Strain-tuning of vacancy-induced magnetism in graphene nanoribbons

Daniel Midtvedt and Alexander Croy

Max-Planck-Institut für Physik komplexer Systeme, 01187 Dresden, Germany

E-mail: croy@pks.mpg.de

Received 9 November 2015, revised 8 December 2015
Accepted for publication 9 December 2015
Published 8 January 2016

Abstract

Vacancies in graphene lead to the appearance of localized electronic states with non-vanishing spin moments. Using a mean-field Hubbard model and an effective double-quantum dot description we investigate the influence of strain on localization and magnetic properties of the vacancy-induced states in semiconducting armchair nanoribbons. We find that the exchange splitting of a single vacancy and the singlet-triplet splitting for two vacancies can be widely tuned by applying uniaxial strain, which is crucial for spintronic applications.

Keywords: graphene, magnetism, strain engineering

(Some figures may appear in colour only in the online journal)

1. Introduction

Spintronics is an interesting prospective technology where spin is used as the information carrier (in contrast to electronic charge in the case of electronics) [1, 2]. Graphene has been proposed as a promising material for realizing this technology [3]. A small spin–orbit coupling facilitates long spin decoherence times and makes information processing based on spin feasible [4, 5]. Magnetic order can can arise in graphene nanoflakes [6–9] and in connection with localized edge states in zig–zag nanoribbons [10]. Further, point defects in graphene, such as vacancies or chemisorpted hydrogen, have been proposed for realizations of spintronic devices [11, 12], since those defects support (quasi) localized electronic states and can induce magnetism [13–16]. In practice, such defects can be created by using electron or ion beams [12, 17].

The magnetic order associated with the magnetic moments depends on the spatial configuration of the defects [15, 18]. For gapped graphene structures, such as nanoflakes [9] or armchair graphene nanoribbons (AGNRs) [15], the defect states are exponentially localized and well separated from the rest of the energy spectrum. Each defect can therefore be considered as a quantum dot (QD).

Two such localized non-degenerate defect states can be thought of as a basic unit of spin-based information processing. In [9], it was shown that a system of two vacancies can be described as a double quantum dot (DQD) system. Further, it was shown that the exchange coupling in such systems can be tuned using a magnetic field.

Such in situ tuning of the magnetic properties is essential for the realization of spintronic devices. In this work, we propose a complementary approach to achieve such tuning based on strain. The electronic properties of graphene are sensitive to strain [19–21], and it is known that GNRs have a strain-tunable band-gap [21, 22]. However, there are only a few studies on the control of magnetism by strain, which so far focus on graphene quantum dots [23, 24], adatoms [25, 26] and magnetic impurities [27, 28]. The influence of compressional strain on vacancy-induced magnetism in bulk graphene was studied in [29].

We use AGNRs as a model system, and characterize the effect of strain on single and double vacancies in such systems. For a single vacancy we calculate the exchange splitting within a mean-field approach to the respective Hubbard model and show that it follows the strain-dependence of the band-gap. In the case of two vacancies, we use the localized defect states to setup a double quantum dot (DQD) model [9, 30]. From this model we calculate the singlet-triplet energy difference and find that it depends exponentially on the product of the distance of vacancies and the applied strain. Our results suggest that strain can be used to non-invasively manipulate the properties of magnetic point defects in graphene. This is expected to be of crucial importance for spintronic applications. In particular, for applications consisting of arrays of...
such DQDs, strain provides a possibility to access and tune each DQD individually. Moreover, by combining vacancy-induced magnetism with mechanical resonators, magneto-mechanical devices based on this principle are within reach.

2. Model

We consider ribbons with armchair edges as sketched in figure 1. In general, the defects can be either (single-atom) vacancies or chemisorbed hydrogen atoms [11], which both effectively lead to the removal of $p_z$ orbitals. In the following, ‘vacancy’ will refer to both types of defects. We note that removing a carbon atom also leads to an unpaired $\sigma$-electron. Experimental results [31] suggest that this electron remains unbound without hybridizing with the extra $\pi$-electron. Thus, both electrons provide independent contributions to the total magnetization. As in previous studies [12, 15] we only consider the $\pi$-electrons in the following.

Uniform strain is applied in the direction parallel to the armchair edges. We include the Poisson effect (narrowing of the ribbon upon stretching) and write the elements of the strain tensor $u = [u_{xx}, u_{xy}, u_{yy}]$ as $u_{xx} = u$, $u_{xy} = -\nu u$ and $u_{yy} = 0$, where $\nu$ is the Poisson ratio $u$ the applied strain. The bond-vectors $\mathbf{r}_{ik}$ connecting atom $i$ and atom $k$ are transformed as $\mathbf{r}_{ik} \rightarrow (\mathbf{1} + \mathbf{u}) \cdot \mathbf{r}_{ik}$ with $\mathbf{1}$ being the $2 \times 2$ identity matrix. For a realistic interatomic potential, this relation is slightly modified [32], and the edges of the vacancies will be reconstructed [11]. These effects depend on the details of the interatomic potential, and are not included here.

To model the electronic properties of the nanoribbon we use a Hubbard model, for which the total Hamiltonian is $H = H_0 + U \sum_i n_i c_i^\dagger c_i c_i^\dagger c_i$. Here, $c_i^\dagger$ creates an electron at site $i$ with spin $s = \{ 1, \uparrow \}$ and $U$ denotes the interaction strength. The non-interacting part, $H_0$, is given by the usual tight-binding model with nearest neighbor hopping (see for instance [33]). Expanding the hopping amplitude $t_0(r)$ and the electron–ion potential $v_0(r)$ up to first order in small displacements of the atoms, yields the following Hamiltonian [22, 34, 35]

$$H_0 = \sum_{\nu = 1}^{N_a} \sum_{i=1}^{N} \left[ \frac{g}{r_0} \sum_{<ij> \nu} \frac{\mathbf{r}_{ij} \cdot \mathbf{u} \cdot \mathbf{r}_{ij}}{r_0} \right] c_i^\dagger c_i$$

$$- t_0(r_0) \sum_{<ij> \nu} \left[ 1 - \frac{\beta \mathbf{r}_{ij} \cdot \mathbf{u} \cdot \mathbf{r}_{ij}}{r_0} \right] c_i^\dagger c_j .$$

The first sum runs over all $N_a$ atoms and the other sums are restricted to nearest neighbors of the atom at site $i$. The on-diagonal contribution is given by the deformation potential and its strength $g/r_0 = \partial \nu \psi_\nu$. The modification of the hopping due to displacement of the atoms is determined by $\beta t_0 = - \partial \nu t_0 r_0$. In the following we use $t_0 = 2.8$ eV, $U = 1.6 t_0$ [36], $g = 4$ eV, $\beta = 3.37$ [20] and $\nu = 0.2$ [37].

3. Results

3.1. Single vacancy

First we consider the case of a single vacancy at the center of the ribbon for $U = 0$. Since the corresponding localized defect state is always located at the Dirac point [13], we expect its energy to follow the behavior of the deformation potential, $v_\nu = \frac{\nu}{2} (\nu_x + \nu_y)$. From figure 2(a) we infer that this is true for strains up to $\approx 3\%$. The localization of the defect state is quantified by the inverse participation ratio $\eta = \sum_n |\psi_n|^4$, where $\psi_n$ are the components of the normalized eigenfunction of the defect state. For a maximally localized state $\eta = 1$, while $\eta \rightarrow 0$ for completely delocalized states and large systems. In figure 2(b) the dependence of $\eta$ on the applied strain and on ribbon width (inset) is shown. The localization at zero strain decreases with increasing width [15]. For a given width, $\eta$ shows a non-monotonic strain-dependence, with a minimum that shifts toward larger strains for decreasing ribbon widths. This behavior can be understood in a qualitative way by recalling that the electronic energy in the Dirac picture is $E = \hbar v_F k$, where $v_F$ is the Fermi velocity and $k$ is the electron momentum which has the unit of inverse length [22]. The relevant energy scale is set by the band-gap $E_g$, and the corresponding length scale is consequently set by $\hbar v_F E_g$. This suggests that the localization length scales inversely with the band-gap. For a semiconducting AGNR the band gap is approximately given by [21]

$$E_g \approx 3 t_0 \min_{n=0,1} \frac{\pi}{\sqrt{3} N_2} \left( n - \frac{1}{3} \right) - \frac{U}{2} (1 + \nu)\mu ,$$

which yields the characteristic zig–zag behavior shown as dashed lines in figure 2(c). Note that for the chosen widths the gap is determined by $n = 0$ (for $N_2 = 19$ the next sub-band starts to contribute around $u = 0.04$). So indeed, comparing the behavior of the participation ratio with the dependence of the band gap on the strain, we find that $\eta(u)\eta(0) \approx E_g(u)/E_g(0)$, shown as dashed lines in figure 2(b).

In the interacting case, Lieb’s theorem [38] predicts that the ground state has total spin 1/2. The energies $\varepsilon_{\text{def,1}}, \varepsilon_{\text{def,2}}$ are, in general, no longer degenerate and the exchange splitting $\Delta_{\text{ex}} = \varepsilon_{\text{def,1}} - \varepsilon_{\text{def,1}}$ is finite. In the ground state only one of
the spin states is occupied, which results in a finite magnetization. We have verified this by performing mean field calculations for the Hubbard Hamiltonian $H$. In figures 2(a)–(c) we show results for the average defect energy $(\varepsilon_{\text{def},1} + \varepsilon_{\text{def},1})/2$, the inverse participation ratio and the band gap. One can see that the observations made for $U = 0$ also hold in the interacting case. In particular, the relation $\eta(u)/\eta(0) \approx E_g(u)/E_g(0)$ is still valid. Figure 2(d) displays the strain dependence of the exchange splitting. Up to a certain strain it monotonically decreases and then increases again. Comparing with the band gap shows that also $\Delta_{\text{ex}}$ follows the strain dependence of $E_g$ given by equation (2). Altogether, we have shown that strain can be used to modify the (localization) properties of the defect state and to tune the exchange splitting.

3.2. Two vacancies

Having characterized the influence of strain on the magnetic properties of a single vacancy, we now add a second vacancy such that their center of mass is at the center of the ribbon. This construct can be thought of as a simple realization of a spin qubit. We only consider vacancies with missing atoms in different sub-lattices and in the ‘tail to tail’ configuration (see figure 1). We first characterize the double-vacancy system in the non-interacting case, and use the obtained results to construct a double quantum dot model for the interacting system.

In the non-interacting case, we find two defect states close to the band center [15]. Linear combinations of the corresponding eigenstates yield states localized at the left and right vacancy, respectively. Figures 3(a) and (b) show the average energy of the two states and their energy difference $\varepsilon_{\text{def},1} - \varepsilon_{\text{def},1}$ for AGNRs of different widths. Inset in (b) shows the dependence of $\eta(0)$ on the ribbon width. Symbols denote results obtained from a TB calculation and dashed lines indicate behavior according to equation (2). Here $N_1 = 100$ (for $U = 0$), $N_1 = 60$ (for $U = 1.6t_0$) and $N_2 = 7, 13, 19$.

![Figure 2](image_url)

**Figure 2.** Strain dependence of (a) the (average) defect energy $(\varepsilon_{\text{def},1} + \varepsilon_{\text{def},1})/2$ of the localized state, (b) the normalized participation ratio $\eta(u)/\eta(0)$, (c) the band gap $E_g$ and (d) the exchange splitting $\varepsilon_{\text{def},1} - \varepsilon_{\text{def},1}$ for AGNRs of different widths. Inset in (b) shows the dependence of $\eta(0)$ on the ribbon width. Symbols denote results obtained from a TB calculation and dashed lines indicate behavior according to equation (2). Here $N_1 = 100$ (for $U = 0$), $N_1 = 60$ (for $U = 1.6t_0$) and $N_2 = 7, 13, 19$. 

The values $N_1$ and $N_2$ correspond to the number of sites in the left and right part of the ribbon, respectively. 

![Figure 3](image_url)

**Figure 3.** Average defect energy $E_{\text{def}}(u)$ and energy difference $\varepsilon_{\text{def}} - \varepsilon_{\text{def}}$ for different widths $N_2$. Symbols denote results obtained from a TB calculation and dotted lines indicate behavior according to equation (2).
Figure 3. Strain dependence of (a) the average energy \( \varepsilon_e \) and (b) the energy difference of the two defect states, and (c) the normalized participation ratio \( \eta(u)/\eta(0) \) for an AGNRs with two vacancies with distance \( d \). Symbols denote results obtained from a TB calculation with \( N_1 = 100 \) and \( N_2 = 7 \). The dashed lines in (a) and (c) indicate behavior according to \( \nu_{\text{TB}} = 3g/2(1 - \nu)u \) and \( E_e(u)/E_e(0) \) with \( E_e \) from equation (2), respectively. The dashed–dotted lines in (b) show \( \Delta \varepsilon(u)/\Delta \varepsilon(0) \) and the inset in (c) displays \( \eta(0) \) versus the distance \( d \).

As we have seen in figure 2(c) the band-gap decreases with strain and therefore at some point the defect states start to overlap with the continuum. For the strains shown in figure 3(b) this only happens for the smallest distance (shown as blue circles), since here the splitting is largest. The inverse participation ratio, shown in figure 3(c), displays a pronounced decrease when the defect states are shifted into the continuum (blue circles). Otherwise \( \eta \) is found to depend only weakly on the distance (see inset of figure 3(c)) and it decreases approximately linearly with the applied strain, but with a distance dependent slope. For vacanices which are far apart the behavior is well described by the ratio \( E_e(u)/E_e(0) \), as expected for nearly independent vacancies.

3.3. Double quantum dot model

According to Lieb’s theorem [38] the ground state of the ribbon for \( U > 0 \) with two single-atom vacancies in different sub-lattices has total spin zero \( S = 0 \) (singlet state) [15]. In this case the highest occupied state, which corresponds to the lower lying defect state \( \psi^{(1)} \), is filled with two electrons of opposite spin. To estimate the energy gap to the triplet states \( S = 1 \), we only consider the defect states \( \psi^{(1)} \) and take them as highest occupied and lowest unoccupied orbitals [9, 30]. By forming linear combinations of \( \psi^{(1)} \), we obtain the states \( \psi^{(L,R)} \) localized at the respective vacancy. Defining corresponding annihilation operators \( a_{n,i} = \sum_s \psi_i^{(n)} \psi_{i,s} \), where \( n = L, R \), we can we write the Hamiltonian for the double quantum dot model as

\[
H_{\text{DQD}} = \sum_i (\varepsilon_L a_i^\dagger a_i + \varepsilon_R a_i^\dagger a_i) + \Delta \varepsilon (n_L a_L^\dagger a_R - n_R a_R^\dagger a_L) + U_{\text{eff}} \sum_n a_i^\dagger a_i^\dagger a_i a_i.
\]

(3)

Here, \( \varepsilon_L = \varepsilon_R \) equals the average energy of the two defect states, \( \Delta \varepsilon \) quantifies the tunnel coupling of the local states and \( U_{\text{eff}} = U \eta \) is the local interaction strength.

In the local basis \( |s_{L,R} \rangle \), where \( s_{L,R} = \{+, -\} \) denotes the spin state of the left and right vacancy, the singlet state of the two-state model is given by \( \Psi_{S=0} = (|+, -\rangle - |-, +\rangle)/\sqrt{2} \) and the triplet states are \( \Psi_{S=1}^{(0)} = (|+, +\rangle + |-, -\rangle)/\sqrt{2} \), \( \Psi_{S=1}^{(1)} = |+, -\rangle \) and \( \Psi_{S=1}^{(-1)} = |-, +\rangle \). The respective energies are found from equation (3) to be

\[
E_{S=0} = U_{\text{eff}} - \sqrt{U_{\text{eff}}^2 + 16\kappa^2}/2 \equiv J,
\]

(4a)

\[
E_{S=1}^{(0)} = E_{S=1}^{(1)} = E_{S=1}^{(-1)} = 0.
\]

(4b)

For \( |t| \ll U_{\text{eff}} \) the exchange energy can be approximated by \( J \approx -4t^2/U_{\text{eff}} \).

Using the data shown in figure 3 we calculate the exchange energy \( J \) as a function of the vacancy distance and the applied strain. The resulting behavior is shown in figure 4. Note that we plot \( J \) versus \( du \). For zero strain \( |J| \) decreases exponentially with increasing distance. Moreover, we find that \( |J| \) is exponentially increasing with increasing \( du \), which is consistent with our observation that \( \Delta \varepsilon \propto \exp(2\kappa du) \) with \( \kappa = \sqrt{3} \beta (1 + \nu)2\nu \). Since the participation ratio depends only weakly on the vacancy distance, but the energy difference strongly decreases, the behavior of \( J \) approaches the strong interaction limit \( |t| \ll U_{\text{eff}} \) for increasing distance. Thus the exchange interaction can be tuned over a wide range by adjusting the distance and/or by applying strain to the ribbon.

4. Conclusions

In summary, we have characterized the influence of geometry and strain on the electronic and magnetic properties of semiconducting AGNRs with one and two vacancies. For a single vacancy we find that the degree of localization and the spin-exchange splitting follows the strain-dependence of the band gap, which is non-monotonously changing. This simple relation connecting the intrinsic vacancy-induced magnetism...
to strain via the band-gap has, to our knowledge, not been reported previously. It implies that the spin-exchange can be changed to large extent by applying strain. Further, the singlet-triplet splitting in the two vacancy system depends exponentially on the product of strain and inter-vacancy distance. This sensitivity with respect to strain may be exploited in the development of quantum-information and sensing applications. In an array of such vacancy-induced DQDs, the strain-tuning of the exchange interaction can in principle be used to gain individual control of the magnetic properties. Combining strain-sensitive magnetic defects with mechanical resonators provides a viable route toward magneto-mechanical devices [39] and might make it possible to couple vacancy-induced DQDs over long distances [40].

References

[1] Awschalom D D and Flate M E 2007 Challenges for semiconductor spintronics Nat. Phys. 3 153–9
[2] Fert A 2008 Nobel lecture: origin, future and development of spintronics Rev. Mod. Phys. 80 1517
[3] Han W K, Gmitra M R K and Fabian J 2014 Graphene spintronics Nanotechnol. 9 794–807
[4] Trauzettel B, Bulac D V, Loss D and Burkard G 2007 Spin qubits in graphene quantum dots Nat. Phys. 3 192–6
[5] Droth M and Burkard G 2015 Spintronics with graphene quantum dots arXiv: 1506.03991
[6] Ezawa M 2007 Metallic graphene nanodisks: electronic and magnetic properties Phys. Rev. B 76 245415
[7] Fernández-Rossier J and Palacios J J 2007 Magnetism in graphene nanoribbons Phys. Rev. Lett. 99 177204
[8] Wang W L, Meng S and Kaxiras E 2008 Graphene nanoflakes with large spin Nano Lett. 8 241–5
[9] Droth M and Burkard G 2015 Tuning antiferromagnetism of vacancies with magnetic fields in graphene nanoflakes Phys. Rev. B 91 115439
[10] Fujita M, Wakabayashi K, Nakada K and Kusakabe K 1996 Peculiar localized state at zigzag graphite edge J. Phys. Soc. Japan 65 1920–3
[11] Yazyev O V and Helm L 2007 Defect-induced magnetism in graphene Phys. Rev. B 75 125408
[12] Yazyev O V 2010 Emergence of magnetism in graphene materials and nanostructures Rep. Prog. Phys. 73 86501
[13] Wakabayashi K 2002 Numerical study of the lattice vacancy effects on the single-channel electron transport of graphite ribbons J. Phys. Soc. Japan 71 2500–4
[14] Pereira V M, Guinea F, dos Santos J M B, Peres N M R and Castro Neto A H 2006 Disorder induced localized states in graphene Phys. Rev. Lett. 96 36801
[15] Palacios J J, Fernández-Rossier J and Brey L 2008 Vacancy-induced magnetism in graphene and graphene ribbons Phys. Rev. B 77 195428
[16] Nair R R, Sepioni M, Tsai I-L, Lehtinen O, Keinonen J, Krasheninnikov A V, Thomson T, Geim A K and Grigorieva I V 2012 Spin-half paramagnetism in graphene induced by point defects Nat. Phys. 8 199–202
[17] Krasheninnikov A V and Banhart F 2007 Engineering of nanostructured carbon materials with electron or ion beams Nat. Mater. 6 723–33
[18] Pisani L, Montanari B and Harrison N M 2008 Defective graphene phase predicted to be a room temperature ferromagnetic semiconductor New J. Phys. 10 1–5
[19] Pereira V M and Castro Neto A H 2009 Strain engineering of graphene’s electronic structure Phys. Rev. Lett. 103 46801
[20] Pereira V M, Castro Neto A H and Peres N M R 2009 Tight-binding approach to uniaxial strain in graphene Phys. Rev. B 80 45401
[21] Lu Y and Guo J 2010 Band gap of strained graphene nanoribbons Nano Res. 3 189–99
[22] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 The electronic properties of graphene Rev. Mod. Phys. 81 109–62
[23] Viana-Gomes J, Pereira V M and Peres N M R 2009 Magnetism in strained graphene dots Phys. Rev. B 80 245436
[24] Cheng S, Yu J, Ma H and Peres N M R 2015 Strain-induced edge magnetism at the zigzag edge of a graphene quantum dot Phys. Rev. B 91 75410
[25] Huang B, Yu J and Wei S-H 2011 Strain control of magnetism in graphene decorated by transition-metal atoms Phys. Rev. B 84 75415
[26] Sharma A, Kotov V N and Castro Neto A H 2013 Effect of uniaxial strain on ferromagnetic instability and formation of localized magnetic states on adatoms in graphene Phys. Rev. B 87 155431
[27] Power S R, Gorman P D, Duffy J M and Ferreira M S 2012 Strain-induced modulation of magnetic interactions in graphene Phys. Rev. B 86 195423
[28] Gorman P D, Duffy J M, Ferreira M S and Power S R 2013 RKKY interaction between adsorbed magnetic impurities in graphene: symmetry and strain effects Phys. Rev. B 88 184505
[29] Santos E J G, Rikken S, Sánchez-Portal D and Ayuela A 2012 Magnetism of single vacancies in rippled graphene J. Phys. Chem. C 116 7602–6
[30] Li Y, He J, Kong X and Kou S-P 2014 Vacancy-induced intrinsic magnetic impurity with quasilocalized spin moment in graphene Phys. Rev. B 90 201406
[31] Nair R R et al 2013 Dual origin of defect magnetism in graphene and its reversible switching by molecular doping Nat. Commun. 4 2010
[32] Midtvedt D, Lewenkopf C H and Croy A 2015 Strain-displacement relations and strain engineering in 2d materials arXiv: 1509.02365
[33] Ramezani M, Moldovan D and Peeters F M 2013 Pseudo magnetic field in strained graphene: revisited Solid State Commun. 175–6 76–82
[34] Suzuura H and Ando T 2002 Phonons and electron–phonon scattering in carbon nanotubes Phys. Rev. B 65 235412
[35] Vozmediano M A H, Katsnelson M I and Guinea F 2010 Gauge fields in graphene Phys. Rep. 496 109–48
[36] Schüler M, Rössner M, Wehling T O, Lichtenstein A I and Katsnelson M I 2013 Optimal Hubbard models for materials with nonlocal coulomb interactions: graphene, silicene, and benzene Phys. Rev. Lett. 111 36601
[37] Perebeinos V and Tersoff J 2009 Valence force model for phonons in graphene and carbon nanotubes Phys. Rev. B 79 241409
[38] Lieb E H 1989 Two theorems on the Hubbard model Phys. Rev. Lett. 62 1201–4
[39] Ganzhorn M, Klyatskaya S and Wernsdorfer W 2013 Strong spin-phonon coupling between a single-molecule magnet and a carbon nanotube nanoelectromechanical system Nat. Nanotechnol. 8 165–9
[40] Burkard G and Imamoglu A 2006 Ultra-long-distance interaction between spin qubits Phys. Rev. B 74 41307