Ab initio study of 3*d*, 4*d*, and 5*d* transition metal adatoms and dimers adsorbed on hydrogen-passivated zigzag graphene nanoribbons

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We performed extensive density-functional calculations of the structural, electronic, and magnetic properties of systems comprising one or two adatoms of Fe, Co, Ni, Ru, Rh, Pd, or Pt adsorbed on a hydrogen-passivated zigzag graphene nanoribbon (GNR). In all cases, the most stable structure featured the adatom(s) at positions near one of the edges of the GNR. However, whereas in the most stable structures of the single-adatom systems Ni/GNR, Ru/GNR, Rh/GNR, and Pd/GNR the adatom was located above a bay of the zigzag edge, Fe/GNR and Co/GNR were found to be most stable when the adatoms were at a first-row hole site, while the two configurations were nearly equienergetic for Pt/GNR. Similarly, whereas the most stable structures of the two-adatom systems Ni₂/GNR, Ru₂/GNR, Rh₂/GNR, and Pd₂/GNR had the adatoms above two neighboring edge bays, Co₂/GNR and Pt_2 /GNR were most stable with the adatoms stacked in a double-decker configuration above a single edge bay, and Fe₂/GNR with the adatoms stacked at a single first-row hole site. Adatom adsorption involved strong hybridization between the metal d states and the GNR states, and adsorption at sites near a GNR edge generally reduced the average magnetic moment of carbon atoms at that edge to near zero, though in some cases-notably two Co₂/GNR configurations—it led to the GNR edges having non-negligible magnetic moments of the same sign even though at the start of the optimization the metal atoms were nonmagnetic and the GNR edges had opposite signs (the preferred configuration of the pristine GNR). The electronic character of GNRs with adsorbed transition metal atoms or dimers depended on the species and concentration of the adsorbate and on the adsorption site(s), different stable or near-stable systems exhibiting semiconducting, zero-gap semiconducting, metallic, or half-metallic behavior.

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I. INTRODUCTION

Graphene nanoribbons (GNRs) are strips of graphene of nanometer scale width.¹⁻³⁴ The properties of a GNR are determined by its width and by the configuration of atoms along its long edges, which depends on its orientation in the graphene plane from which it was conceptually cut and can range from "zigzag" (two bonds of each carbon hexagon are perpendicular to the long edges) to armchair (two bonds in each hexagon are parallel to the long edges). Zigzag GNRs with hydrogen-passivated edges (HPZGNRs), in which all the spins are the same along each edge, are metallic or semiconducting depending on whether the two edges have the same or opposite spins.⁹ The latter configuration, Ferro-A, is slightly more stable than the former, Ferro-F, in which antiferromagnetic coupling between the nearest neighbors is frustrated at the center of the ribbon.^{12,25} GNR-based systems have been shown to have many potential technological applications as spin filter devices,^{9,19} spectrograph sensors,²⁰ internal connectors in integrated circuits,²¹ components of nonvolatile resistance random access memories,²⁶ and displacement detectors.²⁷

In relation to the possible applications of GNRs, it is of great interest to know how the adsorption of transition metals (TMs) may modify the properties of the GNR and/or the adatom or adatoms. However, information in this area is scarce. Rigo *et al.*,²⁵ by means of density-functional-theoretic calculations performed using SIESTA,³⁵ found that the most stable location for a single Ni atom adsorbed on an HPZGNR was above a bay of the zigzag edge; that the adsorption process reduced the magnetic moment of the Ni adatom with respect to its free-atom value due to hybridization between the Ni 3*d* orbitals and carbon 2*p* orbitals; and that the energetic preference for the Ferro-A configuration of the GNR was still maintained on Ni adsorption. Longo *et al.*,³⁰ in a study of oneto four-atom Ni and Fe nanostructures on HPZGNRs, found that the preference for edge bay sites was shared by single Fe adatoms and by Ni and Fe dimers but that Ni nanostructures were more strongly bound than Fe nanostructures, and their atoms had much smaller spin magnetic moments. Moreover, while Ni_n/HPZGNR systems, like pristine HPZGNR, always had lowest energy in the Ferro-A configuration, among Fe_n/HPZGNR systems this only occurred for one- or two-atom adstructures at edge bays and neighboring sites. Thus, as in other TM/all-carbon systems, the properties of TM/GNR systems depend to a large extent on the nature of the TM atom.

To obtain a broader view of this dependence, in the work described here we used SIESTA to study the structural, electronic, and magnetic properties of systems consisting of an HPZGNR bearing adsorbed atoms or homonuclear dimers of TMs from the late 3d, 4d, and 5d transition series. Several adsorption sites were considered (not only those of least energy) because adsorbates can be trapped in metastable states. Computational details are briefly described in Sec. II, our results are presented and discussed in Sec. III, and in Sec. IV we summarize our main conclusions.

II. DETAILS OF THE COMPUTATIONAL PROCEDURE

The computational method used in SIESTA employs localized numerical atomic orbitals as basis sets in the solution of the single-particle Kohn-Sham equations.³⁵ As in Ref. 30, all our calculations were performed using the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA).³⁶ The atomic cores were described by nonlocal norm-conserving Troullier-Martins pseudopotetials³⁷ factorized in Kleinman-Bylander form.³⁸ The pseudopotentials for Fe, Co, Ni, Ru, Rh, Pd, and Pt were generated using the valence configurations $4s^{1}3d^{7}$, $4s^{1}3d^{8}$, $4s^{1}3d^{9}$, $5s^{1}4d^{7}$, $5s^{1}4d^{8}$, $5s^{1}4d^{9}$, and $6s^{1}5d^{9}$, respectively, including nonlinear core corrections. Valence states were described using doubly polarized triple- ζ basis sets. The energy cutoff used to define the real-space grid for numerical calculations involving the electron density was 250 Ry. Using the conjugated-gradient method,³⁹ all structures were relaxed without any geometric or spin constraints until the interatomic forces were smaller than 0.005 eV/Å.

The GNR considered was a (9,0) HPZGNR,⁴ i.e., a GNR with hydrogen-passivated zigzag long edges such that a generic line perpendicular to these edges intersects nine carbon hexagons; in the terminology of Yang et al.¹¹ this is a hydrogen-passivated 10-zigzag GNR, since it has 10 zigzag chains along the direction of growth. Most calculations were performed for a $9.83 \times 50 \times 10$ Å supercell containing four unit cells of this GNR (80 C atoms plus 8 H atoms saturating the dangling bonds at the edges) plus adatoms. Periodic boundary conditions were applied in all directions to make infinite copies of a GNR that was infinite in the x direction and 22.08 Å wide in the y direction, with copies separated by 50 and 10 Å in the y and z directions, respectively. As a check on accuracy, some calculations were also performed using eight unit cells instead of four. A Monkhorst-Pack⁴⁰ grid of $9 \times 1 \times 1 k$ points was used along the x direction for integration in the Brillouin zone. In all calculations, the spins of the adatoms were initially zero, while the GNR was initially in either Ferro-A or Ferro-F form (for each adatom adsorption site configuration, calculations were performed for both these initial GNR forms).

III. RESULTS AND DISCUSSION

For single-adatom X/GNR systems (X = Co, Ru, Rh, Pd, and Pt) we investigated possible adsorption at the same sites as in our earlier study of Ni/GNR and Fe/GNR systems,³⁰ namely a central hole site (CHS), a subcentral bridge site (SCBS), and a subedge atop site (SEAS); see Fig. 1 for graphical definitions of these and other adsorption sites. Additionally, for these systems and for Ni/GNR and Fe/GNR we considered a lateral (first-row) hole site (LHS): for Ni this site was found to be energetically less favorable than SEAS by Rigo *et al.*²⁵ using SIESTA/PBE, but Cocchi *et al.*,³² using PBE in Quantum ESPRESSO (QE/PBE),⁴¹ recently found that for Co it was more favorable than CHS or an edge bay site (EBS).

For each of the above systems, Table I lists the predicted absolute values of the adsorption energies [defined as $E_a = E(\text{GNR} + X) - E(X) - E(\text{GNR}/\text{Ferro} - A)$], together with the spin magnetic moments of the metal adatoms, the average magnetic moments of the C atoms at the two edges of the ribbon, the adatom heights (defined as the difference between the z coordinate of the adatom and the average z coordinate of the C atoms in the GNR plane), and the electronic character of the system. In this table, edge 1 is the



FIG. 1. (Color online) Schematic representation of the positions of adatoms on the (9,0) zigzag GNR (the passivating hydrogens have been omitted for clarity). For dimers, the adatom referred to as TM1 in Table II is depicted in red and TM2 in blue. The exact starting positions of EBS dimer adatoms were the final positions reached by single adatoms started at SEAS positions.

edge nearest to the adatom (except for SCBS; see Fig. 1), and its carbon atoms initially had positive magnetic moments; in no case did the sign of the far-edge magnetic moments change during optimization. The projected density of states (PDOS), spin-density distribution and electronic band structure were calculated in all cases; the corresponding figures are shown here for selected systems, and for the others are included as supplementary material.⁴²

For Ru/GNR, Rh/GNR, and Pd/GNR, as for Ni/GNR, 25,30 the adsorption site in the most stable structure was an EBS reached by displacement from an initial SEAS (by 0.5–1.2 Å, depending on adatom species), but for Fe/GNR and Co/GNR it was an LHS (which for Co/GNR agrees with the results of Cocchi et al.³²), while for Pt/GNR there was little energy difference between adsorption at an EBS and at a nearby lateral bridging site to which the adatom migrated on relaxation from an initial LHS position. In most of these cases, as in most other cases of adsorption at an EBS or an LHS, the absolute value of the average magnetic moment of the near-edge carbon atoms was reduced to values $<0.05 \ \mu_B$ [the main exceptions are Pd(SEAS), Pd(LHS), Ni(LHS), and Ni(SEAS); here and elsewhere, for convenience, specific configuration names such as Pd(SEAS) or Fe(LHS)/Ferro-F refer to starting configurations, not final configurations]: in Pd(SEAS), Pd(LHS), and Ni(LHS) average near-edge magnetic moments of 0.17–0.20 μ_B were retained, and in Ni(SEAS) a moment of $0.13 \ \mu_B$.

In general, adsorption at the preferred site was just marginally less stable (by $\leq 0.02 \text{ eV/supercell}$) when the optimization was begun with the GNR as Ferro-F than as Ferro-A, the form preferred by the pristine GNR (by 0.014 eV/supercell; Ref. 30). The only exceptions were Co(LHS)/GNR and, more markedly, Pd(SEAS)/GNR. In the former case, in which the magnetic moments of the near-edge carbons were near zero regardless of the initial configuration of the GNR, a configuration in which an adatom with about

TABLE I. Absolute values of the adsorption energies E_a of single Fe, Co, Ni, Ru, Rh, Pd, and Pt adatoms on (9,0) GNRs, together with the spin magnetic moments of the adatoms, the average magnetic moments of the C atoms at the two edges of the ribbon, the heights z of the adatoms above the GNR plane, and the electronic character (EC) of the X/GNR systems (S, semiconductor; ZGS, zero-gap semiconductor; M, metallic; HM, half-metallic). Values within parentheses correspond to optimizations begun with the GNR in Ferro-A configuration, and values without to the corresponding starting Ferro-F configuration. The results for the configurations marked with an asterisk were taken from Ref. 30.

Metal Configuration		$\mu_{\mathrm{TM}} \left(\mu_B \right)$	$\langle \mu_{\mathrm{edge1}} \rangle \; (\mu_B)$	$\langle \mu_{\mathrm{edge2}} \rangle \; (\mu_B)$	z (Å)	$ E_a $ (eV)	EC	
Fe	SEAS*	3.07(-3.08)	-0.03(-0.00)	0.28(-0.28)	1.70(1.70)	1.04(1.04)	S (M)	
Fe	SCBS*		Unstable					
Fe	CHS*	2.27(-0.75)	0.27(0.28)	0.27(-0.28)	1.65(1.58)	0.61(0.07)	S (M)	
Fe	LHS	-2.95(-3.11)	-0.08(0.03)	0.29(-0.28)	1.83(1.93)	1.26(1.27)	S (HM)	
Co	SEAS	-0.36(0.15)	0.03(0.02)	0.29(-0.29)	1.70(1.70)	1.25(1.25)	S (S)	
Co	SCBS	1.31(1.28)	0.28(0.28)	0.27(-0.29)	1.86(1.93)	0.53(0.58)	HM (S)	
Co	CHS	1.31(-0.00)	0.28(0.29)	0.28(-0.29)	1.57(1.50)	0.95(0.64)	HM (M)	
Co	LHS	-1.60(-0.85)	-0.02(0.07)	0.28(-0.28)	1.62(1.59)	1.34(1.23)	HM (M)	
Ni	SEAS*	0.47(-0.51)	0.12(0.13)	0.28(-0.29)	1.71(1.71)	1.97(1.98)	S (M)	
Ni	SCBS*	0.10(-0.05)	0.29(0.29)	0.28(-0.28)	1.85(1.83)	1.28(1.30)	S (M)	
Ni	CHS*	-0.03(0.00)	0.28(0.29)	0.28(-0.29)	1.20(1.60)	1.59(1.61)	S (M)	
Ni	LHS	0.40(0.43)	0.17(0.17)	0.28(-0.29)	1.63(1.63)	1.80(1.83)	M (S)	
Ru	SEAS	-1.10(-1.05)	0.02(0.03)	0.28(-0.29)	1.79(1.79)	2.41(2.42)	ZGS (S)	
Ru	SCBS	-1.94(1.93)	0.29(0.29)	0.29(-0.29)	2.07(2.09)	1.07(1.12)	M (S)	
Ru	CHS	1.55(0.00)	0.28(0.29)	0.28(-0.29)	1.76(1.70)	1.70(1.37)	S (S)	
Ru	LHS	-0.81(-0.84)	0.08(0.08)	0.29(-0.29)	1.72(1.72)	2.22(2.24)	M (S)	
Rh	SEAS	-0.06(0.06)	-0.01(0.01)	0.29(-0.29)	1.81(1.75)	3.08(3.09)	S (S)	
Rh	SCBS	-0.76(-0.92)	0.29(0.28)	0.28(-0.28)	2.11(2.12)	1.75(1.82)	M (S)	
Rh	CHS	0.63(0.00)	0.28(0.28)	0.28(-0.28)	1.81(1.80)	2.03(1.93)	S (M)	
Rh	LHS	-0.03(0.03)	-0.01(0.01)	0.28(-0.28)	1.85(1.85)	2.59(2.59)	HM (HM)	
Pd	SEAS	0.19(0.21)	0.19(0.20)	0.28(-0.28)	2.00(2.01)	1.74(1.54)	ZGS (S)	
Pd	SCBS	-0.01(-0.00)	0.28(0.29)	0.28(-0.29)	2.23(2.23)	1.37(1.39)	M (S)	
Pd	CHS	-0.01(0.00)	0.28(0.29)	0.28(-0.29)	2.00(2.01)	1.16(1.10)	M (S)	
Pd	LHS	0.34(0.35)	0.17(0.19)	0.28(-0.29)	2.41(2.40)	1.16(1.18)	M (S)	
Pt	SEAS	0.57(0.55)	-0.01(-0.01)	0.29(-0.29)	1.73(1.75)	2.59(2.57)	S (M)	
Pt	SCBS	0.04(-0.02)	0.29(0.29)	0.29(-0.29)	2.28(2.27)	1.85(1.87)	M (S)	
Pt	CHS	-0.01(0.00)	0.28(0.28)	0.28(-0.28)	1.99(2.35)	1.24(1.92)	M (S)	
Pt	LHS	0.55(0.56)	0.09(0.12)	0.28(-0.29)	2.12(2.15)	2.58(2.60)	S (S)	

half the magnetic moment of free Co $(3 \mu_B)$ couples antiferromagnetically to the far GNR edge was 0.11 eV/supercell more stable than a configuration in which an adatom with a magnetic moment of only 0.85 μ_B couples ferromagnetically to the far edge. In Pd(SEAS)/GNR, in which the near-edge carbons retain about two-thirds of their initial magnetic moments, the Pd atom (which has zero magnetic moment when free) acquired essentially the same magnetic moment as these carbons, and Pd(SEAS)/Ferro-F was 0.20 eV/supercell more stable than Pd(SEAS)/Ferro-A. Thus in this case the GNR retained its initial magnetic configuration, but the Ferro-F form was more stable than the Ferro-A form preferred by the pristine GNR.

The adsorption energy of Co(CHS)/Ferro-F, 0.95 eV/ supercell, is very similar to the 0.97 eV per 4×4 supercell predicted for Co at a hole site on graphene by QE/PBE calculations.⁴³ The greater adsorption energies of Co(LHS)/Ferro-F (1.34 eV) and Co(LHS)/Ferro-A (1.23 eV) are therefore due to the influence of the nearby GNR edge on the interaction between adatom and substrate. The same must hold regarding the relative adsorption energies of Co(SEAS)/GNR (1.25 eV) and Co adsorbed on graphene above a carbon atom (0.44 eV),⁴³ although in this case the edge effect includes the freedom of the GNR-borne adatom to move from an SEAS to an EBS. The influence of the edge is likewise manifest in the magnetic moments: those of Co(LHS) and Co(SEAS) adatoms differ markedly from those of Co adatoms at hole and atop sites on graphene, 1 and 2.8 μ_B , respectively,⁴³ while that of Co(CHS), 1.31 μ_B , is much closer to that found in Co(hole)/graphene. Analogous similarities and differences between the present energy and magnetism results and those obtained on graphene⁴³ are found for Ni and Fe.

Like Johll *et al.*,⁴³ we find that the adsorption energies of Fe, Co, and Ni increase in the order Fe < Co < Ni, regardless of the adsorption site; this behavior is attributable to a decrease in the corresponding interconfigurational energy, i.e., the energy necessary for the transfer of one electron from an *s* orbital to a *d* orbital.⁴³ In the 4*d* TM series, the adsorption energy of Rh is greater than that of Ru, but Pd binds less strongly than Ru at all positions except SCBS, presumably because its *d* shell is complete. Similarly, between-series comparisons show that Ru binds more strongly than Fe, Rh more strongly than Co, and Pt more strongly than Ni or Pd [except that Ni(CHS)/Ferro-F is more stable than Pt(CHS)/Ferro-F], but Pd binds more weakly than Ni in all but the SCBS position.



FIG. 2. (Color online) Spin-density distribution of the system Co(LHS)/Ferro-F, calculated by taking the difference between the spin-up and spin-down densities and integrating along the *z* direction. The number on the adatom is its spin magnetic moment (in μ_B).

The magnetic moments of the TM adatoms on the GNR depend on the adsorption site, but their absolute values are in all cases except that of Pd much smaller than those of the corresponding free atoms (4 μ_B for Fe and Ru, 3 μ_B for Co and Rh, 2 μ_B for Ni and Pt; free Pd has zero magnetic moment) due to hybridization of adatom d states with GNR states to form covalent bonds. By way of example, Figs. 2 and 3 show the spin-density distribution and PDOS of Co(LHS)/Ferro-F (the most stable Co/GNR), in which the magnetic moment of the adatom is $-1.60 \mu_B$, those of the nearest-edge C atoms are near-zero, and those of the far-edge C atoms remain unchanged with respect to those of pristine GNR, $\sim 0.28 \mu_B$ (Table I). Below the Fermi level E_F , the Co PDOS is mainly composed of d-type states resulting from hybridization between the 3dorbitals of Co and the 2p orbitals of neighboring C atoms; 4s peaks, both spin-up and spin-down, are mostly above E_F , i.e., they are unoccupied. Though less than that of the free Co atom, the magnetic moment of the adatom is significant because the spin-down component of the hybrid states is almost entirely below E_F while a large amount of the spin-up component lies above E_F . By contrast with the least-energy systems



FIG. 4. (Color online) As for Fig. 2 but for Pd(SEAS)/Ferro-F.

involving metals that have nonzero magnetic moment as free atoms, Pd(SEAS)/Ferro-F exhibits little electronic interaction between metal and GNR: there is no hybridization between the outer Pd *d* orbitals and carbon orbitals, and the completed *d* shell remains far below the Fermi level (Figs. 4 and 5).

As noted in the Introduction, pristine Ferro-F HPZGNRs are metallic, Ferro-A HPZGNRs semiconducting. Table I shows that these characteristics are not necessarily retained after adsorption of TM atoms. In particular, the most stable Pd system, Pd(SEAS)/Ferro-F, is a zero-gap semiconductor; and the most stable Fe and Co systems, Fe(LHS)/Ferro-A and Co(LHS)/Ferro-F, are both half-metallic. Other low-energy systems with a conduction type different from that of the corresponding pristine GNR (i.e., the starting configuration without its adatom) are Fe(LHS)/ Ferro-F. Co(SEAS)/Ferro-F, Rh(SEAS)/Ferro-F, Pt(SEAS)/Ferro-F and Pt(LHS)/Ferro-F, all of which semiconductors; Ru(SEAS)/Ferro-F (a zero-gap are semiconductor); and Co(LHS)/Ferro-A and Pt(SEAS)/Ferro-A (both metallic). Figure 6 shows the computed electronic band structures in the cases of Co(SEAS)/Ferro-F, Pd(SEAS)/Ferro-F, and Pt(SEAS)/Ferro-A.

For the X_2 /GNR systems with X = Ru, Rh, Pd, or Pt we investigated a starting configuration in which the dimer occupied neighboring SCBS locations (2SCBS), and four



FIG. 3. (Color online) PDOS of the Co atom and an adjacent C atom in Co(LHS)/Ferro-F. The PDOS δ functions have been replaced by Gaussian functions of finite breadth.



FIG. 5. (Color online) As for Fig. 3 but for Pd(SEAS)/Ferro-F.



FIG. 6. (Color online) Electronic band structures of the systems Co(SEAS)/Ferro-F, Pd(SEAS)/Ferro-F, and Pt(SEAS)/Ferro-A. Continuous red lines correspond to spin-up bands and dashed blue lines to spin-down bands.

configurations corresponding to dimer configurations considered in our earlier study of Fe and Ni:³⁰ CHS+NHS (one atom at a CHS and the other at a neighboring hole site closer to one of the edges of the ribbon); EBS+NBS (one atom at an edge bay site and the other at a neighboring site of the same kind on the second zigzag); 2EBS (the two adatoms at two neighboring EBSes); and DD-EBS (a double-decker EBS configuration, i.e., one adatom on top of the other at a single EBS); see Fig. 1. These last three starting configurations correspond to the SEAS + NAS, 2SEAS and DD-SEAS of our previous paper,³⁰ but take into account the evolution of the adatom from an SEAS to an EBS in all the X(SEAS)/GNR systems: in all cases, the EBS adatom(s) started at the final position attained by the single adatom of the corresponding X(SEAS)/GNR system. The fifth configuration previously considered for Fe and Ni was ignored because in our previous study³⁰ it was the second least stable for both Fe and Ni, and had no special features meriting consideration in the present study. For Co, we investigated 2SCBS, CHS+NHS, EBS+NBS, 2EBS, DD-EBS and two configurations prompted by the single-adatom results of the present study, 2LHS (two lateral hole sites occupied) and DD-LHS (one adatom on top of the other at a single LHS). These latter two configurations were also investigated for Fe, given the preference of Fe/GNR for the LHS site. For each of these systems, Table II lists the predicted absolute value of the adsorption energy [defined as $E_a = E(GNR + X_2) - E(GNR + X_2)$ 2E(X) - E(GNR/Ferro - A)], the magnetic moments of the two metal adatoms, the average magnetic moments of the C atoms of the two edges, the distance between the two metal atoms, their heights above the ribbon, and the electronic character of the system. In all cases we computed, for results obtained from both Ferro-A and Ferro-F starting GNR configurations, the PDOS, the spin-density distribution, and the electronic band structure, but for lack of space most of these results are included only in the supplementary material.⁴²

The most stable configuration of the dimer is 2EBS for Ru₂/GNR, Rh₂/GNR, and Pd₂/GNR (as also for Ni₂/GNR; Ref. 30); DD-EBS for Co₂/GNR and Pt₂/GNR; and DD-LHS for Fe₂/GNR. With these dimer locations, only for Co₂ [$|E_a|(Co_2(DD - EBS))/$ Ferro – A) = 3.95 eV, $|E_a|(Co_2(DD - EBS))/$ Ferro – F) = 3.91 eV] and Ni₂ [$|E_a|(Ni_2(2EBS))/$ Ferro – A) = 4.71 eV, $|E_a|(Ni_2(2EBS))/$ Ferro – F) = 4.69 eV] is there more than 0.01 eV difference in energy between the final configurations reached from the Ferro-A and Ferro-F starting configurations of the GNR. Note that the Co dimer locates more laterally than a single Co adatom.

As in the single-adatom systems, the far edge of the GNR generally retained its initial magnetic moment, and the average magnetic moment of the near-edge carbons was reduced to near zero when the adatoms were located laterally. Three exceptions were Ru₂(2SCBS)/Ferro-F, in which the near edge reversed its magnetic moment and the adatoms became virtually nonmagnetic; Co2(DD-LHS)/GNR, in which, regardless of its starting configuration, the GNR adopted Ferro-F form (the near edge retaining 75% of its initial absolute magnetic moment) with the edges coupled antiferromagnetically to both adatoms; and Co₂(DD-EBS)/GNR (the Co₂/GNR configuration of least energy), in which the near edge reversed its magnetic moment (retaining about one-third of its absolute value) and was antiferromagnetically coupled to the adatoms. By contrast, in Fe₂(DD-LHS)/GNR and Pd₂(2EBS)/GNR, in which the near edge also retained about one-third of its initial magnetic moment, the initial configuration of the GNR (Ferro-F or Ferro-A) was maintained, and the adatoms coupled ferromagnetically to the near edge.

Although Johll *et al.*⁴³ found the Co dimer on graphene to be most stable in a double-decker configuration at a hole site, the results obtained in the present study for the single Co atom led us to ignore the analogous $Co_2(DD-CHS)$ configuration.

TABLE II. As for T	Table <mark>I</mark> but fo	r Fe, Co, Ni,	Ru, Rh, I	Pd, and Pt	dimers
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Metal	Configuration	μ_{TM1} (μ_B)	$\mu_{\mathrm{TM2}}~(\mu_B)$	$\langle \mu_{\rm edge1} \rangle \ (\mu_B)$	$\langle \mu_{\rm edge2} \rangle \ (\mu_B)$	d (Å)	z_{TM1} (Å)	z_{TM2} (Å)	$ E_a $ (eV)	EC
Fe	2LHS	-0.47 (-2.59)	3.46(3.49)	0.02(-0.05)	0.27(-0.28)	2.23(2.45)	1.63(1.75)	2.26(2.02)	2.97(3.11)	HM (M)
Fe	DD-LHS	3.15(3.17)	3.32(3.33)	0.11(0.13)	0.28(-0.28)	2.16(2.16)	2.07(2.13)	4.22(4.29)	3.72(3.73)	S (S)
Fe	CHS+NHS*	3.52(3.04)	3.19(-3.09)	0.27(0.28)	0.26(-0.27)	2.52(2.52)	1.58(1.58)	1.58(1.58)	2.55(1.99)	S (M)
Fe	2EBS*	3.45(-3.44)	3.44(-3.44)	0.29(0.29)	0.07(-0.06)	2.48(2.48)	1.93(1.92)	1.93(1.92)	3.54(3.57)	S (M)
Fe	DD-EBS*	2.40(-2.41)	3.21(-3.21)	0.28(0.29)	-0.14(0.12)	2.11(2.37)	1.93(1.81)	4.04(1.93)	3.50(3.52)	S (M)
Fe	EBS+NBS*	3.40(-3.40)	3.42(-3.43)	0.29(0.29)	0.08(-0.09)	2.37(2.37)	1.93(1.93)	1.81(1.81)	3.32(3.34)	S (M)
Co	2LHS	1.68(0.61)	0.13(0.69)	-0.04(-0.02)	0.29(-0.29)	2.35(2.29)	1.82(1.62)	1.59(1.61)	3.19(3.12)	M (S)
Co	CHS+NHS	-2.14(1.37)	-0.22(0.84)	0.28(0.28)	0.28(-0.28)	2.40(2.44)	1.81(1.63)	1.51(1.58)	2.58(2.49)	S (S)
Co	2SCBS	-2.22(1.96)	-2.20(0.25)	0.29(0.29)	0.28(-0.29)	2.14(2.22)	2.12(2.01)	2.13(2.03)	2.96(2.43)	S (S)
Co	DD-LHS	-1.37(1.39)	-2.38(2.38)	0.21(-0.21)	0.28(-0.28)	2.16(2.16)	1.72(1.72)	3.87(3.87)	3.75(3.76)	M (HM)
Co	2EBS	2.36(2.29)	2.28(2.40)	0.08(0.09)	0.28(-0.29)	2.32(2.33)	1.93(1.82)	1.83(2.02)	3.81(3.82)	HM (S)
Co	DD-EBS	1.21(1.27)	2.24(2.25)	-0.11(-0.10)	0.28(-0.29)	2.16(2.15)	1.74(1.76)	3.90(3.89)	3.91(3.95)	ZGS (S)
Co	EBS+NBS	1.90(2.16)	-1.24(2.35)	0.01(0.05)	0.29(-0.29)	2.34(2.24)	1.81(1.82)	1.93(1.94)	3.23(3.58)	HM (HM)
Ni	CHS+NHS*	-0.02(-0.01)	-0.03(0.00)	0.28(0.28)	0.27(-0.28)	2.51(2.51)	1.60(1.80)	1.60(1.80)	3.73(3.75)	S (M)
Ni	2EBS*	0.17(-0.20)	0.71(-0.76)	0.28(0.29)	0.02(-0.03)	2.50(2.50)	1.82(1.83)	1.71(1.71)	4.69(4.71)	S (M)
Ni	DD-EBS*	0.11(0.10)	1.17(1.17)	0.29(0.29)	-0.09(-0.08)	2.44(2.44)	1.71(1.71)	4.15(4.16)	4.55(4.56)	S (M)
Ni	EBS+NBS*	0.42(-0.42)	0.36(-0.44)	0.28(0.29)	0.06(-0.07)	2.47(2.47)	1.60(1.60)	1.60(1.60)	4.27(4.28)	S (M)
Ru	CHS+NHS	-0.07(-2.01)	0.03(-2.01)	0.28(0.28)	0.27(-0.28)	2.26(2.18)	2.16(2.33)	2.14(2.32)	4.62(4.90)	HM (S)
Ru	2SCBS	-0.05(-0.04)	-0.03(-0.03)	0.29(0.29)	-0.28(-0.29)	2.29(2.29)	2.04(2.07)	2.05(2.07)	4.50(4.48)	S (S)
Ru	2EBS	1.49(1.52)	1.41(1.53)	-0.00(0.00)	0.29(-0.28)	2.33(2.33)	1.78(1.78)	2.21(2.22)	5.87(5.86)	S (S)
Ru	DD-EBS	0.24(-0.24)	0.78(-0.79)	-0.02(0.01)	0.28(-0.28)	1.99(1.99)	1.93(1.93)	3.82(3.82)	5.40(5.40)	S (S)
Ru	EBS+NBS	0.47(-0.46)	0.88(-0.88)	-0.00(0.00)	0.29(-0.29)	2.37(2.37)	1.84(1.84)	2.03(2.03)	5.60(5.60)	M (M)
Rh	CHS+NHS	0.87(0.01)	0.90(-0.01)	0.28(0.28)	0.28(-0.28)	2.50(2.49)	2.20(2.17)	2.14(2.14)	5.17(5.23)	ZGS (S)
Rh	2SCBS	0.80(-0.02)	0.80(-0.02)	0.29(0.29)	0.28(-0.29)	2.49(2.49)	2.20(2.20)	2.18(2.18)	5.16(5.15)	S (S)
Rh	2EBS	0.47(0.48)	0.52(0.59)	-0.01(0.01)	0.28(-0.29)	2.52(2.52)	1.62(1.62)	2.17(2.17)	6.55(6.56)	HM (S)
Rh	DD-EBS	0.12(0.32)	0.95(0.84)	-0.03(-0.01)	0.28(-0.29)	2.30(2.30)	1.86(1.85)	4.15(4.14)	5.24(5.25)	ZGS (S)
Rh	EBS+NBS	0.29(0.28)	0.52(0.51)	-0.01(-0.00)	0.29(-0.29)	2.60(2.61)	1.82(1.82)	2.03(2.04)	6.12(6.10)	S (M)
Pd	CHS+NHS	-0.01(0.00)	-0.01(-0.00)	0.28(0.28)	0.27(-0.28)	2.79(2.79)	2.06(2.07)	2.05(2.05)	2.73(2.74)	M (S)
Pd	2SCBS	-0.02(-0.00)	-0.02(-0.00)	0.28(0.29)	0.27(-0.28)	2.76(2.75)	2.28(2.29)	2.26(2.25)	3.07(3.08)	HM (S)
Pd	2EBS	0.20(0.21)	0.26(0.27)	0.09(0.11)	0.28(-0.28)	2.67(2.67)	2.07(2.10)	2.25(2.26)	4.00(4.00)	ZGS (HM)
Pd	DD-EBS	0.09(-0.00)	0.90(0.00)	-0.02(0.00)	0.29(-0.29)	2.52(2.54)	1.91(1.92)	4.42(4.46)	3.38(3.26)	S (HM)
Pd	EBS+NBS	0.29(0.28)	0.23(0.20)	0.06(0.05)	0.29(-0.29)	2.67(2.69)	2.39(2.39)	2.40(2.41)	3.69(3.67)	S (M)
Pt	CHS+NHS	0.47(-0.49)	1.13(-1.14)	0.28(0.28)	0.28(-0.28)	2.43(2.44)	2.25(2.30)	4.68(4.70)	5.17(5.19)	M (S)
Pt	2SCBS	0.72(-0.73)	0.72(-0.73)	0.29(0.29)	0.29(-0.29)	2.56(2.56)	2.35(2.35)	2.33(2.33)	4.80(4.78)	M (HM)
Pt	2EBS	0.23(0.22)	0.35(0.34)	-0.02(-0.02)	0.29(-0.29)	2.57(2.57)	1.70(1.70)	2.16(2.16)	6.53(6.52)	S (M)
Pt	DD-EBS	-0.07(0.07)	-0.83(0.83)	-0.00(0.00)	0.29(-0.29)	2.43(2.44)	1.93(1.91)	4.32(4.30)	6.58(6.58)	HM (HM)
Pt	EBS+NBS	0.31(0.01)	0.43(0.01)	-0.01(0.00)	0.29(-0.29)	2.56(2.57)	2.46(2.47)	2.40(2.40)	6.14(6.07)	S (S)

Since in the present study it is assumed that dimer adatoms started at an SEAS and an EBS would reach the same final position, Johll et al.'s results for a double-decker Co dimer atop a graphene carbon atom may be compared with the present results for Co₂(DD-EBS)/Ferro-A, the most stable Co₂/GNR configuration we found: although the bond length in this latter (2.15 Å), and the magnetic moment of its top adatom (2.25 μ_B), are quite similar to those of Co₂(DDatop)/graphene (2 Å and 2.35 μ_B , respectively),⁴³ the adsorption energy and the magnetic moment of the bottom adatom differ substantially, 3.95 vs. 3.3 eV/supercell and 1.27 vs. 1.89 μ_B ; and analogous similarities and differences between DD-EBS/GNR and DD-atop/graphene are found for Fe2 and Ni₂. In the case of Co₂ in hole site configurations, the influence of the GNR edge is reflected more in the magnetic moments than in energies: the adsorption energy and dimer bond length of Co₂(2LHS)/Ferro-F, 3.19 eV and 2.35 Å, are fairly similar to the 2.86 eV and 2.34 Å observed for adsorption at neighboring hole sites of graphene, but the magnetic moments,

1.68 and 0.13 μ_B , are much smaller than the 2.07 μ_B observed on graphene; while Co₂(DD-LHS)/Ferro-A is quite similar to DD Co₂ at a graphene hole site⁴³ as regards dimer bond length (2.16 vs. 2.03 Å), top-atom magnetic moment (2.38 vs. 2.43 μ_B), and adsorption energy (3.76 vs. 3.58 eV), but not as regards the bottom-atom magnetic moment (1.39 vs. 1.66 μ_B). Strikingly, this last difference is reversed in the case of Fe₂, for which DD-LHS is the most stable configuration: in Fe₂(DD-LHS)/Ferro-A, in which the dimer is bound more strongly, relative to the graphene analog, than in Co₂(DD-LHS)/Ferro-A [| E_a |(DD-LHS)-| E_a |(graphene analog) = 0.73 eV vs. 0.18 eV], the magnetic moment of the bottom adatom is 3.17 μ_B , as against only 2.76 μ_B when the DD Fe dimer is above a graphene hole site.⁴³

By way of illustration, Figs. 7–12 show the spin-density distributions and PDOSes of one X_2 /GNR system that is most stable in the DD-LHS configuration, one that is most stable in the DD-EBS configuration, and one that is most stable in the 2EBS configuration. The PDOSes of Fe₂(DD-LHS)/Ferro-A



FIG. 7. (Color online) As for Fig. 2 but for Fe₂(DD-LHS)/Ferro-A.



FIG. 8. (Color online) As for Fig. 3 but for Fe₂(DD-LHS)/Ferro-A.



FIG. 9. (Color online) As for Fig. 2 but for $\mbox{Co}_2(\mbox{DD-EBS})/$ Ferro-A.



FIG. 10. (Color online) As for Fig. 3 but for $Co_2(DD-EBS)/Ferro-A$.

and Co₂(DD-EBS)/Ferro-A show that, as in the single-adatom systems, the magnetic moments of the adatoms are due to unequal occupation of the spin-up and spin-down components of orbitals resulting from hybridization between adatom 3*d* orbitals and carbon 2*p* orbitals. Hybridization is favored in the fully relaxed system by the axis of the dimer lying at an angle to the GNR plane rather than exactly perpendicular to it. It may also be noted that these Fe or Co atoms have occupied 4*s* states, particularly the top one. In the case of Ru₂(2EBS)/Ferro-F, it may be noted that the magnetic moments of the Ru adatoms are 28–35% larger than that of the single adatom of Ru(SEAS)/Ferro-F (though much smaller than that of a free Ru atom, 4 μ_B); in fact, similar increases in adatom magnetic moment relative to the corresponding single-adatom system



FIG. 11. (Color online) As for Fig. 2 but for Ru₂(2EBS)/Ferro-F.



FIG. 12. (Color online) As for Fig. 3 but for Ru₂(2EBS)/Ferro-F.

were shown by most two-adatom systems, the only exception among the most stable systems being the bottom adatom of $Pt_2(DD-EBS)/GNR$.

Like single-adatom systems, an X_2 /GNR system does not necessarily have the same electronic character as the corresponding pristine GNR. In particular, considering only the most stable X_2 /GNR configuration or configurations for each X, Ru₂(2EBS)/Ferro-F is a semiconductor, Pd₂(2EBS)/Ferro-F is a zero-gap semiconductor, and Pd₂(2EBS)/Ferro-A, Pt₂(DD-EBS)/Ferro-F, and Pt₂(DD-EBS)/Ferro-A are halfmetals. Figure 13 shows the electronic band structures of three of these systems. Note that in two of these three cases (as in numerous others) the electronic type of the two-adatom system differs not only from that of the corresponding pristine GNR, as does that of the corresponding single-adatom system, but also from this latter. For example, whereas the pristine Ferro-A GNR is a semiconductor, Pt(SEAS)/Ferro-A is metallic and $Pt_2(DD-EBS)/Ferro-A$ a half-metal. Thus the electronic character of a TM/GNR system depends not only on the adsorption site and TM species, but also on the adsorbate concentration.

IV. CONCLUSIONS

In this SIESTA/PBE study of one or two TM adatoms on a hydrogen-passivated (9,0) GNR we found that the singleadatom systems Ni/GNR, Ru/GNR, Rh/GNR, and Pd/GNR were most stable with the adatom at a SEAS; Fe/GNR and Co/GNR with the adatom at an LHS; and Pt/GNR with the adatom essentially at either of these positions. In the most stable Ni₂/GNR, Ru₂/GNR, Rh₂/GNR, and Pd₂/GNR species the adatoms adopted a 2EBS configuration, in those of Co₂/GNR and Pt₂/GNR a DD-EBS configuration, and in that of Fe₂/GNR a DD-LHS configuration. In all these systems, marked hybridization between the d states of the metal and GNR states resulted in covalent bonding and a consequent reduction in the magnetic moments of the adatoms with respect to those of the free atoms. Comparison of the predicted adsorption energies and magnetic moments of the Fe, Co, and Ni systems with published results for adatoms and dimers of these metals on graphene⁴³ shows striking differences due to the influence of the GNR edges. Depending on the number and species of adatoms, adsorption of TM atom(s) at certain sites can alter the spin preference of the pristine GNR for the Ferro-A configuration (this effect is most marked for a Pd atom at a SEAS) and/or its electronic type (metallic and semiconducting for pristine Ferro-F and Ferro-A GNRs, respectively). The modulation of the electronic properties of



FIG. 13. (Color online) As for Fig. 6 but for Ru₂(2EBS)/Ferro-F, Pd₂(2EBS)/Ferro-F, and Pt₂(DD-EBS)/Ferro-A.

GNRs by adsorption of TM atoms is of potential utility for nanoelectronics.

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