Bias induced ferromagnetism and half-metallicity in graphene nano-ribbons

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Towards spin selective electronics made of three coordinated carbon atoms, here we computationally propose robust and reversibly bias driven evolution of pristine undoped graphene nano-ribbons (GNR) into ferromagnetic-semiconductor, metal or a half metal, irrespective of their edge configurations. The evolution is a result of a rare ferromagnetic (FM) order emerging among nearest neighbouring (n-n) sites, in positively biased regions in their in-homogeneous bias unit-cells, in attempt to cooperatively minimise on-site Coulomb repulsion and kinetic energy, while maximising localization of electrons at the positively biased sites. The phenomenon appears to be a general property of in-homogeneously biased Coulomb correlated bipartite systems. Consequences are particularly rich in zigzag edged graphene nano-ribbons (ZGNR) due to the contest of bias driven n-n FM order and the inter-edge antiferromagnetic order inherent to ZGNRs, leading to systematic closing of gap for one of the spins, amounting to bias controlled unmissable opening of window for FM-semiconducting and half-metallic transport.

Sheets, ribbons and tubes made of three coordinated sp² hybridized carbon (C) atoms can be semiconducting or metallic, depending on their shape, size and edge configuration. They have been thus long anticipated to constitute a framework for carbon-based electronic circuitry at nano-scale. 2pz electrons of these carbon atoms, if rendered unpaired due to lack of coordination, like at defects or edges, are source of local magnetic moments, and ferrimagnetism in their vicinity. Tuning magnetism of these electrons to add spin-selectivity to carbon based circuit elements, has been an active area of research in the last two decades or so. A large variety of proposals and demonstrations made in this direction based on structural, physical, and chemical functionalization, have promised the possibility of magnetic semiconductors and half-metal primarily in zigzag edged graphene segments, ribbons and tubes. Realization of such proposals into commercially viable devices is challenged by the stringent requirement of precise control over their shape, size, and edge configurations.

In undoped bipartite systems magnetism is known to arise either at strong coupling, where the strength of Coulomb correlation (U) is much higher than kinetic energy, leading to n-n anti-ferromagnetic (AFM) order, or at moderate coupling due to in-equivalence of the two sub-structures, leading to n-n ferrimagnetic (FeM) order. The latter leads to non-zero magnetic moment if the two sub-structures are globally in-equivalent. Majority of proposals referred above are in this category, where the in-equivalence can be due to a host of reasons, like, vacancy defects, substitutional doping, adsorption at sites, application of transverse electric field. On the other hand, nearest neighbour ferro-magnetic (FM) ordering, which we will refer as FM_{n-n}, is rare in bipartite systems and proposed only upon doping by hole or electrons. Description of magnetism sourced at Coulomb correlation among itinerant electrons, as derived within the framework of Hubbard model suggests primarily two classes of mechanisms to rationalize FM_{n-n} ordering in bipartite systems upon deviation from half-filling. With U → ∞, it was shown by Nagaoka that upon doping by a single hole the ground state will have FM ordering in attempt to reduce the kinetic energy of the hole, while avoiding occupancy of a site by more than one electron. However, Nagaoka-FM has been argued to be not relevant to three coordinated systems, since the loops connecting the n-n sites should not pass through more than four sites for Nagaoka-FM to sustain. In the other class of mechanisms, FM ordering is proposed to be exchange driven, but require a flat or nearly flat band, at Fermi energy to accommodate electrons emptied from the doubly occupied states without causing any or much any increase in kinetic energy. Itinerant electrons have been also argued to propagate exchange

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interaction between local moments due to flat bands. An approximate meeting ground of the two pathways lead to the Stoner criteria, which argues that a high $U$ and non-zero density of states (DOS) at Fermi energy is necessary for the unequal number of electrons with the two spins to be energetically favorable. Flat-band based mechanisms, or more generally the Stoner Criteria, for $FM_{n-n}$ is thus supported only by the doped armchair edged graphene nano-ribbons (AGNR) on account of the flat or nearly flat bands which are located below and above the valence and conduction band edges and represent $pi$-bonds parallel to the ribbon edges. In zigzag edged graphene nano-ribbons (ZGNR), $FM_{n-n}$ has been proposed to be possible with topological line defects owing to their non-bipartite nature.

Based on mean-field and ab-initio computation of spin resolved electronic structure, in this work we suggest an alternate approach to manipulate magnetism in graphene nano-ribbons (GNR), wherein, any GNR irrespective to their non-bipartite nature.

Results and Discussion

We calculate spin polarized electronic structure of non-uniformly biased AGNR and ZGNR unit-cells shown in Fig. 1, first using the mean-field approximation of Hubbard model as a function of bias potential $V_g$ and $U$, and then compare with density functional theory (DFT) based first principles calculation.

To probe the nature of magnetic ordering we calculate the average $n-n$ spin correlation as:

$$S = \frac{1}{N_f} \sum_{i,j} \frac{1}{n_i n_j} \sum_{\sigma} \hat{S}_i \sigma \hat{S}_j \sigma$$

where $N_f$ is the number of sites per unit-cell, $n_i$ the number of $n-n$ sites around the $i$-th site, and $\hat{S}_i \sigma \equiv \langle n_i, \sigma \rangle - \langle n_i \rangle$, with $\langle n_i, \sigma \rangle$ being the population of electron with spin-$\sigma$ at the $i$-th site due to the occupied states calculated using the mean-field approximation of Hubbard model. Positive and negative values of $S$ plotted in Fig. 1 imply existence of FM and AFM or FeM ordering respectively. Existence of both thus imply spatial separation between FM and FeM ordering.

Negative spin correlation. For AGNRs, Fig. 1(a–f) imply rapid consolidation of AFM (FeM) ordering above $U-2|t|$ with zero (positive) $V$. For $V = 0$ this is reminiscent of Mott transition at half-filling ($n = 1$) in bipartite lattices. The trend that with increasing $V$ the transition from non-magnetic to the FeM ground state happens with increasing $U$, is similar to that observed in case of non-magnetic to AFM transition in bipartite lattices with increasing deviation from half-filling, and is understood in terms of the additional correlation required to dominate over the kinetic energy of the excess charges. The similarity in trend is expected since with non-zero $V$, the biased and unbiased regions both deviate locally from half-filling. With $U > 0$ at $\nu = 0$, ZGNRs expectedly...
show n-n FeM ordering and AFM ordering globally between the two substructures. With increasing $V_g$, quenching of magnetic ordering in ZGNRs below an increasing threshold of $U$ can be understood as the dominance of positive bias over on-site Coulomb correlation, leading to occupation of biased sites by electrons with both the spins.

Positive spin correlation. Emergence of FM$_{n-n}$ ordering is marked by the positive spin correlation [Fig. 1] and the associated lifting of spin degeneracy of the band-structures [Fig. 2] over a range of $V_b$ with $U$ moderate and higher. FM ordering quenches rapidly in AGNRs [Fig. 1(a–f)] as the biased region moves away from the edges or are widened. Similarly in ZGNRs, positive spin correlation is much prominent if the biased region cover zigzag chains of carbon atoms parallel to the edges. Notably, an FM phase of generalized Nagaoka type is known to occur in the mean-field phase diagram of cubic bipartite lattice$^{31}$ at deviation from half-filling. Although Nagaoka may not be feasible$^{31}$ in three coordinated bipartite lattices, it is beyond the scope of this work to comment on whether it will be effective on the background of increased correlation due to confinement. However, the trend that the onset of the FM$_{n-n}$ order is more prominent if the biased region is narrow and located closer to the ribbon edges, clearly suggest that localization of electrons, and consequently the enhanced Coulomb correlation, are likely the key associated factors leading to FM$_{n-n}$. Notably, in case of ZGNRs, if the biased sites cover zigzag(transverse) C-C bonds then the spin at those FM$_{n-n}$ ordered sites would prefer to be FM(AFM) ordered with sites at both the edges, mediated by the inherent n-n FeM order prevalent outside the biased region. Thus in case of biased zigzag sites, mixing of FM$_{n-n}$ ordered state with the dominant spin, and the nearest localized edge state, can stabilize both, leading to relative ease in occurrence of FM$_{n-n}$ order compared to that in case of biased transverse sites. This is consistent with less positive spin-correlation [Fig. 1(j–l)] in case of biased C-C transverse bonds.

Band-structure. FM$_{n-n}$ order at the positively biased sites inherently implies lifting of spin-degeneracy since it consolidates one of the spins in the biased region. Emergence of the FM-semiconducting, FM-metallic and half-metallic phases are thus naturally expected as consequences of FM$_{n-n}$ order if the biased region covers C-C zigzag(transverse) bonds. As shown schematically in Fig. 3, the contest supports the edge-states with spin-1 at edge-1, but suppresses the edge-state with spin-2 at edge-2. The consequent systematic closure of gap [Fig. 2(f,g)] exclusively for spin-2, [Fig. 3] can be understood as a result of effective increase in on-site energy for electrons with spin-2 at edge-2 due to accumulation of electrons with spin-1 at that edge on account of FM$_{n-n}$ ordering. Expeditious to recall, equal probability of finding an electron at both the edges, implying same effective on-site term at both the edges, leads to closure of band-gap, as happens for both the spins in the absence of Coulomb correlation. Indeed, the reduction in n-n FeM order near edge-2 due to the competing magnetic orders, implies reduction of the effective Coulomb correlation near edge-2 where
to those considered in Fig. 1, has similar trend as [Fig. 2(f)], marked by lifting of spin-degeneracy and reduction in band-gap for one of the spins [Fig. 4] within a range of ramp potential. This qualitative agreement between correlation. Furthermore, the reported agreement of DMRG, QMC and ED results[42,47], with DFT in rationalizing mean-field and DFT results is an important validation of the former, which only incorporates on-site Coulomb beyond nearest neighbours in a ferrimagnetic ground state. Furthermore, the robust emergence of the FM\(_n\) for which the FM\(_n\) states appear to indicate that the ribbons should maintain their structure intact in the range of ramp potential \(U\) and low \(V_g\) and is thereby qualitatively different from previous proposals of bias induced opening of half-metallic window reported so far.

**From first principles.** Band-structure calculated from first principles using density functional theory (DFT) with sawtooth potential\(^{48}\) applied in the transverse direction [Fig. 4(a)] of ZGNR to resemble biased region akin to AGNRs. Nevertheless, with biased region covering C-C zigzag bonds [Fig. 2(f)], the inter-edge AFM ordering clearly evolves into inter-edge FM ordering, leading to evolution of the valence band edge for spin-2 into a partially occupied dispersive band, which offers a robust window for half-metallic transport. This reiterating that bias coverage of zigzag C atoms is more effective than that of biased transverse C atoms in emergence of FM\(_{n-\sigma}\) order. However, the systematic reduction of band-gap for one of the spins, as argued above, happens in ZGNRs irrespective of whether the biased region covers C-C zigzag or transverse bonds, paving the way for robust bias controlled FM-semiconducting and half-metallic transport. Thus the same is offered by more realistic wider biased regions as well, at moderate \(U\) and low \(V_g\), which might be technologically relevant.

Notably, the emergence of the half-metallic window in this case is rooted at the emergence of the FM\(_{n-\sigma}\) order, and is thereby qualitatively different from previous proposals of bias induced opening of half-metallic window in ZGNRs where the sub-lattice asymmetry due to transverse electric field\(^{13}\) or defects\(^{24,25}\), lead to FM ordering beyond nearest neighbours in a ferrimagnetic ground state. Furthermore, the robust emergence of the FM\(_{n-\sigma}\) order in the positively biased regions of the unit-cell, irrespective of location of the biased region with respect to the edges, and configuration of the ribbon edges, namely, zigzag or armchair or mix of both, clearly imply no explicit pre-requisition of flat or nearly flat bands at Fermi energy for the observed FM\(_{n-\sigma}\) order to emerge. Thus the spatially non-uniform bias induced FM\(_{n-\sigma}\) order proposed in this work is fundamentally different than the bias induced FM order\(^{42}\) and half-metallic transport\(^{13,25}\), reported so far.

**Minimal model & mechanism.** To check the generality of our results beyond the three coordinated networks we resort to a minimal unit-cell, which can exhibit the FM\(_{n-\sigma}\) order if it exists. We choose a unit-cell of four consecutive sites, of which two neighboring sites are biased [inset, Fig. 5(b)]. Spin-correlation between the two biased sites [inset, Fig. 6] as a function of \(V_g\) and \(U\) has similar generic features as in Fig. 1, thus hinting at the generality of the n-n FM order as a property of non-uniformly biased bipartite systems. Notably, if we do not consider non-zero crystal momentum, then the positive spin-correlation does not exist, although the trend of spin-correlation as a function of \(V_g\) and \(U\) obtained using the mean-field Hubbard model, agrees qualitatively with that obtained using exact-diagonalization(ED). Itinerant electrons described by dispersive bands at Fermi energy are thus likely to play important role in manifestation of FM\(_{n-\sigma}\) order, as suggested by Fig. 2.
Figure 4. ZGNR in presence of sawtooth potential: (a) potential profile; (b) band structure (above) & spin density (below). DFT results are qualitatively similar to their counterparts [Fig. 2] based on mean-field Hubbard model. Bands marked by the green dots are exclusively due to space charge.

Figure 5. Density (up, down) and band structure of 4-site linear chain from mean-field Hubbard for $U = 15.0 \cdot V_g = 10.0 \text{ eV (a,b)}; V_g = 15.0 \text{ eV (c,d)}; V_g = 20.0 \text{ eV (e,f)}$. The evolution of band structure is qualitatively similar to those in Fig. 2, implying generality of the FM order.
The evolution of spin polarized charge densities [Fig. 5(a,c,e)] with increasing $V_g$ suggests spin-separation between biased and unbiased region similar to that observed in ribbons. Such a spin-separation can possibly be rationalized by noting that increased occupancy of the biased sites by electrons with both the spins, upon increased $V_g$, would in turn increase potential energy due to on-site Coulomb repulsion. Thus to keep potential

Figure 6. Biased site spin-correlation plot (inset) and different energy contributions for $U = 15.0$ from: mean-field Hubbard model(a–d) & analytic WF based calculation(e–h). The light red and blue backgrounds used in (a) to (h) represent FeM and FM ordering respectively between the biased sites. The qualitative similarity of the energetics responsible for emergence of the FM$_{n-n}$ order, imply that the mean-field results are valid beyond the mean-field approximation.
energy low, each of the biased sites will prefer to be dominated by electrons with one of the two spins. However if two such neighboring sites have opposite spins, as would be in a FeM ground state, then the wave-functions for both the spins will have rapid variation from site to site, leading to high kinetic energy. Instead, if wave-functions of one type of spin spans the biased sites more than those with the other spin, as evident from the charge densities [Fig. 5(a,c,e)], then the wave-functions can be smoother than their FeM counterparts, implying lesser kinetic energy while allowing lower on-site Coulomb repulsion as well. The evolution of charge densities [Fig. 5(a,c,e)] clearly implies electrons to be more itinerant for one spin than for the other upon emergence of FeM, leading to lifting of spin degeneracy [Fig. 5(c,d)] akin to that in [Fig. 2(a,c)]. Upon further increase of \( V^g \) [Fig. 6(b–d)] the lowering of potential energy due to \( V^g \) dominates over the increase of potential energy due to on-site Coulomb repulsion, leading to occupancy of bias sites by both spins, resulting into return of non-magnetic ground state and spin degenerate band-structure [Fig. 5(e,f)]. Thus with higher \( U \) a higher \( V^g \) is required for the FeM\(_{\text{non}}\) order to quench, which is also consistent with the trend observed in Fig. 1.

To quantitatively justify the mechanism anticipated above, we partition the total energy [Fig. 6(a)] of the unconstrained(UC) ground state into kinetic energy and potential energies due to on-site Coulomb repulsion and applied bias, and compare those with their counterparts in a non-magnetic(NM) and FeM ground states. NM ground state is obtained by assigning same charge density for both the spins. For the FeM ground state, charge density for one of the spins is assigned to be the mirror image of that for the other spin about the centre of the unit-cell. We choose the energetics of the NM ground state to be the reference. Figure 6(c,d) suggests that the UC ground state with FeM\(_{\text{non}}\) order has lower kinetic energy than NM and FeM ground states, owing initially to lowering of potential energy due to gate bias, but subsequently and primarily due to lowering of on-site Coulomb repulsion facilitated by separation of spin between positively biased and unbiased sites. Notably, although the FeM ground state has a lower kinetic energy than the UC ground state, the degree of localization at the positively biased site offered by the former is much lower than that due to the latter. Thus an FeM ordered state with the same degree of localization as offered by the UC ground state must have higher kinetic energy than the latter. Thus the observed FeM\(_{\text{non}}\) order is a result of attempts to minimize on-site Coulomb repulsion and kinetic energy in conjunction with each other, while maximizing localization of electrons at the positively biases sites.

In addition to agreement with DFT results, to demonstrate further that the observed FeM\(_{\text{non}}\) order is not limited by the mean-field approximation, we resort to simple analytical models for Wannier functions(WF), to represent the ground state of the four site unit-cell at half-filling. WFs are linear combination of wave-functions and can be chosen to be real and localized largely within a unit-cell in one dimension. Thus in place of 2\( N \) wave-functions for each spin, \( N \) being the number of allowed wave-vectors in the first Brillouin zone, we can choose two WFs for each spin to represent four electrons. We approximate WFs to be non-zero only within a unit-cell. Such approximate WFs describing the non-magnetic(NM) ground state can be of the following general form:

\[
\phi_{1,1}^{\text{NM}} = (a,b,c,d),
\]
\[
\phi_{2,1}^{\text{NM}} = \left[ e + \frac{c f}{a} g + \frac{df}{b}, -f - \frac{ae}{c}, -f - \frac{gb}{d} \right],
\]

which are constrained to be orthogonal to each other. Similarly, two orthogonal WFs to describe the FeM ground state can be approximated as:

\[
\phi_{1,1}^{\text{FeM}} = (a,b,c,d),
\]
\[
\phi_{2,1}^{\text{FeM}} = \left[ e + \frac{c f}{a} g + \frac{df}{b}, -f - \frac{ae}{c}, -f - \frac{gb}{d} \right],
\]
\[
\phi_{6,1}^{\text{FeM}} = (d,c,b,a),
\]
\[
\phi_{6,2}^{\text{FeM}} = \left[ f + \frac{gb}{d} e + \frac{ae}{c}, -g - \frac{df}{b}, -e - \frac{cf}{a} \right],
\]

where the \( |\phi_{2,1}^{\text{NM}}| \) is mirror image of \( |\phi_{1,1}^{\text{NM}}| \) with respect to the middle of the unit-cell. Finally, orthogonal WFs with FeM\(_{\text{non}}\) order can be approximated as:

\[
\phi_{1,1}^{\text{FeM}} = (a,b,c,d),
\]
\[
\phi_{2,1}^{\text{FeM}} = (c,d,-d,-c),
\]
\[
\phi_{1,1}^{\text{FeM}} = (e,f,f,e),
\]
\[
\phi_{2,1}^{\text{FeM}} = g, h, -h, -g.
\]

The number of independent variables chosen to express the WFs are determined by the symmetry of the spin densities [Fig. 5(a,c,e)] and orthogonality of the states. Total energies of ground states are calculated in the basis of the approximate WFs within the Hubbard model without mean-field approximation. For each class of WFs, ground state is obtained by finding the global minima of total energy using the cylindrical algebraic decomposition algorithm\(^{49}\). Kinetic energy and potential energies due to Coulomb repulsion and external bias are estimated using the WFs corresponding to the ground states. Notably, Fig. 6(e–h) implies emergence of FeM\(_{\text{non}}\) order in exactly the same pathway as suggested within the mean-field approximation of Hubbard model [Fig. 6(a–d)]. These agreements indeed confirms the induced FeM\(_{\text{non}}\) order to be a genuine attribute of in-homogeneously
biased bipartite systems and should be observed beyond mean-field computation, as also suggested by DFT. Thus the FM$_{n-n}$ order proposed in this work indeed appears to be a general property of non-uniformly biased bipartite systems. Although it remains to be specifically tested, available studies suggest that similar emergence of FM$_{n-n}$ order may be even easier in non-bipartite systems.

Conclusion
To summarize, in this work we computationally propose the possibility of bias driven nearest neighbour (n-n) ferromagnetic (FM) order and half-metallic transport as a result of interplay of localization and Coulomb correlation. Results suggest emergence of n-n FM order in positively biased regions of non-uniformly biased bipartite systems, as a generic outcome of efforts to minimize Coulomb repulsion with minimal loss of the itinerant nature of electrons, while maximizing localization of electrons in the positively biased sites. The n-n FM order is computationally demonstrated here to exist in graphene nano-ribbons irrespective of their edge configurations, as well as in a minimal model system, which emphasizes the generality of the observed localization induced n-n FM order at half filling. The associated lifting of spin-degeneracy leads to exotic metallic (normal, ferromagnetic and half-metallic) phases. In armchair edged semiconducting ribbons the metallic phases are presided by direct to indirect transition, while in zigzag edged graphene ribbons, their inherent inter-edge AFM order contests the bias driven FM$_{n-n}$ order, leading to systematic closer of gap for one of the spins resulting into robust window for FM semiconducting and half-metallic transport. These results are expected to encourage a conceptually new pathway for voltage controlled opening of windows for half-metallic transport in two dimensional systems in general. In view of recent advancements, in implementing gates at sub-micron length-scale, these results might encourage implementation of the proposed pathway for voltage controlled systematic opening of windows for half-metallic transport in ribbons and sheets of graphene and other two dimensional systems.

Method
To compute spin-polarized electronic structure in the realistic AGNR and ZGNR unit-cells, we resort to the mean-field approximation of Hubbard model within the n-n tight-binding framework:

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} + \frac{1}{2} \sum_{i, \sigma} c_{i,\sigma}^\dagger c_{i,\sigma} (U(n_{i,\sigma}) - V_i^f + V_i^s)$$

(2)

$\langle n_{i,\sigma} \rangle$ being the population of electron with spin-$\sigma$ at the i-th site due to the occupied states. Eqn. (2) implies a self-consistent computation of electronic structure as a function of the strength of on-site Coulomb repulsion ($U$)\textsuperscript{13,14}, between opposite spins, and the gate bias ($V_i^f$), given the lowering of energy due to hopping between n-n sites represented by $t = -2.7 eV$\textsuperscript{15–17}. Coulomb potential ($V$) due to electrons at nearest neighboring sites and beyond is calculated using the Ewald summation scheme\textsuperscript{18}. We compare our mean-field Hubbard model based results with their counterparts obtained from first principles using density functional theory (DFT). We use a plane-wave based implementation\textsuperscript{19} of DFT, wherein, we have used a gradient corrected functional\textsuperscript{59} of density to approximately estimate the exchange–correlation contribution to total energy.

Standard computational techniques have been used in this work to calculate electronic structure of systems detailed in the figures.

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**Author Contributions**
The corresponding author has planned the work and written the manuscript. The first author has performed all the calculations and analysis presented in the work.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

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