Probing divacancy defects in a zigzag graphene nanoribbon through an RKKY exchange interaction

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Abstract
We investigate the effects of vacancy defects on the electronic and magnetic properties of zigzag graphene nanoribbons (zGNRs) by making use of the Green’s function formalism in combination with a tight-binding Hamiltonian. We explain the evolution of indirect exchange coupling, known as the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, including single, double, and multiple 5-8-5 divacancy (DV) defects. Our numerical calculations show that changes in the electronic structure and exchange coupling of zGNRs depend to a significant degree on the location of DV defects with respect to the ribbon edges and the number of DV defects. In the case where both impurities are located on the edge, the magnitude of the exchange coupling is several orders of magnitude higher than when they are placed on the interior of the nanoribbon. Furthermore, a periodic DV causes a dramatic change in the magnetic ground state of the ribbon. In the limit of a high vacancy potential, the strength of the RKKY interaction is approximately independent of the Fermi energy. We demonstrate that, on the one hand, the defect engineering of atomic vacancies is a promising way to modify the magnetic properties of graphene nanoribbons, and, on the other hand, unusual RKKY oscillations around the DVs are a new technique for directly probing the local vacancies in a zGNR through the RKKY exchange interaction.

Keywords: divacancy defect, Green’s function formalism, Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, tight-binding Hamiltonian, graphene nanoribbon

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

1. Introduction
Graphene, a two-dimensional (2D) allotrope of carbon formed by a single layer of graphite [1], has attracted great attention, owing to the Dirac-like energy spectrum of its charge carriers and the resulting spectacular properties [2–4]. Despite significant advancements in the synthesis and processing of atomically precise graphene nanoribbons (GNRs), various structural defects generated during preparation are broadly considered to be inevitable. Compared to ideal 2D graphene, the electronic, chemical, thermal, and mechanical properties of real 2D graphene are profoundly influenced by the presence of structural defects, lattice imperfections [2, 3], wrinkles, and even the ripples that always exist in graphene sheets [5, 6]. These ubiquitous defects are considered the limiting factors for electronic transport in graphene, as they cause charge impurities [7, 8], rippling [9] or resonant scattering [10–12] and can also give rise to pseudo-magnetic gauge fields [4]. Similar effects can be expected from topological lattice defects, which spontaneously lead to corrugations in
graphene [13]. The ion-induced formation of lattice defects can be considered to be a potential source of intervalley scattering in defective graphene that causes diverging resistivity at low temperatures, indicating an insulating behavior of graphene [14].

As one of the intrinsic point defects in graphene, vacancies have recently received enormous attention because of their major implications for graphene devices [15–30]. Such defects can be used to tailor or improve the physical characteristics of graphene [31–37] and generate unusual phenomena [24–28].

For example, while pristine graphene is strongly diamagnetic, graphene with single-carbon-atom defects can exhibit paramagnetism [38], such that the localized state of atomic defects is split into two densities of states peaks, with energy separations of several tens of meV. Surprisingly, the effective g factor around the atomic defect has been measured at about 40, which is about 20 times larger than the g factor for electron spins. A large electron–hole asymmetry may arise from local lattice deformation around the monovacancy and the electron scattering due to the charged defect [4]. Moreover, vacancy defects are predicted to change the semimetallic nature of graphene into metallic behavior [39]. These structural defects also cause so-called resonant scattering at the Dirac points and are considered to impose a limit on graphene conductivity [12]. Another exciting aspect of graphene vacancy defects is that they can be used to produce negative differential resistance devices [40], filter the electronic or phononic valleys [41], and produce gas sensors [42]. Although the mechanical properties are degraded by the presence of vacancy defects [43–47], these defects are predicted to play an effective role in the thermal conductance [48], control of the mechanical and thermoelectric properties [49], and the electronic transport [4] of GNRs.

Vacancy defects can be artificially created in graphene by electron or ion irradiation [15, 33] and visualized at an atomic resolution by high-resolution transmission electron microscopy [17] and scanning probe microscopy [50, 51]. As a simple, controllable, and scalable method, acid treatment is known to be the simplest approach for vacancy-defect creation [52]. The most probable form of defects generated by ion irradiation is single vacancies [34] that give rise to magnetic moments in single-layer graphene [15, 33].

In a ribbon, vacancies are a common type of defect that can influence the electronic characteristics, such as bandgap and conductivity [36, 37]. For instance, the vacancy state of graphene can be strongly modified in the presence of edges in semi-infinite graphene sheets [53]. It has been shown that GNRs possess a finite bandgap [54–56] owing to quantum confinement and edge effects, and show promise to be suitable for the development of realistic graphene-based nanodevices, such as graphene ribbon field-effect transistors [57–59], thermoelectric generators [60–62] and optoelectronic applications [63–65].

First-principles calculations [66] show that vacancy defects introduce localized states near the Fermi level and local magnetic-moment magnetism in a monolayer C3N and the newly synthesized two-dimensional polyimine, and consequently, the bandgap and magnetism of monolayer C3N can be tuned by the introduction of defects and atom substitution. In contrast to graphene, all the vacancies of C3N have a metallic character because of altered stoichiometry [67].

In the framework of spin-polarized density functional theory (DFT) [68], it has been shown that the magnetic moment of graphene and silicene with vacancies decreases with an increase in the concentration of vacancies. However, germanene remains non-magnetic, irrespective of the vacancy concentration. With the formation of vacancy defects, silicene and germanene show a transition from semimetals to semiconductors, while graphene becomes metallic. Therefore, they should be taken into account in 2D-materials-based applications [36, 37]. Many theoretical studies have mainly focused on the effects of vacancies on the electronic properties of GNRs and the resulting device characteristics [69, 70].

Divacancies (DVs), a type of defect created either by the coalescence of two single vacancies or by removing two neighboring carbon atoms, may appear naturally as a stable defects during growth; alternatively, they can be created on purpose by electron or ion irradiation [17, 34, 71–74]. It has been shown that DVs in graphene are energetically favored, compared to monovacants defects, because the formation energy of DVs is lower than that of two isolated monovacancies, and isolated monovacancies have a tendency to coalesce into a DV [75–79]. Moreover, monovacancies that coalesce to form a DV reconstruct it without a dangling bond [80] and these DVs are the most important ones in terms of changes in transport properties [81, 82], even at a low concentration i.e. an order of magnitude of about 0.03.

Ab initio calculations of the dynamics and stability of DVs in graphene show that DVs are one of the most abundant defects in irradiated graphene [78, 83, 84] and have various reconstructed structures, such as triple-pentagon–triple-heptagon (555–777) and pentagon–octagon–pentagon (5–8–5) patterns [52, 85]. A double-vacancy (5–8–5) defect is formed by the removal of two carbons, leaving a surface with two pentagonal rings and one octagonal ring [77]. On the other hand, Stone–Wales (SW) topological defects, non-hexagonal ring defects in graphene generated by the reconstruction of the hexagonal lattice, may play a significant role in the mechanical failure of 2D materials [86–88]. A Stone–Wales defect is the rearrangement of the six-membered rings of graphene into two five-member (pentagons) and two seven-member (heptagons) rings. This rearrangement is the result of the π/2 rotation of a C–C bond [17]. Recall that graphene fracture begins when a nanocrack appears at an SW defect, where one of the C–C bonds shared by a heptagon and a nearby hexagon breaks at a critical strain [77]. At higher concentrations of S-W defects (≥7%), a conversion from a brittle to a ductile fracture occurs, due to the relocation of atoms around SW defects, which traps and blunts the advancing crack tip [89].

The formation of reconstructed DVs close to the edges of zigzag graphene nanoribbons (zGNRs) can be a practical way to make them partially ferromagnetic [90]. This effect takes place even though the DVs are produced by removing two atoms from opposite sublattices, which were balanced before being reconstructed into 5–8–5 defects. There is a strong interaction between the defect-localized and edge
bands, which mix and split away from the Fermi level. According to Lieb’s theorem [91], one way to attain ferromagnetic graphene nanostructures is to impose a sublattice imbalance. For instance, graphene systems with vacancies [70, 92–94] have a non-zero spin due to sublattice imbalance. When these defects are present in zGNRs, they give rise to localized states and can consequently lead to spin effects and ribbon magnetization [92, 95]. Moreover, it has been found that zGNRs have spin-polarized edges, antiferromagnetically coupled in the ground state with a total spin of zero [96], and can be ferromagnetic due to the presence of reconstructed 5-8-5 DV defects near one edge.

DFT, in conjunction with a Green’s function analysis [97], shows that zGNR devices with vacancies in the edge regime turn out to exhibit perfect spin-filter activity for well-defined choices of the strain and the bias, carrying completely polarized minority-spin currents. In an alternative structure, characterized by vacancies in the bulk regime, spin currents with the majority orientation prevail. With respect to both their sign and size, magneto current ratios are found to depend strongly on vacancy locations.

In semiconducting armchair ribbons and two-dimensional graphene without a global sublattice imbalance, there is a maximum defect density above which local magnetization disappears [92]. Overall, zGNRs with 5-8-5 DV defects may show either zero spin polarization [98] or spin-polarized transport in ribbons with narrow widths [95]. Very recently, in a systematic theoretical investigation, Kot et al [30] studied the band dispersion of graphene with randomly distributed structural defects using two complementary methods: the exact diagonalization of a tight-binding (TB) Hamiltonian and the implementation of a self-consistent T-matrix approximation. It was shown that in all instances, except the case of vacancies placed in a single sublattice, there is no bandgap opening near the Dirac point. Further, da Cunha et al [99] developed a model to describe charge transport on 2D honeycomb lattices in the presence of vacancy defects. It was found that the positioning of vacancies plays a major role in the scattering of charge carriers, in the sense that their overall mobility is determined by where the defect is located. It was also observed that the position of the vacancy on the lattice was crucial in defining the kind of scattering process of the polaron by the vacancy.

For pristine graphene, with a low concentration of vacancy defects, when the Fermi energy lies in the energy region where the density of states (DOS) is linear, indirect exchange coupling, known as the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [100–102], mediated by a background of conduction electrons in the host material, decays as $R^{-3}$ [103]. Otherwise, the presence of vacancies pushes the exponent ($-3$) toward more negative values. The effect of a few percent of vacancies surpasses both atomic-scale oscillations and Friedel oscillations due to the Fermi surface for a remarkable range of chemical potential values [103].

As mentioned earlier, the chemical, thermal and mechanical properties of GNRs in the presence of 5-8-5 DVs have been studied extensively [17, 34, 71–74, 90, 104]. However, indirect exchange coupling for GNRs in the presence of DVs has not been systematically reported. Therefore, it is necessary to systematically study the effects of DVs on the electronic and magnetic properties of GNRs. Motivated by the effects of DVs on the electrical [105–108] and magnetic [90, 109] properties of GNRs, in this paper, we explain the evolution of indirect exchange coupling in zGNRs in the presence of a sublattice staggering potential. Within the TB model, we exploit the Green’s function formalism to reveal the RKKY interaction between two magnetic impurities (MIs) placed on a zGNR.

Our calculations show that changes in the electronic structure and the exchange coupling of zGNRs depend on the location of the DVs with respect to the ribbon edges and the number of DVs. Introducing vacancies into zGNR changes the spatial variation of the RKKY interaction, particularly those magnetic moments located around the vacancies. We show that different values of the vacancy potential in the same zGRN give rise to different changes in the electronic and magnetic properties. A periodic DV created in a zGRN causes a dramatic change in the magnetic ground state of the ribbon. It is established that the presence of DVs in zGNRs leads to the remarkable properties and applications of GNRs.

The remainder of this paper is organized as follows. In section 2, we describe the systems under consideration, i.e. zGNRs in the presence of 5-8-5 DVs. To do so, a TB model Hamiltonian is presented for a 2D graphene lattice and the theoretical framework then is introduced to calculate RKKY using a real-space Green’s function. In section 3, we discuss our numerical results for the exchange interaction and the electronic properties of zGNRs in the presence of 5-8-5 DVs. Finally, we summarize our findings in section 4.

2. Theory and model

As mentioned above, the DV is one of the most abundant and most important defects in crystalline materials. We therefore consider DVs produced by the removal of two neighbor carbon atoms (representing $p_z$ orbitals in the TB model), causing so-called 5-8-5 defects, so that the two sublattices are balanced [92]. It should be noted that we ignore lattice distortion.

It has been shown that due to strain, the self-healing of vacancy defects is inevitable, and defects exhibit reconstruction and coalescence near the ribbon edge; however, such an analysis is beyond the scope of our paper. A number of techniques and proposals for vacancy assessment have emerged over the years [59, 92, 110–115]. On the one hand, most of the first-principles calculations based on DFT methods are limited to a few hundred atoms. On the other hand, although calculations using empirical classical interatomic potentials are fast and can deal with many atoms, the validity and reliability of the calculation results are questioned. It is therefore desirable to have a computational tool that is fast enough to handle calculations for several thousands of atoms and is thus accurate enough that the calculation results can provide a meaningful understanding of the structures of vacancy defects in graphene. In this regard, TB approximation can bridge the gap between first-principles calculations and simulation using empirical classical potentials. Similarly
to the approach used in our work, several techniques and proposals [59, 92, 110–115] have been developed based on the TB approximation for GNRs.

It is worth mentioning that each edge carbon atom in GNRs is only bounded by two neighboring carbon atoms, and the resulting dangling carbon bond offers a remarkable opportunity to manipulate the electronic properties of GNRs [103]. Detailed first-principle calculations reveal that the chemical modification of GNRs results in a considerable deformation of the bond lengths and bond angles near the edge [116]. In this regard, different edge-functionalization groups result in different types of bonds, namely sp² (for ZGNRs terminated by one hydrogen atom) and sp³-like (by adsorption of two hydrogen atoms), respectively, at the edges of the GNRs, which leads to a significant impact on the electronic structure near the Fermi level [117–119].

Using a non-equilibrium Green’s function combined with DFT, the transport properties have been investigated, including the spin-filtering and rectifying behaviors of zigzag silicon carbon nanoribbons [119] and zigzag graphene nanoribbons [117, 118] with different edge hydrogenations. The results show that a perfect spin-filtering effect with 100% spin polarization and a rectifying behavior with a ratio larger than 10⁵ can be obtained by dihydrogenation, which can also be modulated by changing the widths of the two component ribbons. Several theoretical studies [55, 120, 121] have shown that owing to lateral quantum confinement, GNRs with hydrogen-passivated armchair edges are semiconducting at widths below 10 nm, while those with zigzag edges are metallic, owing to edge states at the Fermi level. Moreover, other researchers have shown that the chemically modified edges of ZGNRs are in a half-metal state [121–124]. On the other hand, half-metallicity may be realized in a ZGNR either by applying a high in-plane homogeneous electric field or by chemically functionalizing the zigzag-edges of the GNR with different groups such as H, COOH, OH, NO₂, NH₃, CH₃, etc [121, 122, 125]. The unique magnetic properties of chemically modified ZGNR edges were also revealed by experiment [125, 126]. Wu et al found high magnetic anisotropic energies of ZGNRs due to edge modification with F, Cl, or Br atoms [127], and Huang et al [128] reported that ZGNRs allow spin interactions and robust spiral magnetism through edge functionalization with Ti and V atoms. Notable breakthroughs in bottom-up methods have allowed for the fabrication of atomically precise GNRs with perfect edges, where perfect-edged GNRs as well as more complex nanostructures with controlled atomic arrangements [124, 129] were obtained by the assembly of small specific monomers. For instance, using the self-assembly of suitable monomers on a gold surface [130], one can produce an edge-modified structure. Datta et al [12] reported that graphene samples can be etched along their crystallographic axes by a hydrogenation mechanism with the help of metallic nanoparticles. Also, besides hydrogen, many other elements, such as fluorine, oxygen, boron, nitrogen, and a hydroxyl group (OH) have been used for edge passivation in GNRs [132–135].

Increments of the C–C bonds and bonding angles at the nanoribbon edge have been reported based on TB approximation calculations [136–138]. It has been shown that a reduced interatomic distance enhances hopping integrals and results in changes to the electronic properties of GNRs [139]. On the other hand, to take account of the effect of deformation on the graphene ribbon edge, a phenomenological hopping parameter is introduced in the TB approximation calculations [116]. In some TB approximation calculations in which the dangling bonds are saturated by hydrogen atoms [137, 140], it has been assumed that all transfer integrals between the nearest-neighbor (NN) sites are set to the same values. Using combined first-principles and TB calculations, Wang et al [116] simulated the effects of chemical edge modifications on the structural and electronic properties of GNRs, by introducing a phenomenological hopping parameter for NN hopping to represent various chemical edge modifications. Surprisingly, the introduction of this hopping parameter into the TB scheme accurately captured the effects caused by chemical edge modifications. However, in the traditional TB method, due to H saturation, the edge-hopping parameter is changed from t to 1.2t, where t = 2.7 eV is the NN hopping integral of graphene [55]. It is worth noting that while boundary saturation has a great influence on the properties of GNRs, such an analysis is beyond the scope of our paper.

A schematic picture of a ZGNR with two DVs, where the defect regions are denoted by a gray color, is shown in figure 1 (left panel). The dashed rectangle represents a pristine unit cell. Following the conventional notation [56, 141–145], the length (L) and the width (N) of the nanoribbon with zigzag-shaped edges on both sides are defined as the number of unit cells and zigzag lines across the ribbon’s width, respectively. As shown in this figure, each atom is labeled with a pair of numbers (m, n), for which m, n represent the x and y coordinates of the lattice points.

According to this notation, the positions of the two magnetic impurities are labeled by (n₁, m₁) and (n₂, m₂), with (m, n) as the indices of the sublattices, and accordingly the location of each DV defect is labeled by (nᵢ, mᵢ), in which nᵢ is the unit cell number of the ith DV and mᵢ is the position of the upper vacancy in the ith DV. Here, the locations of the first and second DVs are (n₁, m₁) = (4, 4) and (n₂, m₂) = (8, 8), respectively.

The TB Hamiltonian for the itinerant electrons in graphene is given by [3]:

\[
\mathcal{H}_{\text{NN}} = -t \sum_{\langle ij \rangle, \sigma} \left( a_{i \sigma} \dagger b_{j \sigma} + \text{h.c.} \right) -t' \sum_{\langle ij \rangle, \sigma} \left( a_{i \sigma} \dagger a_{j \sigma} + b_{i \sigma} \dagger b_{j \sigma} + \text{h.c.} \right),
\]

(1)

Here, \( a_{i \sigma} (a_{i \sigma} \dagger) \) is the annihilation (creation) operator for a particle with a spin \( \sigma \) (\( \uparrow, \downarrow \)) at site \( \mathbf{R}_i \) on a sublattice A (an equivalent definition is used for \( b_{i \sigma} (b_{i \sigma} \dagger) \) on a sublattice B).
The subscripts \((i, j)\) and \((\langle i, j \rangle)\) denote the NN and next-nearest-neighbor (NNN) pairs of atoms, respectively, where \(t\) is the NN hopping energy between different sublattices. The value of the NNN hopping integral \(t'\) (hopping between the same sublattices) is not well-known but \textit{ab initio} calculations [148] predict a value of \(0.02 \leq t' \leq 0.2t\), depending on the type of TB parameterization. A TB fit to cyclotron-resonance experiments [149] suggests \(t' \approx 0.1\) eV.

Based on dedicated measurements of the DOS in graphene, by using high-quality capacitance devices, the NN and NNN terms are obtained as \(t \approx 3\) eV and \(t' \approx -0.3\) eV, respectively [150]. From the density functional calculations using the linear muffin-tin orbital method and linear augmented-plane-wave method, the TB hopping integrals with signs chosen such that \(t, t' > 0\) were obtained as \(t \approx 2.91\) eV and \(t' \approx 0.16\) eV, respectively for graphene [151]).

The optimized structural geometry for the vacancy in GNRs as reported in the literature varies widely. While some have found planar structures [152–157], others have reported non-planar structures with out-of-plane displacements varying from \(\delta z \approx 0.12 \pm 0.47\) Å [104, 158–161]. Furthermore, it has been found that a paramagnetic relaxation yields a non-planar structure \(\delta z \approx 0.27\) Å, while Faccio et al [156] obtained a planar structure, using spin-polarized calculations. It has been shown that symmetry strictly forbids the admixture of \(\sigma\) and \(\pi\) states for planar relaxation around vacancies, leading to flat \(\sigma\) bands. The \(\pi\) bands are not flat, owing to hybridization with continuum \(\pi\) states. There are several reviews devoted to the energetics of formation, transformation, migration, coalescence and healing of defects in graphene. For instance, the general feature of orbital exchange in the course of the structural relaxation process has been presented by Max Pinheiro Jr et al [162], using DFT calculations. Another comprehensive review by Skowron et al [163] provided an overview of the energetic characteristics of various thermally activated and irradiation-induced reactions in the interior of graphene and at graphene edges. The processes of defect formation, healing and changes of defect type due to bond realignment and atomic emission reactions are determined in this review.

In this work, a fully relaxed mono-vacancy GNR is constituted as a planar Jahn–Teller (JT) distorted carbon triangle around each vacancy, with the carbon atoms outside the triangle relaxed by a much smaller amount [164]. Density functional calculations plus the all-electron spin-polarized linear augmented-plane-wave formalism [164] show that the three \(sp^2\sigma\) dangling bonds adjacent to the vacancy introduce localized states (\(V\sigma\)) in the mid-gap region, which split due to the crystal field and a JT distortion, while the \(p, \pi\) states introduce a sharp resonance state (\(V\pi\)) in the band structure. This simple model [164] suggests a JT distortion of the carbon triangle surrounding the vacancy. The vacancy site was modeled by simply removing a lattice site, corresponding to the vacancy potential \(U_0 = \infty\). In a real material, however, \(U_0\) is a large value. Translational symmetry is broken by the presence of localized defects such as vacancies and impurities. Vacancies have been modeled by adding an on-site perturbation, \(V\), to the unperturbed NN TB Hamiltonian \(\mathcal{H}_0 = -t \sum_{i \alpha} c_{i \alpha}^\dagger c_{i \alpha} + H.c.,\) with the Greek subscripts \(\alpha\) indicating the sublattice indices, so that

\[
\mathcal{H}_{\text{vacancy}} = \mathcal{H}_0 + V,
\]

where the localized form of the impurity potential can be written as

\[
V = U_{0A} c_{0A}^\dagger c_{0A} + U_{0B} c_{0B}^\dagger c_{0B},
\]

where \(U_{0A} (U_{0B})\) is the strength of the potential due to the vacancy on the sublattice \(A (B)\). This simple model suggests that hoppings to the vacant sites are forbidden.

In graphene, the \(sp^2\sigma\) states are removed from \(E_F\) due to the strong interaction with neighboring orbitals along the C–C bonds. However, with a vacancy present, the three \(sp^2\sigma\) orbitals of the three NN carbon atoms with their lobes pointing
towards the vacancy have their usual bonding partners missing, so that they occur near $E_F$, with their on-site energies $\epsilon_{\sigma}$ slightly below the $\sigma$ orbital energies because of the $s$ orbital component present in the $\sigma$ states.

Crystal-field splitting, however, can also lift the three-fold degeneracy of the ground state into a double-degenerate state and a single-degenerate state. The remaining degeneracy of the double-degenerate state is lifted in the presence of the JT distortion of the triangle, which is described by the unequal hopping $t_{ij} \neq t'_{ij}$. Two of the three hopping terms are then modified into $t'_{ij}$ as indicated in figure 1 (right panel). From the DFT band-structure fitting, and taking into account the 2NN hopping $t$ between the three dangling bonds in the undistorted triangle, the two unequal hopping parameters are obtained as $t_{ij} \approx 1.6$ eV and $t'_{ij} \approx 1.2$ eV.

2.1. RKKY interaction in zGRNs with defects

To study the magnetic interaction between two local moments in the system, we consider the indirect exchange coupling between magnetic impurities as an RKKY form, mediated by conduction electrons. Using a second-order perturbation [100–102], the effective magnetic interaction between two magnetic moments at positions $\mathbf{r}_i$ and $\mathbf{r}_j$ was given by [165, 166],

$$J_{\text{RKKY}} = \frac{\lambda^2 S(S + 1)}{4\pi S^2} \int d\omega \sum_{\mathbf{r}} |G(\mathbf{r}, \mathbf{r}, \omega)|^2,$$

(4)

where $S$ is the magnitude of the impurity spin, $\lambda$ is the coupling constant between the on-site impurity spins and the spin of the itinerant electrons, and $f(\omega) = \left[ e^{(\omega - \mu)/T} + 1 \right]^{-1}$ is the Fermi–Dirac distribution function at energy $\omega$, temperature $T$, and chemical potential $\mu$. Note that we use units such that $\hbar = a = 1$ in all calculations. Making use of the Lehman representation of the Green’s function, the eigenfunctions $E_\sigma$ and the wave functions $\psi_n(\mathbf{r}_i)$ can be obtained by diagonalizing the real-space Hamiltonian of zGNRs with vacancies

$$\mathcal{H}_{\text{Defected zGNR}} = \mathcal{H}_{\text{NNN}} + V$$

(5)

where $n$ denotes the band index and $i$ and $j$ are the carbon site index of magnetic impurities which are located at position $\mathbf{r}_i$ and $\mathbf{r}_j$. Using the appropriate spectral functions in the low-temperature limit, the integration over energy in equation (4) is therefore

$$J_{\text{RKKY}} = -\text{Re} \int_{\epsilon < \mu} d\epsilon \int_{\epsilon' > \mu} d\epsilon' \sum_{\mathbf{r}} \langle \hat{\psi}_n(\mathbf{r}) \hat{\psi}_n^*(\mathbf{r}) \rangle \langle \hat{\psi}_m(\mathbf{r}) \hat{\psi}_m^*(\mathbf{r}) \rangle \delta(\epsilon - \epsilon' - H_{\sigma}),$$

(6)

Finally, after straightforward calculations, the normalized RKKY interaction can be expressed as the following desired result [141–145]

$$J_{\text{RKKY}}(\mathbf{r}, \mathbf{r}) = -\sum_{n,h} \left[ \frac{f(E_n) - f(E_n')}{E_n - E_n'} \right]$$

$$\times \langle \hat{\psi}_n(\mathbf{r}) \hat{\psi}_n^*(\mathbf{r}) \rangle \langle \hat{\psi}_m(\mathbf{r}) \hat{\psi}_m^*(\mathbf{r}) \rangle.$$  

(7)

This result, which is the main equation of this work, is a well-known formula in linear-response theory.

3. Numerical results and discussions

In this section, we present our main results for RKKY exchange coupling in DV zGNRs. We evaluate the static spin susceptibility using equation (7) in real space for various configurations of the MI and DV defects. We consider the same strength of vacancy potential for sublattices $A$ and $B$, i.e. $U_{0A} = (U_{0B}) = U_0$.

First, we investigate the spatial behavior of the RKKY interaction (as a function of the dimensionless distance $R/a$) for two MIs in a zGNR with $M = 20, N = 300$, for different strengths of the impurity potential $U_0/\hbar = 0, 2, and 5$ eV, including single, double and multiple DVS (see figure 2). In panels (a), (b) and (c), both the MIs are located on the same edge at positions $(5, 1)$ and $(n, 1)$, with $n = 6, 7, 8, ...$, and in panels (d), (e) and (f), both are located inside the zGNR, for a configuration with the first impurity at $(5, 10)$ and the second at $(n, 10)$, with $n = 6, 7, 8, ...$

Panels (a) and (e) show a zGNR with one DV at position $(150, 4)$; (b) and (f) represent a zGNR with two DVs at positions $(145, 4)$ and $(155, 4)$; (c) and (g) refer to a zGNR with 11 DVs at positions $(5, 4), (34, 4), (63, 4),..., (295, 4)$ (DV defects with a period of $\Delta R_\text{DV}/a = 30$), and finally, panels (d) and (h) illustrate a zGNR with 30 DVs at positions $(5, 4), (15, 4), (25, 4),... (295, 4)$ (DV defects with a period of $\Delta R_\text{DV}/a = 10$) are periodically situated in the zGNR.

The effect of the presence of the DV is apparent in this figure; the magnetic RKKY coupling shows different spatial distributions for DV zGNRs with different numbers of DVSs and various spatial configurations. Not only the magnitude but also the sign of the exchange coupling can be controlled by changing the spatial distribution of both the magnetic impurities and the DVSs as well as the number of DVSs. It is worth mentioning that regardless of whether the MIs are at the edge or not, the RKKY coupling is short-range and falls off rapidly an increase in the impurity distance, for a high concentration of DVSs for an example, panels (d) and (h): here, for impurity distances larger than $R/a 50$, the RKKY coupling is nearly zero. We also consider the effect of the impurity potential $U_0$ to determine how this perturbation affects the spatial profile of the RKKY coupling under different numbers of local DV defects. Most importantly, as shown in figure 2, one can observe that a significant sharp-peak perturbation appears in the spatial profile of the RKKY coupling when the second MI approaches a DV, regardless of whether the MIs are at the edge or in the interior of the ribbon. This type of perturbation of the regular RKKY oscillations around DVs is a method of directly probing the local vacancies in a zGNR by using the RKKY exchange interaction.

Besides, it has been shown that when impurities are located at the edge, the magnitude of the exchange coupling is several orders of magnitude greater than when impurities are in the bulk. Most importantly, zGNRs with one or two DVSs
have the highest difference between the edge and bulk RKKY interactions, in comparison with samples with more DVs. For instance, when impurities are located on the edge, the magnitude of the exchange coupling is approximately four orders of magnitude greater than when the impurities are in the bulk, for zGNRs with one and two DVs.

For clarity, we show the result for the case of the pristine sample (a zGNR without defects) with $M = 20$, $N = 300$, for different spatial configurations of the MIS in figure 3. The red curve represents the case where both MIS are located on the top edge at positions (95, 1) and (105, 1) and the black curve represents the case where both MIS are located in the interior region of the zGNR, at positions (95, 10) and (105, 10). The RKKY coupling shows a few oscillations in $R$, and then it decays rapidly with short-range behavior when both the impurities are situated within the interior of the nanoribbon and there is no discontinuity in the spatial profile of the RKKY coupling.

Here, we systematically examine how the exchange magnetic coupling of zGNR depends on the position of 5-8-5 DV defects (see figure 4). We show the range function of the RKKY interaction as a function of the distance between localized DVs (in units of the unit cell length), for a zGNR with $M = 20$, $N = 200$ (in the intrinsic case $E_F = 0$, ±1, ±2. Panels (a), (b), and (c) correspond to situations where both the DV defects are placed close to the upper edge. We fix one of the DVs at the position (95, 4) and the location of the second DV is at (105, 4) and in panels (d), (e) and (f), we consider the case when both the DV defects are away from the edge at positions (95, 10) and (105, 10). In panels (a) and (d), both MIS are located on the same zigzag edge at sites (95, 1) and (105, 1); in panels (c) and (d), both are inside the zGNR on sublattices (95, 10) and (105, 10). In panels (a) and (c), two DV defects are located at positions (5, 4) and ($n_2$, 4) with $n_2 = 6, 7, 8, ..., (5, 4)$ (a zGNR with 5-8-5 defects placed close to the upper edge) and in panels (b) and (d), DV defects are located at positions (5, 10) and ($n_2$, 10) with $n_2 = 6, 7, 8, ..., (5, 10)$ (a zGNR with defects placed relatively farther away from the top edge).

As shown in this figure, $J_{RKKY}$ displays an oscillatory behavior with respect to the distance between two DVs. Moreover, it is obvious that for the case when $U_0/t \neq 0$, the RKKY interaction falls off very rapidly and becomes zero after $\Delta R_{DV}/a = 100$. In the case when $U_0/t = 0$, the trend is reversed, as the RKKY coupling becomes zero for $\Delta R_{DV}/a < 100$, except in the case when DV defects are placed farther away from the edge and both magnetic impurities are located on the same edge.

In figure 5, we display the calculated results for the scaled RKKY interaction as a function of the vacancy potential $U_0/t$, for a zGNR with $M = 20$, $N = 200$ for various Fermi energies $E_F = 0, \pm 1, \pm 2$. Panels (a), (b), and (c) correspond to situations where both the DV defects are placed close to the upper edge. We fix one of the DVs at the position (95, 4) and the location of the second DV is at (105, 4) and in panels (d), (e) and (f), we consider the case when both the DV defects are away from the edge at positions (95, 10) and (105, 10). In panels (a) and (d) both MIS are located on the same zigzag edge at sites (95, 1) and (105, 1); in panels...
Figure 3. Scaled RKKY interaction as a function of the impurity distance for an zGNR without defects (a pristine sample) with $M = 20, N = 300$, for different spatial configurations of the MIs: The red curve represents the case where both impurities are located exactly at the edge at positions (95, 1) and (105, 1) and the black curve represents the case where both impurities are located in the bulk of the zGNR at positions (95, 10) and (105, 10).

(b) and (e), both are located inside the zGNR on the sublattices (95, 10) and (105, 10), and finally, in panels (c) and (f), both MIs are fixed at the counterpart zigzag edges at lattice sites (100, 1) and (100, 20).

As we have shown, the presence of DVs profoundly alters the magnetic ground state of zGNRs with defects. The quenching of the RKKY interaction at and above a certain vacancy potential is clear in these figures. Therefore, the Fermi energy and the spatial configuration of both MIs and the DVs have a very significant impact on the vacancy potential engineering of magnetic coupling in 2D zGNRs. It is worth mentioning that, regardless of whether DVs are close to the edge or not, the RKKY interaction has a peak structure with a maximum or minimum value. In all cases, the main peak shifts toward higher-vacancy potentials with an increase in the Fermi energy, for positive Fermi energies. By contrast, in the absence of the NNN hopping $t'$, the local density of state (LDOS) is a symmetric function with respect to a change of sign of the energy $E \rightarrow -E$, with a sharp peak exactly at $E = 0$ (not shown here). When the DV defect is moved toward the center of the ribbon in a double DV defect, the local DOS decreases rapidly.

To further investigate the presence of DVs in zGNRs, we also calculated the RKKY coupling as a function of the Fermi energy for different configurations of the MIs in figure 6. The position of both the DVs and the MIs are the same as in figure 5: in panels (a), (b) and (c), two DVs are located at positions (95, 4) and (105, 4), and in panels (d), (e) and (f), MIs are located at positions (95, 10) and (105, 10). In panels (a) and (d), both MIs are fixed at the same zigzag edge at sites (95, 1) and (105, 1); in panels (b) and (e), both are located inside the zGNR on sublattices (95, 10) and (105, 10); and finally, in panels (c) and (f), both MIs are fixed at the counterpart zigzag edges at lattice sites (100, 1) and (100, 20).

We find here that the RKKY coupling depends on the DV positions and more strongly on the distance from the edge. We now show that different types of vacancies in the same zGNR give rise to different changes in the electronic and magnetic properties. Interestingly, in the limit of a high vacancy potential, the strength of the RKKY interaction is approximately unchanged in terms of the Fermi energy i.e. the magnetic ground state of the system is constant, either positive (ferromagnetic) or negative (antiferromagnetic), with variations of the Fermi energy, and depends on the DV distance from the edge as well as the positions of two MIs. Also, in the limit of a high vacancy potential, when both impurities are located inside the zGNR, as shown in panels (b) and (e), the RKKY coupling nearly becomes zero.

Furthermore, to understand the effects of the positions of the MIs and the DVs on the RKKY properties of zGNRs, we study the local density of states (LDOS) of the zGNRs. The corresponding site-resolved LDOS for the ith site, at a given position $r$ and energy $E$, is obtained from the imaginary part of the unperturbed Green’s function as

$$LDOS(r, E) = -\frac{1}{\pi} \text{Im} G^0(r, r; E)$$

(8)

where the unperturbed Green’s function matrix $G^0(r, r; E)$ is expressed as

$$G^0(r, r; E) = \frac{1}{(E + i\eta)I - \hat{H}}$$

(9)
Figure 5. Scaled RKKY interaction as a function of the vacancy potential $U_0/t$ for zGNRs with $M = 20, N = 200$ for various Fermi energies $E_F = 0, \pm 1, \pm 2$ eV. In panels (a), (b) and (c), two DVs are located at positions (95, 4) and (105, 4) (a zGNR with 5-8-5 defects placed close to the upper edge) and in panels (d), (e) and (f), two DVs are located at positions (95, 10) and (105, 10) (a zGNR with 5-8-5 defects placed relatively farther away from the top edge). In panels (a) and (d), both MIs are located on the same zigzag edge at sites (95, 1) and (105, 1), and in panels (b) and (e), both are located inside the zGNR on sublattices (95, 10) and (105, 10); and finally, in panels (c) and (f), both MIs are fixed at the counterpart zigzag edges at lattice sites (100, 1) and (100, 20).

Figure 6. Scaled RKKY interaction as a function of the Fermi energy for zGNRs with $M = 20, N = 200$ for various vacancy potentials $U_0/t = 0, 2$. The positions of both the DVs and the MIs are the same as shown in figure 5: in panels (a), (b) and (c), two DVs are located at positions (95, 4) and (105, 4) (a zGNR with DV defects placed close to the upper edge) and in panels (d), (e) and (f), DVs are located at positions (95, 10) and (105, 10). In panels (a) and (d), both MIs are located on the same zigzag edge at sites (95, 1) and (105, 1), and in panels (b) and (e), both are located inside the zGNR on sublattices (95, 10) and (105, 10); and finally, in panels (c) and (f), both MIs are fixed at the counterpart zigzag edges at lattice sites (100, 1) and (100, 20).
where \( \eta \) is a positive infinitesimal number which is taken as 1 meV in our calculations without specification. Next, we discuss the effects of multiple DVs located near the edge as a function of the electron energy. The calculated LDOS for a zGNR with \( M = 24, N = 300 \) and \( U/\hbar t = 2 \) is shown in figure 7. Panels (a) and (c) are for a zGNR with two DVs located at the (95, 4), (105, 4) sites and the (95, 10), (105, 10) sites, respectively and panels (b) and (d) are for a zGNR with one DV located at the (95, 4) sites in panel (c), and located at the (95, 10) sites in panel (d).

The effect of the presence of the DV is clear; similarly to the RKKY coupling, the LDOS depends on the DV positions and more strongly on the distance from the edge. Zigzag GNRs with different numbers of DVs and different DV positions have different electronic LDOSs at a certain site. When a DV defect is placed close to one of the edges, the LDOS becomes more sensitive to the site position. It is worth mentioning that, regardless of whether DVs are close to the edge or not, the LDOS has a sharp peak for edge sites. In all cases, this main peak in the vicinity of the zero energy is asymmetric because in the TB model equation (1) we take into account the fact that NNN \( t' \) leads to electron–hole asymmetry and a shift of the zero LDOS peak toward lower energies. By contrast, electronic LDOS becomes different from that of a defect-free zGNR because in the TB approximation, we have investigated the combination with the TB approximation, we have investigated the evolution of the RKKY interaction mediated by a background of conduction electrons of zGNRs with defects including single, double, and multiple DVs. DVs are modeled by removing two adjacent carbon atoms from sites where hoppings to vacant sites are forbidden. The calculations show that changes in the electronic LDOS and the exchange coupling of zGNRs depend on the location of the DVs with respect to the ribbon edges and the number of DVs. We have found that introducing vacancies into zGNRs changes the spatial variation of the RKKY interaction, particularly for those magnetic impurities located on lattice sites near the vacancies. Zigzag GNRs with one or two DVs have the highest difference between the edge and bulk RKKY interaction, in comparison with samples that have more DVs. We have shown that different values of the vacancy potential in the same zigzag nanoribbon give rise to different changes in the electronic and magnetic properties. A periodic DV created in a zGNR causes a dramatic change in the magnetic ground state of the ribbon. A strong perturbation of the RKKY oscillations appears in the spatial profile of the RKKY coupling when the magnetic impurities approach a DV. Our results suggest that, on the one hand, the defect engineering
of atomic vacancies is a promising way to modify the magnetic properties of graphene nanoribbons, and, on the other hand, unusual RKKY oscillations around the DVs are a new technique for directly probing the local vacancies in a zGNR through the RKKY exchange interaction, which can lead to remarkable properties and applications in spintronics based on monolayer zGNRs.

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