Hidden multiferroic order in graphene zigzag ribbons

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The insulating magnetic phase in graphene zigzag ribbons, predicted both by density functional and mean field Hubbard model calculations, is described without additional approximations with a BCS wave function of two phase-locked condensates of spin-polarized electron-hole pairs. The associated order parameter is the spin dipole operator that features both magnetic and electric order and accounts for the spin-resolved ferroelectricity of the system. Each condensate is associated to a spin-dependent dipole and their relative phase locking sets the total electric dipole and total magnetization equal to zero.

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The quest of novel electronic phases, characterized by new order parameters, and the interplay between electric and magnetic degrees of freedom are two of the major themes in condensed matter physics. The coexistence of magnetic and electric order is associated to transition metal perovskites, whereas spintronics proposals are based on materials where either spin-orbit interactions or d electrons play a prominent role. Here I show that the magnetic ground state predicted in graphene zigzag ribbons, a chemically simple system without d electrons and negligible spin orbit coupling, is indeed a new electronic phase whose order parameter is the product of the spin and the electric polarization. This new electronic state may be studied experimentally thanks to recent progress in the fabrication of graphene and graphene based flat nanostructures.

Early theory work predicts that graphene is a zero gap semiconductor, with electron-hole symmetry and linear conduction and valence bands. These features arise naturally from a tight-binding model with one Π orbital per atom in a honeycomb lattice at half filling and they are related to fact that the honeycomb lattice is bipartite. The electronic structure of graphene nanoribbons depends dramatically on their atomic structure. Here I focus on graphene ribbons with zigzag edges. The single-particle description of this system features two almost degenerate quasi-flat bands at the Fermi energy. These flat bands are associated to edge states. When Coulomb repulsion is added to this picture within a mean field Hubbard model, local moments of opposite signs form in the edges, with a total zero spin, and a gap opens at the Fermi energy. The predictions of this model are robust with respect to the addition of more orbitals, second neighbour hoppings and long range Coulomb interactions, all present in density functional (DFT) calculations. DFT results and the mean field Hubbard model yield very similar results for the low energy sector of the electronic structure both for zigzag graphene ribbons and nanoislands. This permits a significant computational simplification as well as conceptual advantage through the use of exact results valid for the Hubbard model.

In this paper three things are done. First, I show that the mean field wave function of the Hubbard model for graphene ribbons with zigzag edges is that of two phase locked BCS condensates of spin-polarized electron-hole pairs living in the edge bands, the only bands affected by the interactions. Second, the BCS electron-hole coherence implicit in the wave function is associated to the existence of spin-resolved transverse electric polarizations that yield a zero total electric dipole and spin when summed. Therefore, the standard mean field magnetic phase of zigzag graphene ribbons is an excitonic insulator phase with a hidden ferroelectric order. Third, the mean field bands are written in terms of the BCS gap and diagonal self-energies.

Zigzag graphene ribbons are described with a single-orbital tight-binding model plus a on-site Hubbard repulsion treated in the mean field approximation at half filling.

\[ \mathcal{H} = \sum_{\vec{r}, \vec{r}'} t_{\vec{r}, \vec{r}'} c_{\vec{r} \sigma}^\dagger c_{\vec{r}' \sigma} + U \sum_{\vec{r}} n_{\vec{r}, \uparrow} n_{\vec{r}, \downarrow} \]  

where \( c_{\vec{r} \sigma}^\dagger \) creates an electron at the Π orbital of atom located at \( \vec{r} \) with spin \( \sigma \), \( n_{\vec{r}, \sigma} = c_{\vec{r} \sigma}^\dagger c_{\vec{r} \sigma} \) is the occupation operator. The first term in the Hamiltonian describes the first-neighbour hopping (\( t = 2.5eV \)) in the graphene ribbon and the second describes on-site Coulomb repulsion. I take \( U = 2eV \). The zigzag ribbon is a one dimensional crystal whose unit cell, shown in fig. 1a, is repeated along the x direction. The position \( \vec{r} \) is determined by a unit cell index, \( x \) and a intra-cell index \( I \). Notice that the top and bottom atoms belong to different sub-lattices. In a unit cell there are with \( N_P \) pairs of A and B atoms, and the width of the ribbon is \( W \approx \sqrt{3}N \), with \( N = 2N_P \).

The spectrum of the self-consistent mean field Hamiltonian for a ribbon with \( N \) atoms per unit cell has \( N \) bands per spin channel, half of which are occupied. Figure 1b shows the well known non-interacting (\( U = 0 \)) bands for a ribbon with \( N = 18 \). Solid (dashed) lines represent full (empty) states. The two flat bands in the outer region of the Brillouin zone correspond to states that are localized in the edges of the ribbon. As shown in figure 1d, they are not really degenerate except for...
ka = ±π. At zero temperature the lower (valence) band is full and the upper (conduction) band is empty. The operators that annihilate an electron in those bands are:

\[ c_{k,\sigma} = C_{k\sigma} = \frac{1}{\sqrt{L}} \sum_{x,I} e^{ikx} \psi_{c,k}(I) c_{x,I,\sigma} \]

\[ h^{\dagger}_{k,\sigma} = V_{k\sigma} = \frac{1}{\sqrt{L}} \sum_{x,I} e^{ikx} \psi_{c,k}(I) c_{x,I,\sigma} \tag{2} \]

where \( \frac{1}{\sqrt{L}} e^{ikx} \psi_{c,v,k}(I) \) are the Bloch eigenstates and \( L \) is the length of the ribbon. The gap between these bands is proportional to the penetration of the edge states towards the bulk region.

Figure 1c shows the mean field interacting bands, shifted rigidly by \(-U/2\). A gap opens at the Fermi energy, in agreement with DFT calculations. The average spin-resolved charges along a unit cell are shown in figures 2a,2c. Spin up (down) electrons pile at the top (bottom) edge of the ribbon and leave a charge deficit in the opposite side, also in agreement with DFT calculations. Therefore, the edges have local magnetization with opposite sign. For a given spin, there is an excess of electrons in one edge that are missing in the other. The total electronic charge turns out to be the same in all the atoms.

[FIG. 1: (Color online). (a) Zigzag ribbon unit cell. (b) Band structure of N = 18 zig-zag ribbon with U = 0 (c) and U = 2eV. Only half of the Brillouin zone is shown. (d) Comparison of low energy bands. Interacting bands have been shifted downwards by U/2. (e) U = 0 single particle gap at the edge states.]

It is crucial to realize that the non-interacting and the shifted mean field bands are identical except for the lowest energy empty band and the highest energy occupied band which differ in the outer sector of the Brillouin zone, shown in figure 1c. These bands are denoted by – and + and \( v \) and \( c \) for the interacting and the non-interacting case. It turns out that both – and + can be expressed as linear combinations of \( c \) and \( v \) only, with an accuracy better than 99%. Thus it is possible to relate the two interacting states – and + with the non-interacting conduction and valence band through

\[
\begin{pmatrix}
    f^{\dagger}_{-k\sigma} \\
    f^{\dagger}_{+k\sigma}
\end{pmatrix} =
\begin{pmatrix}
    u_k & v_k e^{i\phi_k} \\
    -v_k e^{-i\phi_k} & u_k
\end{pmatrix}
\begin{pmatrix}
    V_{k\sigma} \\
    C_{k\sigma}
\end{pmatrix}
\tag{3}
\]

Importantly, the spin dependence is limited to the phases. The moduli of the coefficients \( |u_k|^2 \) and \( |v_k|^2 \), are shown in figure 2b. We find that \( v_k^2 + u_k^2 > 0.99 \). Using this relation we formulate the interacting theory in terms of electrons and holes in the non-interacting valence and conduction band. The mean field ground state, which is formed by filling all the mean-field bands below the gap, is written as \( |\Phi\rangle = |\Phi\rangle_1 \times |\Phi\rangle_2 \) where:

\[ |\Phi\rangle_\sigma = \prod_{k} f_{-k\sigma}^{\dagger} |G\rangle_\sigma \]

where \( |G\rangle_0 \) is the non-interacting ground state with no holes in the valence band and no electrons in the conduction band. Equation (4) is one of the important results of this work: the mean field ground state implicit in eq. (1) that yields the bands of fig 1c and the density profile of fig. 2c and 2d can be written as the product of two BCS condensates of spin polarized electron-hole pairs. This wave function is found in the context of excitonic insulators and non-equilibrium exciton condensates.

Importantly, this BCS state implies the existence of non-magnetic long-range order for the interband operators. The numerical calculations systematically show that the interband coherence

\[ \langle \Phi | e_{k\uparrow}^{\dagger} h_{k\downarrow}^{\dagger} | \Phi \rangle = v_k^* u_k e^{-i\phi} = -\langle \Phi | e_{k\downarrow}^{\dagger} h_{k\uparrow}^{\dagger} | \Phi \rangle \tag{5} \]
are finite and their relative phase is locked: \((\phi_1 - \phi_1) = \pi\). Interband coherence is zero for \(U = 0\) and is related to observables that mix the valence and conduction band. These acquire an anomalous expectation value in the \(U > 0\) phase. The interband coherence is associated to electric polarization\(^{25}\) in non-equilibrium exciton condensates and to electronic ferroelectricity in the case of Bose-condensation of slave bosons in the case of mixed-valence compounds.\(^{26}\) Hence, I look for the connection between the interband coherence implicit in eq. (4) and the spin-resolved electric dipole implicit in figs. 2a,2c. The electric dipole is written as the sum of the spin-resolved dipole \(P_y = P_{y1} + P_{y1}\) where

\[
P_{y\sigma} = \sum_{k,\nu,\nu'} y_1 e n_{x,\sigma} + \sum_{k,\nu,\nu'} \frac{d_{\nu,\nu'}(k)}{e} \psi_{\nu,\nu'}(I) \psi_{\nu,\nu'}(I) \tag{6}
\]

are the spin-resolved components of the dipole operator, and the dipole matrix elements are given by

\[
d_{\nu,\nu'}(k) = \sum_{\nu} e y_1 \psi_{\nu,\nu'}(I) \psi_{\nu,\nu'}(I) \tag{7}
\]

The labels \(\nu, \nu'\) run over the non-interacting bands. The ribbon is centered at \(y = 0\). Because of the mirror symmetry of the zigzag unit cell, \(d_{\nu,\nu'}(k) = 0\), so that only the band-mixing terms on eq. (7) can yield a contribution. The average dipole operator in the state \(|1\rangle\) is:

\[
\langle P_y \rangle = \frac{1}{L} \sum_{k,\sigma} d_{C\nu}(k) v_{k}^* e^{-i\phi_\sigma} + \text{h.c.} = \frac{1}{L} \sum_{k,\sigma} P_{y\sigma}(k) \tag{8}
\]

Whereas \(\langle P_y \rangle = 0\) the spin resolved components \(P_{y\sigma}(k)\), shown in fig. 2d are finite and with opposite sign. A zero net dipole resulting for the sum of two opposite spin-resolved dipoles is expected from inspection of figures 2a and 2c and the homogeneous spin-summed charge distribution. Thus, the spin resolved dipoles are related to the interband coherence and the absence of net electric dipole is related their phase locking in eq. (4). In order to characterize this new kind of electronic order, I introduce the spin dipole operator:

\[
P_{\sigma,\sigma'}(y, z) = e \sum_{I} y_1 n_{I\sigma} S_{\sigma,\sigma'}^z = \begin{pmatrix} P_{y1} & 0 \\ 0 & -P_{y1} \end{pmatrix} \tag{9}
\]

where \(S_{\sigma,\sigma'}^z\) is the Pauli matrix. Thus, the relevant order parameter associated to the electronic state \(|1\rangle\) is \(\text{Tr}_\sigma \langle \Phi | P(y, z) | \Phi \rangle\). Spin rotational invariance permits to choose \(z\) along any direction in the spin space. This order parameter is invariant under the combined action of time reversal and mirror symmetry, and provides a natural explanation to the spin-polarization of the system when subject to a transverse electric field, predicted by DFT calculations. Notice that this phase is different from the non-magnetic ferroelectric phase predicted in\(^{6}\), which is not found in DFT.

The mean field state \(|1\rangle\) invites to write the interacting bands in terms of a BCS-like gap related to interband coherence. To do that, I project out all the bands except \(C\) and \(V\):

\[
\epsilon_{xI,\sigma}^\dagger \approx \frac{1}{\sqrt{L}} \sum_{k} e^{-ikx} \left( \psi_{kC}(I) C_{k\sigma}^\dagger + \psi_{kV}(I) V_{k\sigma}^\dagger \right) \tag{10}
\]

The occupation of the sites is expressed as \(n_{I\sigma} = \frac{1}{2} + \sigma m_I\), where \(\sigma = \pm\). This automatically ensures that the occupation in each site is 1. Using transformation eq. (10), the mean field Hamiltonian reads:

\[
\mathcal{H} = \sum_{k,\sigma} \left( C_{k\sigma}^\dagger V_{k\sigma} \right) \left( \xi_{\sigma\sigma}(k) \Delta_{\sigma}(k) \right) \left( C_{k\sigma} V_{k\sigma} \right) \tag{11}
\]

with

\[
\xi_{\sigma\sigma}(k) = \epsilon_{\sigma}(k) + \frac{U}{2} + U \sigma \sum_{l} \psi_{l\sigma}(I) \psi_{l\sigma}(I) \langle m_l \rangle \tag{12}
\]

where \(\epsilon_{\sigma}(k)\) are the \(U = 0\) bands and \(\nu = c, v\). The second term in (12) is the rigid shift of the bands \(U \sigma\) and the third term is the diagonal self energy \(\Sigma_{\nu,\nu}\). The off-diagonal self-energy reads:

\[
\Delta_{\sigma}(k) = \pi U \sum_{l} \psi_{l\sigma}(I) \psi_{l\sigma}(I) \langle m_l \rangle \tag{13}
\]

Notice that \(\Delta_{\sigma}(k) = -\Delta_{\sigma}(k)\), which explains the phase locking of eq. (4). Notice also that in the Hubbard model the self energies for spin \(\sigma\) electrons depend on the density of carriers with opposite spin \(\overline{\sigma}\). For each \(k\sigma\) the mean field two by two matrix can be written as \(\overline{\mathcal{H}} + \overline{\Delta}(k)\overline{\sigma}\) where \(\overline{\sigma}\) are the Pauli matrices, and the effective field can be written as:

\[
\overline{\Delta}_{\sigma}(k) = \left( \text{Re}(\Delta_{\sigma}(k)), \text{Im}(\Delta_{\sigma}(k)) \right) \tag{14}
\]

The eigenvalues of this two by two matrix are

\[
E_{\pm,\sigma}(k) = \frac{1}{2} \left( U \pm \sqrt{\xi_{\sigma,\sigma}(k)\xi_{\sigma,\sigma}(k) + 4|\Delta_{\sigma}(k)|^2} \right) \tag{15}
\]

The transformation \(\Phi\) permits to diagonalize (11), obtaining \(\mathcal{H} = \sum_{k,\sigma,\tau = \pm} E_{\tau,\sigma}(k) f_{k\sigma}^\dagger f_{k\tau}\). At zero temperature only the lower branches \(E_{\tau,\sigma}(k)\) are occupied. The mean field dispersion \(E_{\tau,\sigma}(k)\) depends on \(\xi_{\sigma\sigma}(k)\) and on \(\Delta_{\sigma}(k)\) which in turn depend on the magnetization:

\[
m(I) = \sum_{k} \psi_{k\sigma}(I) \psi_{k\sigma}(I) u_k v_k^* + \text{h.c.} \tag{16}
\]

The magnetization depends on the transformation factors, \(u\) and \(v\), which depend on the energies through:

\[
|v_k|^2 = \frac{1}{2} \left( 1 - \frac{\overline{h}_{\sigma\sigma}(k)}{\overline{h}_{\sigma\sigma}(k)} \right) u_k v_k e^{i\phi_\sigma} = \frac{-\overline{h}_{\sigma\sigma}(k)}{|\overline{h}_{\sigma\sigma}(k)|} \tag{16}
\]

Equations (12),(13),(14),(15),(16) form a self-consistent set. The numerical solutions of the mean field Hubbard model
also satisfy these equations. This permits to relate the mean field dispersion to the diagonal self energy \( |\Sigma_{\nu,\sigma}(k)| \) and the off-diagonal self-energy \( |\Delta(k)| \), shown in fig. 3. They are spin independent. It is apparent that these self-energies are finite in different regions of the Brillouin zone. The diagonal self-energy is related to the non hybridized edge states located in the outer region of the Brillouin zone whereas the off-diagonal self-energy occurs for weakly hybridized edge states, at smaller \( |k| \).

Further reduction of \( |k| \) opens the single-particle gap, which overshades the self-energies. These results also permit to unveil the origin of the gaps \( \Delta^1 \) and \( \Delta^0 \) introduced in \( \Sigma \) (see fig. 3). It is apparent that the \( \Delta^1 \) gap is given by the diagonal self-energy whereas the \( \Delta^0 \) gap is related to the non-diagonal self-energy. Accordingly, \( \Delta^1 \) is insensitive to the ribbon width and can be approximated by \( \Delta^1 \approx 2U|m| \) where \( |m| \) is the magnetization of the edge atoms. In contrast, \( \Delta^0 \) decreases as the ribbon width increases due to the smaller inter-edge hybridization.

The long range order implicit in this and previous mean field theories of graphene zigzag ribbons is known to be destroyed in one dimension because of long-wavelength spin wave modes associated to the breaking of a continuous symmetry. I have verified that the results of this work remain valid for finite length graphene ribbons and tubes for which Goldstone modes have a confinement gap. Therefore, the results of infinite ribbon systems are relevant for finite systems.

In summary, the BCS wave function describing two phase-locked Fermi-liquid electron hole pairs is the the collective wave function behind the insulating ferrimagnetic phase in graphene zigzag ribbons portrayed by mean field Hubbard, model, which yields the same results than DFT calculations. The underlying electron-hole coherence in each spin-channel is related to mirror symmetry breaking of the charge density for a given spin. Their relative phase-locking warrants that the total spin and electric dipole are zero. The natural order parameter for this electronic state with magnetic and spin-hidden electric order is the spin-dipole operator (eq. \( \langle \mathbf{d} \rangle \)). The reformulation of the mean field theory in terms of a 2-band BCS model rationalizes the shape of the mean field bands in terms of diagonal and non-diagonal self-energies. The joint presence of electric and magnetic order anticipates non-trivial magneto-electric effects in graphene zigzag ribbons.

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