Evidence Of Electric-Field Induced Magnetic Phase Transition In Graphene Nano-Fragments

Tushima Basak
Department of Physics
Mithibai College
Vile Parle (W), Mumbai - 56, INDIA
Tushima.Basak@mithibai.ac.in

Tista Basak
Department of Basic Science and Humanities
Mukesh Patel School of Technology Management & Engineering, NMIMS University
Vile Parle (W), Mumbai - 56, INDIA
Tista.Basak@nmims.edu

Abstract—Employing the Pariser-Parr-Pople model Hamiltonian, we predict theoretically that the ferromagnetic ground state of graphene nano-fragments can undergo phase transition to a non-magnetic state on the application of an external electric field. Our results indicate that the energy gaps for up and down spins are degenerate in the absence of electric field. However, this degeneracy is lifted under the influence of an external electric field. This selective tuning of the different magnetic states as well as their energy gaps in graphene nano-fragments by an externally applied electric field can be efficiently exploited in designing nano-scale spin polarized field effect transistors.

Keywords—*graphene nano-fragments; electric field; phase transition.*

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I. INTRODUCTION

The successful isolation and fabrication of graphene nano-fragments (GNF) has triggered a plethora of investigations [1-6] in recent years due to its intriguing properties such as high carrier mobility, long spin diffusion length, long lifetime and intrinsic magnetism. This properties of graphene nano-fragments make them a potential candidate for nano-electronic devices. In addition, recent theoretical studies have elucidated that quantum confinement, edge nature, shape and application of an external electric field play an important role in manipulating the magnetic properties of graphene based nano-fragments. This opens up new frontiers for the practical application of graphene nano-fragments in fabricating novel spintronic devices.

Recent theoretical investigations have revealed that the spin-ordered edge states of zigzag edged graphene nano-fragments can undergo energy-level shifts under the influence of an external electric field, leading to a phase transition between the different magnetic phases. In addition, it has been predicted that the application of electric field to the anti-ferromagnetic (AFM) phase of graphene nano-fragments lifts the spin degeneracy resulting in a half-semiconducting behavior. However, it is observed that most of the literature reported, till date, focuses in analyzing magnetism in regular shaped graphene nano-fragments while very few studies exist on irregular shaped graphene nano-fragments. This has inspired us to explore the effect of electric field on the different magnetic states of GNF with minimum (C_{2v}) symmetry.

The organization of the rest of the paper is as follows. A brief overview of the theoretical methodology is presented in Sec. II which is followed by results and discussion in Sec. III. Finally, the conclusions are given in Sec. IV.

II. COMPUTATIONAL METHODOLOGY

The geometric configuration of the hydrogenated GNF consisting of 40 carbon atoms is given in Fig. 1. It will be denoted as GNF-40, in the remainder of the paper.

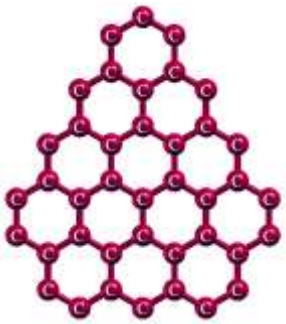


Fig. 1. Geometric configuration of GNF-40.

In our calculations, the bond-lengths and bond-angles between the carbon-carbon atoms have been fixed at 1.4 Å and 120°, respectively. The longer extent of the GNF is assumed to lie along the y axis while the shorter dimension is along the x-axis.

The calculations have been done by employing the effective π-electron Pariser-Parr-Pople (PPP) [7-8] model Hamiltonian

$$H = -\sum_{i,j,\sigma} [t_{ij} (c_{i\sigma}^{+} c_{j\sigma} + c_{j\sigma}^{+} c_{i\sigma})] + U \sum_{i} (n_{i\uparrow} n_{i\downarrow}) + \sum_{i<j} [V_{ij}(n_i-1)(n_j-1)] \quad (1)$$

where $c_{i\sigma}$ ($c_{i\sigma}^{+}$) denotes the creation (annihilation) operator acting on a π orbital localized on the i^{th} carbon atom of spin σ while the matrix elements t_{ij} represents the one-electron hops which has been restricted to nearest neighbours in our calculations. The value of hopping matrix elements have been fixed at 2.4 eV, consistent with our earlier studies on polymers [9], polycyclic aromatic hydrocarbons [10] and hydrogenated

graphene nano-fragments [11]. The term n_i represents the total number of electrons of the i^{th} carbon atom having spin σ. The parameters in the second and third terms of eqn. (1) depict the on-site and long-range Coulomb interactions, respectively. These Coulomb interactions have been parametrized according to the Ohno relationship

$$V_{ij} = U/\kappa_{i,j}\,(1+0.6117\,R_{i,j}^{2})^{1/2} \quad (2)$$

where $\kappa_{i,j}$ represents the dielectric constant for taking into account the screening effects of the system while $R_{i,j}$ denotes the distance (in Å) between the i^{th} and j^{th} carbon atoms. In this work, the computations have been done at the restricted Hartree-Fock (RHF) and the unrestricted Hartree-Fock (UHF) level for the non-magnetic and magnetic states, respectively using a code developed in our group. The values of the parameters adopted for our calculations are U = 8.0 eV and $\kappa_{i,j}$ = 2.

III. RESULTS ÀND DISCUSSION

A. *Energetic ordering and phase diagram of the different magnetic states of GNF-40*

The computed Hartree-Fock energy of the different magnetic states of GNF-40, in the absence of electric field, indicates that the ferromagnetic (FM) phase is the ground state which is followed by anti-ferromagnetic (AFM) state. The non-magnetic (NM) configuration constitutes the second excited state of the system.

Fig. 2 represents the magnetic phase diagram of GNF-40 as a function of an external electric field. It is observed that the FM configuration is the ground state, in the absence of electric field. Further, the FM ground state remains stable under the influence of an electric field along the x-direction (i.e., longitudinal electric field E_x).

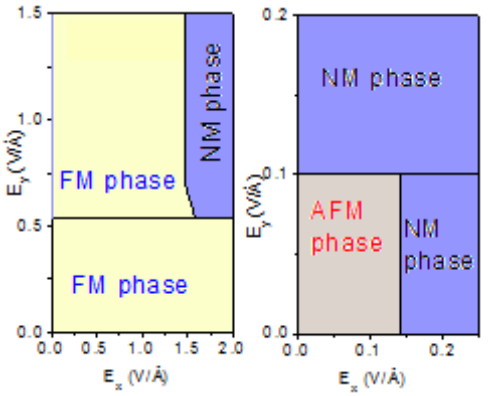


Fig. 2. Magnetic phase diagram of GNF-40 as a function of an external electric field.

However, the first excited AFM state undergoes a phase transition to the second excited NM phase when the magnitude of $E_x \geq 0.14$ (V/Å). Similarly, the AFM state is destroyed resulting in a NM phase when the magnitude of electric field along the y-direction (i.e., transverse electric field E_y) > 0.1 (V/Å). In addition, this phase transition is also observed under the simultaneous application of longitudinal and transverse electric field.

At high values of transverse electric field, a phase transition from ground (FM) to NM state occurs when the magnitude of $E_y \geq 0.54$ (V/Å). However, this NM phase is very unstable and transforms back to the FM phase at the instant E_x is also applied. Further, this NM state becomes energetically stable when the magnitude of the applied electric field $E_x \geq 1.57$ (V/Å) and $E_y \geq 0.54$ (V/Å).

Thus, a phase transition occurs initially from the first excited AFM state to the second excited NM phase at low values of electric field which is subsequently followed by a phase change from the FM ground state to the NM configuration. This implies that the magnitude as well as direction of applied electric field is responsible for manipulating the phase transitions exhibited by GNF-40.

B. *Spin density plots of the different magnetic states of GNF-40 as a function of electric field*

Fig. 3 (a-b) represents the spin density distribution for the AFM phase of GNF-40 in the absence and presence of an external transverse electric field (E_y = 0.06 V/ Å), respectively. The up(α)/down(β) spin orientation of the carbon atoms are depicted by (yellow/blue) spheres in the figure.

It is observed that in the absence of electric field (Fig. 3a) the spin density corresponding to the up spin direction of the carbon atoms is localized on the upper edge of GNF-40 while the carbons atoms with down spin orientation are concentrated on the lower edge. The local magnetism of the AFM phase with zero net spin is due to this spatial asymmetry of the spin distribution.

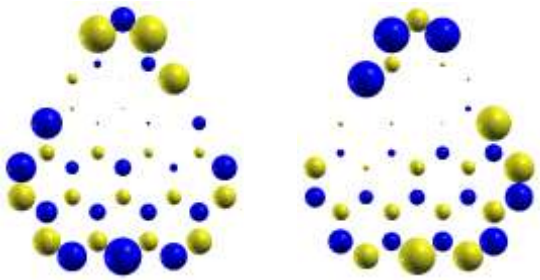
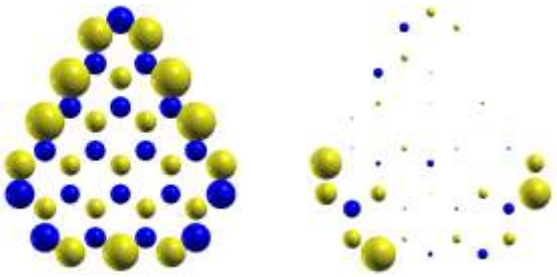


Fig. 3(a-b). Spin-density plots of the AFM phase of GNF-40 in the absence and presence of transverse external electric field, respectively. The yellow/blue spheres represent the up/down spin orientation of the carbon atoms.

When GNF-40 is exposed to a transverse electric field of magnitude E_y = 0.06 V/ Å, a transfer of spin distribution among the carbon atoms is observed. This eventually leads to a NM state with further increase in electric field.

Fig. 4 (a-b) represents the spin density plot for the FM phase of GNF-40 in the absence and presence of an external diagonal electric field (E_x = 1.4 V/ Å and E_y = 0.7 V/ Å), respectively. Fig. 4(a) indicates that the spin distribution is mostly concentrated on the zigzag edges and it rapidly reduces as we approach the centre of the graphene nano-fragment, in the absence of electric field. In addition, the number of carbon atoms having up spin is more than the down spin carbon atoms imparting FM character to the GNF.



(a) (b)

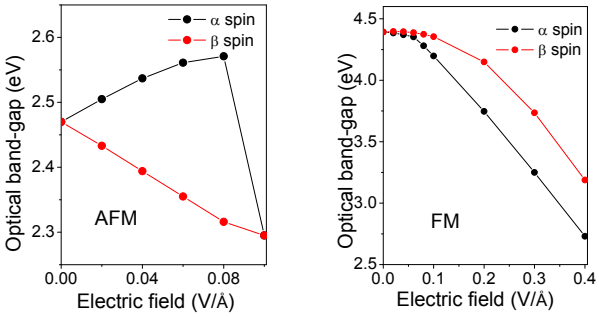
Fig. 4(a-b). Spin-density plots of the FM phase of GNF-40 in the absence and presence of external diagonal electric field, respectively.

However, with the application of an external diagonal electric field (Fig. 4b), the electrons of individual carbon atom rearrange their mutual spin to reduce the up/down spin orientations of each carbon atom. This eventually destroys the FM character of GNF-40 and gives rise to NM state.

This implies that the magnitude and direction of external electric field plays an important role in redefining the spin orientation of the carbon atoms, which aids in tuning the magnetic properties of GNF-40.

C. Variation of spin-polarized band gaps of the AFM and FM phases as a function of an external electric field.

Fig. 5 (a-b) depicts the dependence of spin-polarized optical band gaps of AFM and FM configurations of GNF-40 on an externally applied transverse electric field.



(a) (b)

Fig. 5(a-b). Plot of spin-polarized optical band gap of AFM and FM phases as a function of externally applied transverse electric field, respectively.

It is observed that the optical band gap of the up/down spin orientations of the carbon atoms is degenerate for both the AFM and FM states in the absence of electric field. However, this spin-degeneracy is lifted on application of electric field. In case of the AFM phase, the application of electric field results in an uniform decrease/increase of the optical band gap of spin down(β)/up(α) electrons. However, the optical band gap corresponding to spin down electrons never become zero due to quantum confinement of GNF-40 resulting in half-semiconducting behaviour. Eventually, the optical band gap of spin down/up electrons becomes degenerate with increase in the magnitude of applied external electric field.

The spatial concentration of the up/down spin distribution at the opposite edges of GNF-40 is primarily responsible for the splitting of the optical band gap in AFM state (Fig. 3a). However, a spin transfer occurs on application of electric field, resulting in a decrease in the splitting of the optical band gap. Finally the spin-polarized optical band gaps become degenerate at the instant the AFM state undergoes a phase transition to the NM phase.

In case of the FM phase, the spin-polarized optical band gap exhibits an electric field induced splitting, in agreement with the behaviour observed for the AFM state. However, the band gaps for both α and β spins decreases with increasing electric field. In addition, the rate of decrease of β spin is slower as compared to that of α spin under the influence of electric field. However, the spin-polarized band gaps never becomes degenerate even for extremely high values of electric field which is in contrast to the trends exhibited by the AFM phase. Further, this band gap splitting is observed under the application of in-plane transverse and diagonal electric fields, while it remains degenerate when the electric field is applied along the longitudinal direction.

The spatial concentration of the spin-density (Fig. 4a) of the same spin orientation is greater on one side of the GNF as compared to the other side which is responsible for the optical band gap splitting in the presence of electric field.

Thus, the spin-dependent band gaps of GNF-40 can be effectively tailored by external electric fields of different alignments and magnitude. This unique property can be successfully exploited for designing spintronic devices.

IV. CONCLUSION

In conclusion, we have demonstrated that GNF-40 is an intriguing system which exhibits well-defined magnetic states that can undergo phase transition by precise modulation of a suitably aligned external electric field. Our studies have elucidated the dependence of spin-polarized optical band gaps on the strength and direction of the electric field which opens up new possibilities for developing carbon based spintronic devices.

REFERENCES

[1] Y.-W. Son, M. L. Cohen, and S. G. Louie, "Half-metallic graphene nanoribbons", *Nature* (London), vol. 444, pp. 347-349, Nov. 2006.
[2] L. A. Agapito, N. Kioussis, and E. Kaxiras, " Electric-field control of magnetism in graphene quantum dots: *Ab initio* calculations", *Phys. Rev. B*, vol. 82, pp. 201411, Nov. 2010.
[3] H. Zheng and W. Duley, "Field effects on the electronic and spin properties of undoped and doped graphene nanodots", *Phys. Rev. B*, vol. 78, pp. 155118, Oct. 2008.
[4] S. Bhowmick and V. B. Shenoy, "Edge state magnetism of single layer graphene nanostructures", *J. Chem. Phys.*, vol. 128, pp. 244717, June 2008.
[5] A. Zhou,W. Sheng, and S. J. Xu, "Electric field driven magnetic phase transition in graphene nanoflakes", *Appl. Phys. Lett.* vol. 103, pp. 133103, Sept. 2013.
[6] W.-L. Ma and S.-S. Li, "Electric-field-induced spin depolarization in graphene quantum dots", *Phys. Rev. B*, vol. 86, pp. 045449, July 2012.
[7] J. A. Pople, " Electron Interaction In Unsaturated Hydrocarbons", *Trans. Faraday Soc.*, vol. 49, pp. 1375-1385, July 1953.
[8] R. Pariser and R. G. Parr, "A SemiEmpirical Theory of the Electronic Spectra and Electronic Structure of Complex Unsaturated Molecules. II", *J. Chem. Phys.*, vol. 21, pp. 767-776, May 1953.
[9] P. Sony and A. Shukla, " Photoinduced absorption in disubstituted polyacetylenes: Comparison of theory with experiments", *Phys. Rev. B*, vol. 71, pp. 165204, Apr. 2005.
[10] K. Aryanpour, A. Shukla, and S. Mazumdar, "Electron correlations and two-photon states in polycyclic aromatic hydrocarbon molecules: A peculiar role of geometry", *J. Chem. Phys.*, vol. 140, pp. 104301, Mar. 2014.
[11] T. Basak, H. Chakraborty, and A. Shukla, "Theory of linear optical absorption in diamond-shaped graphene quantum dots", *Phys. Rev. B*, vol. 92, pp. 205404, Nov. 2015.