C\textsubscript{2}H and (b) C\textsubscript{2}F.](image-url)
and wannier90 for the electronic Hamiltonian, we used the code [16].

FIG. 2. (Color online) Band structure and density of states (DOS) for C2H and C2F obtained from non-spin-polarized calculations. Contributions from the impurity orbitals (s for H and sp for F) are shown by color.

A and fully relaxed. To construct a localized basis for the electronic Hamiltonian, we used the wannier90 code [16].

Fully relaxed structures of C2H and C2F as well the MLWF are shown in Fig. 1. All orbitals are well localized providing an intuitive picture of the chemical bonding. In each case, the MLWF basis includes three bond-centered orbitals, corresponding to the sp2-like hybridization of carbon atoms (σCC), one bond-centered sp-like orbital localized between carbon and hydrogen/fluorine atoms (σCH/σCF), and one pz-like orbital centered at the non-bonded carbon atom. In the case of C2F, there are three additional orbitals resulting from the F-centered sp2-type hybrids (σF). In contrast to C2H, the σCF and p orbitals in C2F are more localized, implying stronger binding and enhanced stability of the fluorinated system (Table 1).

In Fig. 2 we show the density of states (DOS) and band structure projected onto the orbitals associated with the MLWF localized at the impurity orbitals of C2H and C2F. In both cases there is a density of states at the Fermi level, indicating the presence of uncompensated electrons, which are localized mainly at the pz-orbital of carbon with some contribution from the impurity orbitals.

The MLWF formalism allows us to represent the electronic Hamiltonian in the tight-binding form,

\[ H = \sum_i \varepsilon_i n_i + \sum_{ij} t_{ij} c_i^\dagger c_j, \tag{1} \]

where summation runs over the Wannier orbitals, \( \varepsilon_i \) is the energy of the ith orbital, \( t_{ij} \) is the hopping parameter between ith and jth MLWFs, and \( c_i^\dagger \) (\( c_j \)) is the creation (annihilation) operator of electrons localized at the ith (jth) MLWF. In Fig. 3 we show the most relevant hopping parameters obtained from the non-spin-polarized Hamiltonian for C2H and C2F. In contrast to graphene, where nearest-neighbor hoppings only are essential to describe the main characteristics of the ground-state electronic spectrum, the case of graphene derivatives is considerably more complicated due to the lowering of symmetry. In view of the complexity of the Hamiltonian, a simple analytical model, which would be appropriate for studying magnetic properties of C2H and C2F, is not readily available.

If the spin polarization is switched on, the exchange interactions split the energies of electrons with opposite spins, resulting in the formation of magnetic states. Interestingly, spin-polarized DF calculations yield different ground states for C2H and C2F, corresponding to the ferromagnetic (FM) and antiferromagnetic (AFM) configurations with a small band gap (∼0.5–1.0 eV), respectively [8–10]. Exploiting exponential localization of the MLWF in real space [13], the magnetic moments can be associated with the respective Wannier orbitals. Accordingly, the exchange splitting on the ith Wannier orbital can be calculated from diagonal elements of the spin-polarized MLWF Hamiltonian as \( \Delta_i = H_{ii} - \varepsilon_i \), whereas the corresponding magnetic moment is easily obtained from the density of states (DOS) \( g_{ii}^s(\varepsilon) \) projected onto the ith MLWF, \( M_i = \int_{-\infty}^{E_F} d\varepsilon \left[ g_{ii}^s(\varepsilon) - g_{ii}^p(\varepsilon) \right] \). The corresponding values are listed in Table 1 for different Wannier orbitals. Apart from the magnetic moment localized in the pz orbital, there is a non-negligible contribution from the impurity orbitals, which is more pronounced for C2H (σCH orbital). Below, we show that this contribution plays an essential role in determining the magnetic behavior of C2H.

Owing to the possibility of a localized representation of magnetic moments in C2H and C2F, the magnetic in-
interactions can be analyzed in terms of the Heisenberg model,

\[ H = - \sum_{i \neq j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j, \]

where \( J_{ij} \) is the exchange coupling between \( i \) and \( j \) sites, and \( \mathbf{s}_i, \mathbf{s}_j \) are unit vectors pointing in the direction of local magnetic moments at sites \( i \) and \( j \), respectively. Thus, we consider the mapping of DF calculations onto classical Heisenberg model [18]. At this mapping, the exchange parameters can be calculated via the second variations of the total energy with respect to infinitesimal rotations of the magnetic moments. For a lattice with a basis, this can be written in the following form [18]

\[ J_{ij}^{\alpha \beta} = \frac{1}{4 \pi} \int_{-\infty}^{E_F} d\varepsilon \ \text{Im} \left[ \Delta_\alpha \Delta_\beta (\varepsilon) \Delta_\beta \Delta_\alpha (\varepsilon) \right], \]

where \( i, j \) and \( \alpha, \beta \) denote unit cell and sublattice (orbital) indices, respectively. \( \Delta_\alpha(\varepsilon) \) is the exchange splitting of the orbital \( \alpha \) (\( \beta \)), \( E_F \) is the Fermi level, and \( G_{ij}^{\alpha \beta} (\varepsilon) \) is the real-space Green’s function, whose reciprocal-space representation is given by,

\[ G_{k}^\sigma (\varepsilon) = [\varepsilon - H^\sigma (k) + i\eta]^{-1}, \]

\( \eta \to +0 \). Here, \( H^\sigma (k) \) is the reciprocal-space Hamiltonian for spin \( \sigma = \uparrow, \downarrow \), whose matrix elements are obtained in the MLWF basis from spin-polarized DF calculations, corresponding to the most favorable magnetic state (FM for \( \text{C}_2\text{H} \), and row-wise AFM for \( \text{C}_2\text{F} \)). The Green’s functions are evaluated by taking \( \approx 10^6 \) \( k \)-points in the full Brillouin zone and the parameter \( \eta = 0.02 \).

In Fig. 4 we show the calculated exchange parameters for both \( \text{C}_2\text{H} \) and \( \text{C}_2\text{F} \) as functions of the distance between the nearest-neighbor interactions in \( \text{C}_2\text{H} \) and \( \text{C}_2\text{F} \) can qualitatively be explained by the difference in the overlap between the \( p_z \) and \( \sigma_{CH(\text{CF})} \) orbitals, resulting from the unequal spreads (Table I) and interorbital distances (Fig. 1). Thus, this kind of exchange interaction is directly related to the overlap of the wave functions involved. The second contribution to the exchange \( (p_z-p_z) \) interactions) exhibits a more complicated behavior, which is typical for the indirect superexchange interactions. By comparing the hopping parameters given in Fig. 3 it can be deduced that the difference in the \( p_z \) coupling between \( \text{C}_2\text{H} \) and \( \text{C}_2\text{F} \) is related to the presence of the \( 2p \) fluorine orbitals \( (\sigma_F) \) in \( \text{C}_2\text{F} \), which provide an additional superexchange pathway compared to \( \text{C}_2\text{H} \). For both systems, however, a conventional perturbative treatment of the superexchange (e.g., in terms of the relation \( J_{ij} \sim t_{ij}^2/U \)) is probably not correct due to the small magnitude of the Coulomb interactions \( U \) in \( sp \) systems.

We now turn to the problem of magnetic ordering in \( \text{C}_2\text{H} \) and \( \text{C}_2\text{F} \). In both cases, the presence of a significant AFM interaction on the triangular lattice of \( p_z \) orbitals suggests the instability of any collinear spin alignment [19]. Surprisingly, the exchange interactions in \( \text{C}_2\text{F} \) represent almost an ideal realization of the Heisenberg model with nearest-neighbor AFM couplings (\( J = -10 \)

### Table I. Linear spreads (\( \Omega \)), magnetic moments (\( M \)) and exchange splittings (\( \Delta \)) associated with the Wannier orbitals of \( \text{C}_2\text{H} \) and \( \text{C}_2\text{F} \). The orbitals are denoted according to Fig. 1

<table>
<thead>
<tr>
<th></th>
<th>( \text{C}_2\text{H} )</th>
<th></th>
<th>( \text{C}_2\text{F} )</th>
</tr>
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<tbody>
<tr>
<td>( \Omega, \Delta )</td>
<td>0.86</td>
<td>1.02</td>
<td>1.25</td>
</tr>
<tr>
<td>( \Delta ), eV</td>
<td>0.29</td>
<td>0.62</td>
<td>2.54</td>
</tr>
<tr>
<td>( M, \mu_B )</td>
<td>0.02</td>
<td>0.17</td>
<td>0.76</td>
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FIG. 4. (Color online) Calculated exchange parameters as functions of the distance between the \( p_z \) (red curve) and \( p_z \) \( \sigma_{CH(\text{CF})} \) (blue curve) orbitals in \( \text{C}_2\text{H} \) (left panel) and \( \text{C}_2\text{F} \) (right panel). The interactions between the other orbitals are negligibly small and not shown. In the inset, the \( J(R) \) parameters are shown with a prefactor \( R^\beta \).
meV), whose classical solution corresponds to the 120° Néel state [Fig. 4(b)]. In contrast to C₂F, the ground state of C₂H is not obvious due to the presence of a larger number of competing interactions of different signs. In this case, we seek the ground state spin configuration in the general form of a coplanar spin spiral, 
\[ S_{\alpha(\beta)}(r) = S_{\alpha(\beta)} \left( \cos(Q \cdot r + \phi_{\alpha(\beta)}), \sin(Q \cdot r + \phi_{\alpha(\beta)}) \right), \]
where Q is the spiral ordering vector, and \( \phi = \phi_{\alpha} - \phi_{\beta} \) is the phase shift between the spins on different sublattices. Minimizing the total energy with respect to Q and \( \phi \) we find that the ground state corresponds to an incommensurate spin spiral with Q=(0.31,0.79) and \( \phi=41.5° \). The corresponding spin configuration is shown schematically in Fig. 5(a).

The problem of magnetic frustration in C₂H and C₂F becomes more complicated if the quantum effects are taken into account. If we assume that the unsaturated carbon atoms in C₂F carry \( S = 1/2 \) spin, its ground state would correspond to the three-sublattice magnetic order, similar to the classical case, which is a widely accepted scenario for the spin-1/2 quantum Heisenberg antiferromagnet on a triangular lattice [20]. However, the magnitude of the local magnetic moment in C₂F (\( M_p \approx 0.5\mu_B \)) strongly suggest itinerant-electron magnetic behavior, which cannot be properly described by the quantum Heisenberg model. Although multispin models can provide a consistent description of the magnetism on the triangular lattice [21], the way of the parametrization of such models is far from being clear. The most natural model for studying itinerant-electron magnetism is the Hubbard model. Previous applications of this model to the triangular lattice reveal a spin liquid state at intermediate values of the \( U/t \) parameter with the transition to the ordered Néel state at higher \( U/t \) values [21,22]. Given a relatively small magnitude of U in sp materials due to the delocalization of electrons [23], the spin liquid state appears to be a possible scenario for the ground state of C₂F.

The case of C₂H turns out to be even more complicated due to the presence of the two magnetic sublattices comprising the honeycomb lattice. Although recent studies of the Hubbard model on the honeycomb lattice do not exclude the existence of a spin liquid phase in some range of the \( U/t \) parameters [24], their results cannot be directly applied to C₂H having two nonequivalent sublattices with \( M_p \approx 0.76\mu_B \) and \( M_{pH} \approx 0.17\mu_B \). An adequate description of such a system requires a more sophisticated analysis in terms of the multiorbital Hubbard model and represents an important issue for further studies.

In conclusion, we have studied the exchange interactions in C₂H and C₂F and analyzed the possibilities of the magnetic ordering in these systems. In each case, we have found the presence of AFM interactions on the triangular lattice of magnetic moments, leading to the instability of the collinear magnetic ordering due to frustration. Although the true quantum ground state remains to be determined, both systems are expected to exhibit highly correlated magnetic behavior at low temperatures and can be considered as promising candidates for the quantum spin liquid.

We acknowledge support by the EC under the Graphene Flagship (contract no. CNECT-ICT-604391) and by the scientific program no. 14.18.21.0076 (Russia).