Single-Molecule Magnet Mn$_{12}$ on GaAs-supported Graphene: Gate Field Effects from First Principles

Shuanglong Liu,$^{1,2,3}$ Maher Yazback,$^{1,2,3}$ James N. Fry,$^{1}$ Xiao-Guang Zhang,$^{1,2,3}$ Hai-Ping Cheng$^{1,2,3}$

$^1$Department of Physics, University of Florida, Gainesville, Florida 32611, USA
$^2$Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA
$^3$Center for Molecular Magnetic Quantum Materials, University of Florida, Gainesville, Florida 32611, USA
Abstract

We study gate field effects on the heterostructure Mn$_{12}$O$_{12}$(COOH)$_{16}$(H$_2$O)$_4$ | graphene | GaAs via first-principles calculations. We find that under moderate doping levels electrons can be added to but not taken from the single-molecule magnet Mn$_{12}$O$_{12}$(COOH)$_{16}$(H$_2$O)$_4$ (Mn$_{12}$). The magnetic anisotropy energy (MAE) of Mn$_{12}$ decreases as the electron doping level increases, due to electron transfer from graphene to Mn$_{12}$ and change in the band alignment between Mn$_{12}$ and graphene. At an electron doping level of $-5.00 \times 10^{13}$ cm$^{-2}$, the MAE decreases by about 18% compared with zero doping. The band alignment between graphene and GaAs is more sensitive to electron doping than to hole doping, since the valence band of GaAs is close to the Fermi level. The GaAs substrate induces a small band gap in the supported graphene under zero gate field and a nearly strain-free configuration. Finally, we propose a vertical tunnel junction for probing the gate dependence of MAE via electron transport measurements.

I. INTRODUCTION

Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$, where R represents –CH$_3$ or other ligands, is a prototypical single-molecule magnet (SMM) [1] whose magnetic and electronic properties have been studied since the late 90s [2–6]. This molecule is also interesting as a spin system because its total magnetic moment puts it near the boundary between classical and quantum regimes. Tunneling magnetism measurements show its quantum nature [7], but its big magnetic moment ($S = 10$) makes it almost classical. The magnetic anisotropy energy (MAE) of Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$, which forms the barrier for magnetic tunneling, depends on the type of ligand [8–32] as well as the charge state of the molecule. In experiments, one or two electrons reduced Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$ have been synthesized by adding PPh$_4^+$ or other cations to the molecular crystal [13, 33–37]. The resulting negatively charged Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$ with integer number of electrons yields a decreased MAE for –CHCl$_2$ [35] or –C$_6$F$_5$ [13] ligands. Based on computations, a decreased MAE has also been reported for negatively charged Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$ with $-\text{H}$ [6] or $-\text{C}_6\text{H}_5$ [38] ligands. When a magnetic molecule is adsorbed on a surface, a fractional number of electrons may be transferred to/from the molecule, modifying its MAE [39–42].

*hping@ufl.edu
Most earlier experiments are performed either in solution or in molecular crystals. Recently, Hebard’s group experimentally investigated the gate-voltage dependence of transport properties of Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$ on graphene surfaces (supported by Si) with different ligands. The applied gate voltage is believed to affect transport properties by modulating the charge transfer between graphene and Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$. However, such experiments were unable to determine whether the MAE of Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$ is also tuned by the gate voltage and the charge transfer induced by it. It is also not clear how the coupling to a semiconductor substrate changes the magnetic and electronic properties of the molecule. In this study, we aim to answer these questions through a first-principles calculation using Mn$_{12}$O$_{12}$(COOH)$_{16}$(H$_2$O)$_4$ (Mn$_{12}$) as an example.

We choose GaAs-supported graphene (Gr|GaAs) as substrate. Compared to a Si substrate, GaAs provides free carriers at lower temperatures. This allows transport measurements at lower temperatures, where the magnetic properties of SMMs are better observed. Common stable GaAs surfaces include (100) and (111) with various surface reconstructions. The GaAs (111) surface has closest lattice match with the graphene lattice. Munshi et al. reported the growth of GaAs nanorods on few-layer graphene, where a GaAs(111) surface is in contact with the top graphene layer. Several epitaxial atomic structures of the interface between GaAs(111) and graphene have been proposed in literature but all with relatively large strain in graphene. Here, we propose a different atomic structure where the strain in graphene is close to zero. Using this structure, we simulate gate field effects on the Gr|GaAs interface with and without the adsorption of Mn$_{12}$. For brevity, we denote the heterostructure with Mn$_{12}$ by Mn$_{12}$|Gr|GaAs.

The rest of the paper is organized as follows. We describe the computational details in Section II. We present the atomic structure, the electronic structure, and the magnetic anisotropy of the Mn$_{12}$|Gr|GaAs heterostructure in Sections III A–III C. In Section III D, we propose a vertical tunnel junction based on the Mn$_{12}$|Gr|GaAs heterostructure. Finally, we conclude in Section IV.

II. METHOD

All calculations are based on density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) and the SIESTA package. We
use VASP to relax atomic structures with no applied electric field and SIESTA to calculate electronic structures in the presence of a gate electric field. The atomic structure is kept at the relaxed configuration with no electric field.

In VASP calculations, we apply an energy cutoff of 500 eV for plane waves and projector augmented wave (PAW) pseudopotentials \[57\]. We adopt the exchange correlation energy functional proposed by Klimes et al., optB86b \[58\], to include the van der Waals interaction between graphene and Mn$_{12}$ (or GaAs). Given the large supercell size \((a = b \approx 3.2\,\text{nm}, c = 5.2\,\text{nm})\), only the Γ point is sampled in reciprocal space. The energy tolerance for electronic self-consistency and the force tolerance for ionic relaxation are set to \(1 \times 10^{-6}\,\text{eV}\) and \(0.02\,\text{eV/Å}\) respectively. We use Gaussian smearing with a smearing parameter of \(0.2\,\text{eV}\) to facilitate the electronic self-consistent procedure. In order to eliminate interaction between periodic images in the perpendicular direction (with respect to the GaAs slab), a vacuum layer of at least 18 Å is added and electric dipole corrections (for both energy and force) are enabled. On-site Coulomb interaction \((U)\) within the DFT+\(U\) method and spin-orbit interactions are not considered for ionic relaxations.

In SIESTA calculations, we apply double-\(\zeta\) polarized (DZP) basis functions \[56\] for Mn and O atoms and single-\(\zeta\) polarized (SZP) basis functions for C, H, Ga, and As atoms. Such a mixed basis set allows us to describe the magnetic properties (due to Mn atoms) accurately with less computational load. A SZP basis set is often not sufficiently accurate for structural relaxation, but it usually produces reasonably good electronic structure for a fixed atomic structure. The basis functions are optimized for Mn$_{12}$, graphene, and the GaAs slab separately. Detailed specifications of the basis functions are presented in Appendix A. Since the optB86b functional is not available in SIESTA and the atomic structure is fixed, we use the Perdew-Burke-Ernzerhof (PBE) exchange correlation energy functional \[59\] instead. We apply norm-conserving pseudopotentials as generated by the Troullier-Martins scheme \[60\] and a mesh cutoff of 200 Ry for real space sampling. To accurately determine the Fermi energy, we adopt a \(6 \times 6\) \(k\)-grid for sampling reciprocal space \[61\] and the 4\textsuperscript{th} order Methfessel-Paxton smearing method \[62\] with a smearing temperature of 200 K. Results of convergence tests with respect to the smearing temperature and with respect to the \(k\)-grid are given in Tables B1 and B2 respectively (see Appendix B). The effects of a single back gate are modeled via the effective screening medium (ESM) method \[63\]. In the single gate configuration, the boundary condition for the back-gate (vacuum) side is constant electrostatic potential.
(vanishing first derivative of the potential). Such a non-periodic boundary condition for the electrostatic potential is imposed by the corresponding Green’s function in the ESM method. In our simulations, the back-gate (vacuum) boundary is 15 Å below (above) the bottom (the top) of the system under study. In order to improve the numerical results for band alignment within the heterostructure Mn$_{12}$|Gr|GaAs, we treat the semicore Ga $d$ electrons as valence electrons and adopt the DFT+1/2 approach for GaAs [64,65]. A DFT+1/2 cutoff radius of 3.8 Bohr is applied to limit the range of self-energy potential for As 4$p$ orbitals [66]. The DFT+1/2 band gap of bulk GaAs is calculated to be 1.526 eV, in good agreement with the experimental value of 1.52 eV at low temperatures [44], as opposed to 0.236 eV without this approach. For the same purpose of improving the band alignment, we apply the DFT+$U$ method proposed by Dudarev et al. [67] and set the on-site Coulomb interaction $U$ to 4 eV for Mn atoms. This value for $U$ yields good agreement of the density of states of Mn$_{12}$ compared with X-ray photoemission spectra (XPS) and X-ray emission spectra (XES) measurements [68].

We also use the SIESTA package to calculate the MAE of Mn$_{12}$ on graphene without the GaAs substrate (to be justified later). Spin-orbit interactions are included via the pseudopotentials [69,70] and evaluated in an on-site approximation [71]. At high electron doping levels, the self-consistent calculation fails to converge with the Methfessel-Paxton smearing method. This convergence problem is solved by using the Fermi-Dirac smearing method. To improve the numerical accuracy, we apply a $24 \times 24$ $k$-grid together with a smearing parameter of 0.041 eV and an energy tolerance of $1 \times 10^{-6}$ eV for electronic self-consistency. We set the spin-orbit coupling strength parameter to be 1.34, such that the calculated MAE (5.2 meV, or 61 K) of Mn$_{12}$O$_{12}$(COOCH$_3$)$_{16}$(H$_2$O)$_4$ is close to the experimental value [72]. The DFT+$U$ method is not applied for calculating the MAE.

III. RESULTS

A. Atomic structure

Fig. 1 shows the atomic structure of the heterostructure Mn$_{12}$|Gr|GaAs. The GaAs(111) surface is modeled by a slab consisting of six Ga atomic layers and six As atomic layers. The top two atomic layers are stabilized by a $2 \times 2$ reconstruction with Ga vacancies [49].
Each As atom at the bottom is terminated by a pseudo hydrogen atom with 0.75 electrons to avoid fictitious surface bands. The lattice constants of bulk GaAs and graphene are 5.653 and 2.461 Å, respectively. We found a good lattice match for the supercell shown in Fig. 1, which contains $4 \times 4$ GaAs unit cells (with surface reconstruction) and $13 \times 13$ graphene unit cells. This allows graphene to match the GaAs lattice with only a 0.04% compression.

During atomic relaxation, all atoms are relaxed except the bottom three Ga (As) atomic layers in order to mimic the bulk environment of GaAs. Without the Mn$_{12}$ molecule, graphene already buckles slightly due to the nonuniform interaction with GaAs. The maximal out-of-plane displacement of graphene (carbon atoms) is about ±0.08 Å, which is one order of magnitude larger than in-plane displacements. After the adsorption of Mn$_{12}$, graphene is further distorted, with a maximal out-of-plane displacement of about ±0.03 Å. Due to relatively weak chemical bonds between the core of the Mn$_{12}$ molecule and the surrounding ligands, the molecule is prone to distortion and losing parts of ligands. For example, Mn$_{12}$ loses its structural integrity when deposited on a Au(111) surface [73]. In contrast, previous DFT calculations suggest that Mn$_{12}$ remains intact on graphene [4]. In the current study, the structure of Mn$_{12}$ also remains intact with slight structural distortion when it is adsorbed on Gr|GaAs. Figs. 2a and 2b show histograms of the number of chemical bond lengths and bond angles versus change in the bond length or bond angle. All bond lengths or bond

![Diagram of Mn$_{12}$-Gr-GaAs heterostructure](image-url)
angles of Mn$_{12}$ change by no more than 0.03 Å or 4°. A fraction 69.5% of all chemical bond lengths and 60.4% of bond angles of Mn$_{12}$ change within the range of $[-0.005 : 0.005]$ Å and $[-0.25 : 0.25]$ deg. However, there are 8 Mn-O bonds which change by more than 0.015 Å in length. Each of these Mn-O bonds stems from a Mn$^{3+}$ ion of the outer Mn$_8$O$_8$ ring, and all of them point towards graphene (from Mn to O). Also, there are two Mn-O-H bond angles that change by more than 3.5 deg. For both of these Mn-O-H entities, the O-H bond belongs to a H$_2$O unit and the Mn-O bond length changes by more than 0.015 Å.

![Bar chart of bond length changes](image)

![Bar chart of bond angle changes](image)

**FIG. 2.** Statistics of (a) bond length changes and (b) bond angle changes of Mn$_{12}$. The comparison is between the Mn$_{12}$ molecule adsorbed on Gr|GaAs and an isolated free Mn$_{12}$ molecule.
B. Electronic structure

Now, we turn to the electronic structure of the Mn$_{12}$|Gr|GaAs heterostructure under both zero and finite gate electric fields. Without spin-orbit coupling, isolated graphene is a semi-metal, without an energy gap at the Fermi level. When graphene is supported on the GaAs(111) surface, calculation using SIESTA shows an energy gap of 2.2 meV at the Dirac point. There are two possible factors that can induce such an energy gap in graphene, 1) a structural distortion in graphene itself, and 2) the non-uniform potential due to the GaAs substrate. To identify which factor is responsible for the gap, we remove the GaAs substrate and compute the band structure for isolated graphene but with the same structural distortion. The resulting band structure is gapless to within our numerical precision (≈ 0.1 meV). From this we conclude that the 2.2 meV energy gap is due to the non-uniform potential of the GaAs substrate. The band gap of graphene does not change after adsorption of Mn$_{12}$.

![Band structure of Mn$_{12}$|Gr|GaAs. Squares, circles, and triangles represent, respectively, Mn$_{12}$, graphene, and GaAs states. The size of a symbol (square, circle, triangle) is proportional to the projected density of states of the Mn$_{12}$ molecule, graphene layer, or 1st GaAs layer. The Fermi level is set to zero.](image)

FIG. 3. Band structure of Mn$_{12}$|Gr|GaAs. Squares, circles, and triangles represent, respectively, Mn$_{12}$, graphene, and GaAs states. The size of a symbol (square, circle, triangle) is proportional to the projected density of states of the Mn$_{12}$ molecule, graphene layer, or 1st GaAs layer. The Fermi level is set to zero.
In the Mn$_{12}|$Gr$|$GaAs heterostructure, both graphene and GaAs are nonmagnetic, and according to our spin-polarized DFT calculations, both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Mn$_{12}$ have the same spin. We define this spin to be spin up. Fig. [3] shows the spin-up energy bands of this heterostructure. The Fermi level lies within the 2.2 meV energy gap of graphene. Relative to the Fermi energy, the HOMO orbital of Mn$_{12}$, the LUMO orbital of Mn$_{12}$, the valence band maximum (VBM) of GaAs and the conduction band minimum (CBM) of GaAs lie at $E_{\text{HOMO}} = -0.681$ eV, $E_{\text{LUMO}} = 0.192$ eV, $E_{\text{VBM}} = -0.035$ eV, and $E_{\text{CBM}} = 1.496$ eV. Compared with these four typical energies, the band gap of graphene is much smaller. For this reason, and for convenience of discussion, we will denote the Dirac point as the middle of the apexes of the upper and lower Dirac cones, even though the two cones are not quite connected. The LUMO energy $E_{\text{LUMO}}$, the energy of the Dirac point $E_{\text{Dirac}}$, and the valence band maximum $E_{\text{VBM}}$ together dictate the band alignment between Mn$_{12}$, graphene, and GaAs.

![Graph showing typical energies](image)

**FIG. 4.** The typical energies $E_{\text{LUMO}}$, $E_{\text{Dirac}}$, and $E_{\text{VBM}}$ of Mn$_{12}|$Gr$|$GaAs versus charge doping level.

Fig. [4] shows how $E_{\text{LUMO}}$, $E_{\text{VBM}}$, and $E_{\text{Dirac}}$ are affected by carrier density, i.e., the dependence of the band alignment on electrostatic doping. A negative (positive) carrier density means electron (hole) doping. All energies are measured relative to the Fermi energy, which is set at zero. Overall, all these three typical energies decrease with electron doping and increase with hole doping level. $E_{\text{Dirac}}$ in particular is more sensitive to electron doping than hole doping. For example, $E_{\text{Dirac}}$ is $-0.195$ eV at a charge density of $\rho = -0.50 \times 10^{13}$ cm$^{-2}$,
but only +0.008 eV at +0.50 \times 10^{13} \text{cm}^{-2}. The asymmetric response of \( E_{\text{Dirac}} \) to charge doping can be understood from two aspects. First, electrons are mainly added to (taken from) graphene before the HOMO of \( \text{Mn}_{12} \) (the VBM of GaAs) is brought to the Fermi level, whence \( \text{Mn}_{12} \) (GaAs) becomes charged (doped). However, the VBM of GaAs is much closer to the Fermi level than the HOMO of \( \text{Mn}_{12} \). Second, GaAs has a much higher density of states than graphene. Therefore, the same amount of charge causes a smaller shift in the energy bands when GaAs is doped than when graphene is doped. At \( \rho = -1.00 \times 10^{13} \text{cm}^{-2} \), the LUMO orbital of \( \text{Mn}_{12} \) is only a few meV above the Fermi level. According to our calculations, the LUMO of \( \text{Mn}_{12} \) becomes partially occupied, and thus \( \text{Mn}_{12} \) is negatively charged. It is noteworthy that the Dirac point of graphene becomes lower in energy than the VBM of GaAs at a point between \( \rho = 0.50 \times 10^{13} \text{cm}^{-2} \) and \( \rho = 1.00 \times 10^{13} \text{cm}^{-2} \).

We also simulate gate field effects on the band alignment of \( \text{Gr}|\text{GaAs} \) without \( \text{Mn}_{12} \). By comparing with \( \text{Mn}_{12}|\text{Gr}|\text{GaAs} \), we find that the influence of \( \text{Mn}_{12} \) on both \( E_{\text{Dirac}} \) and \( E_{\text{VBM}} \) is smaller than 1 meV within the charge density range of \([-0.50 : 1.00] \times 10^{13} \text{cm}^{-2} \). At \( \rho = -1.00 \times 10^{13} \text{cm}^{-2} \), \( E_{\text{Dirac}} \) (\( E_{\text{VBM}} \)) increases by 3.3 (2.0) meV upon the adsorption of \( \text{Mn}_{12} \).
| Doping level ($\times 10^{13}$ cm$^{-2}$) | Mn$_{12}$ ($\times 10^{-3}$) | Graphene ($\times 10^{-3}$) | 1$^{st}$ Ga layer ($\times 10^{-3}$) | 1$^{st}$ As layer ($\times 10^{-3}$) | 2$^{nd}$ Ga layer ($\times 10^{-3}$) | 2$^{nd}$ As layer ($\times 10^{-3}$) | 3$^{rd}$ Ga layer ($\times 10^{-3}$) | 3$^{rd}$ As layer ($\times 10^{-3}$) |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| −1.00                           | 0.61            | 1.67            | −6.36           | −3.38           | 0.26            | 0.03            | 0.17            | −0.14           |
| −0.50                           | 0.00            | 0.91            | −3.15           | −1.66           | 0.13            | 0.02            | 0.08            | −0.06           |
| −0.10                           | 0.00            | 0.17            | −0.59           | −0.31           | 0.03            | 0.01            | 0.01            | −0.01           |
| −0.05                           | 0.00            | 0.09            | −0.30           | −0.15           | 0.01            | 0.00            | 0.01            | −0.01           |
| 0.00                            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            |
| 0.05                            | 0.00            | −0.07           | 0.25            | 0.10            | 0.00            | −0.01           | −0.01           | 0.00            |
| 0.10                            | 0.00            | −0.18           | 0.62            | 0.30            | −0.02           | −0.01           | −0.01           | 0.01            |
| 0.50                            | 0.00            | −0.19           | 0.56            | 0.13            | −0.13           | −0.20           | −0.06           | −0.07           |
| 1.00                            | 0.00            | −0.17           | 0.41            | −0.03           | −0.21           | −0.36           | −0.12           | −0.20           |

Table I shows the distribution of excess charges at the interface of Mn$_{12}$|Gr|GaAs based on Mulliken charge analysis. The electron distribution for Mn$_{12}$|Gr|GaAs under zero doping level is subtracted as a reference. As seen from the table, the number of electrons on Mn$_{12}$ barely changes except at $\rho = −1.00 \times 10^{13}$ cm$^{-2}$, where 0.06 ($\approx 0.61 \times 10^{-3} \times 100$) electrons are added to Mn$_{12}$. Graphene gains 0.56 ($\approx 1.67 \times 10^{-3} \times 338$) at a doping level of $\rho = −1.00 \times 10^{13}$ cm$^{-2}$, and it loses 0.06 ($\approx |−0.17| \times 10^{-3} \times 338$) electrons at a doping level of $+1.00 \times 10^{13}$ cm$^{-2}$. This is consistent with our previous observation that electron doping results in a larger shift of the Dirac point than hole doping. The 1$^{st}$ GaAs layer tends to lose (gain) electrons when graphene gains (loses) electrons. This is likely due to the Coulomb repulsion between these two adjacent atomic layers. The number of electrons gained by the 1$^{st}$ GaAs layer does not change monotonically with the hole doping level, but reaches a maximum at $\rho = +0.10 \times 10^{13}$ cm$^{-2}$. This observation supports that GaAs is doped with holes at a doping level between $\rho = +0.10 \times 10^{13}$ cm$^{-2}$ and $\rho = +0.50 \times 10^{13}$ cm$^{-2}$.
FIG. 5. Mulliken charge analysis for Mn$_{12}$ within Mn$_{12}$|Gr|GaAs at a doping level of $\rho = -1.00 \times 10^{13}$ cm$^{-2}$. The charge distribution at zero doping is subtracted as a reference. O$_{\text{Mn}^{3+}}$ (O$_{\text{Mn}^{4+}}$) denotes oxygen atoms in the Mn$_8$O$_8$ ring (Mn$_4$O$_4$ center).

Compared with zero doping, the Mn$_8$O$_8$ ring, the Mn$_4$O$_4$ core, the COOH groups, and the H$_2$O units of Mn$_{12}$ gain $8.18 \times 10^{-3}$, $1.84 \times 10^{-3}$, $47.70 \times 10^{-3}$, and $3.59 \times 10^{-3}$ electrons respectively at the charge doping level of $\rho = -1.00 \times 10^{13}$ cm$^{-2}$. Although the COOH groups gain much more charge than the Mn$_8$O$_8$ ring in total, one Mn$^{3+}$ ion (in the Mn$_8$O$_8$ ring) gains more electrons than one atom in the COOH groups on average (see Fig. 5). The average amount of electrons gained by one Mn$^{3+}$ ion is about four times larger than that gained by one Mn$^{4+}$ ion (in the Mn$_4$O$_4$ core). For both Mn$^{3+}$ and Mn$^{4+}$ ions, the spin-up channel gains and the spin-down channel loses electrons. Since the highest occupied spin down molecular orbital is well below the Fermi level and thus remains fully occupied, the loss of electrons in the spin down channel is due to the deformation of occupied states. According to Boukhvalov et al. [74], redistribution of electron density affects the magnetic exchange interactions between Mn atoms.

Let $V_H(\rho, z)$ be the plane-averaged (over the x-y plane) Hartree potential of Mn$_{12}$|Gr|GaAs at position $z$ for charge doping density $\rho$. Fig. 6 shows $\delta V_H = V_H(\rho, z) - V_H(0, z)$, which can be viewed as the gate potential. We focus on three regions: 1) the region between GaAs and graphene, 2) the region between graphene and Mn$_{12}$, and 3) the region beyond Mn$_{12}$. Let regions $i$ ($i = 1, 2, \text{and } 3$) begin at $z_i^1$ and end at $z_i^2$. We define the gate potential buildup across region $i$ to be $\Delta_i = \delta V_H(z_i^2) - \delta V_H(z_i^1)$, where the argument $\rho$ is dropped for brevity. Within the charge density range $[-0.50 : 1.00] \times 10^{13}$ cm$^{-2}$, $\Delta_1$ is effectively
FIG. 6. Hartree potential difference $\delta V_H = V_H(\rho, z) - V_H(0, z)$ of Mn$_{12}$|Gr|GaAs. The horizontal arrows indicate the three regions indexed by 1, 2, and 3. H$_{Mn12}$ denotes a –H ligand of Mn$_{12}$. The inset zooms in on the region shaded in gray.

tuned, whereas $\Delta_2$ is not. This is consistent with Fig. 4 in the sense that the band alignment between graphene and GaAs (Mn$_{12}$) is (is not) effectively tuned. Within the same charge density range, $\Delta_3$ remains almost zero, which signifies that the gate electric field does not extend across Mn$_{12}$. At $\rho = -1.00 \times 10^{13}$ cm$^{-2}$, both $\Delta_2$ and $\Delta_3$ are significantly tuned as a result of Mn$_{12}$ being doped with electrons. The gate electric field $E_i$ in region $i$ is determined by $eE_i = \Delta_i/(z_i^2 - z_i^1)$ where $e$ is the unit charge (a positive value). $E_1$, $E_2$, and $E_3$ are 0.69, 0.08, and 0.05 V/nm respectively at $\rho = -1.00 \times 10^{13}$ cm$^{-2}$. Recall that GaAs becomes doped with holes at a doping level between $\rho = 0.10 \times 10^{13}$ cm$^{-2}$ and $\rho = 0.50 \times 10^{13}$ cm$^{-2}$. As consequence, $E_1 = -0.06$ V/nm at $\rho = 0.10 \times 10^{13}$ cm$^{-2}$ is larger in magnitude than $E_1 = -0.05$ V/nm at $\rho = 0.50 \times 10^{13}$ cm$^{-2}$, although the doping level for the latter is higher. Note that the adsorption of Mn$_{12}$ does not affect the Hartree potential between GaAs and graphene by much (less than 1 meV) within the charge density range $[-1.00 : 1.00] \times 10^{13}$ cm$^{-2}$. This implies that the electron tunneling rate between GaAs and graphene in transport measurements is similar with and without the presence of Mn$_{12}$. 

C. Magnetic anisotropy

Next, we examine how electrostatic doping affects the magnetic anisotropy energy of Mn$_{12}$. We have shown in Section III B that electrons can be added to but cannot be taken from Mn$_{12}$ at moderate doping levels. Therefore, we consider the effects of electron doping on MAE in particular. When the charge doping density is higher in magnitude than $-1.00 \times 10^{13}$ cm$^{-2}$, there are only graphene and Mn$_{12}$ states near the Fermi level. According to second order perturbation theory [75], the MAE is dominated by pairs of occupied and unoccupied states around the Fermi level. Therefore, it should be a good approximation to calculate MAE without GaAs. Based on the heterostructure Mn$_{12}$|Gr without GaAs, we calculate the MAE as $\text{MAE} = E_\perp - E_\parallel$, where $E_\perp$ ($E_\parallel$) is the DFT total energy for the spin of Mn$_{12}$ perpendicular (parallel) to the magnetic easy axis. The calculated MAE of Mn$_{12}$|Gr versus the charge doping density is shown in Fig. 7. As seen from the figure, the MAE decreases as the electron doping level increases. The MAE at $\rho = -5.0 \times 10^{13}$ cm$^{-2}$ decreases by about 18% compared with the value at zero doping. It is noteworthy that the MAE of Mn$_{12}$|Gr at zero doping is 1% smaller than the MAE of an isolated Mn$_{12}$ [4].

![Graph showing MAE versus charge doping density](image)

**FIG. 7.** Magnetic anisotropy energy (MAE) versus charge doping density for Mn$_{12}$|Gr.

We can relate the decrease in MAE in terms of electron transfer from graphene to Mn$_{12}$. Fig. 8 shows the number of electrons transferred from graphene to Mn$_{12}$ versus the charge doping density. The number of electrons added to Mn$_{12}$ increases with the electron doping density, and about 0.18 electrons are added to Mn$_{12}$ at $\rho = -5.0 \times 10^{13}$ cm$^{-2}$. Along with the electron transfer, the magnetic moment of Mn$_{12}$, in units of Bohr magneton, increases
by nearly the same amount as the number of electrons transferred. The magnetic moment of Mn_{12} increases rather than decreases since the spin polarization of the LUMO orbital, which receives the added electrons, is parallel to the total spin of the whole Mn_{12} molecule. Previously, Park and Pederson considered potassium addition to introduce extra electrons on Mn_{12} \footnote{6}. They found that the MAE of Mn_{12} decreases by 15\%, 37\%, and 56\% with 1, 2, and 4 extra electrons respectively. As a numerical experiment, we add extra electrons to a single isolated Mn_{12} molecule which has the same atomic positions as the Mn_{12} molecule of the Mn_{12}|Gr heterostructure. The MAE of the isolated Mn_{12} molecule decreases as the number of added electrons increases from zero to one. The MAE of isolated Mn_{12} decreases by 15\% with one additional electron, coincident with Park and Pederson’s findings. This confirms that electron transfer from graphene to Mn_{12} is responsible for the decrease in the MAE of Mn_{12}|Gr under electron doping.

However, with 0.18 additional electrons, the MAE of isolated Mn_{12} decreases by 2\%, which is much smaller than the decrease of 18\% in the MAE of Mn_{12}|Gr. This can be understood within second order perturbation theory, where pairs of occupied and unoccupied states can be classified into three types, Mn_{12}-Mn_{12}, graphene-graphene, and Mn_{12}-graphene. The 2\% decrease in the MAE of the isolated Mn_{12} can be understood as a decrease in the contribution from the Mn_{12}-Mn_{12} pairs. Since contributions to the MAE from graphene-graphene pairs are negligibly small (as seen from isolated graphene), we owe the extra reduction in the MAE of Mn_{12}|Gr to a decrease in the contribution from the Mn_{12}-graphene pairs. Such an argument is supported by the observation that electron doping dramatically changes the band alignment between Mn_{12} and graphene and thus the pairs of occupied graphene (Mn_{12}) states and unoccupied Mn_{12} (graphene) states around the Fermi level. Note that the change in the band alignment between Mn_{12} and graphene is mainly caused by electrostatic doping rather than by electron transfer between Mn_{12} and graphene. Thus, the change in the band alignment between Mn_{12} and graphene is another factor that is responsible for the decrease in the MAE of Mn_{12}|Gr under electron doping.

In order to investigate the possible role of a local electric field between Mn_{12} and graphene, we take the isolated Mn_{12} molecule again and move it close to (2.46 Å away from) the plane where the boundary condition of constant electrostatic potential is enforced. In this way, we retain a strong local electric field below Mn_{12} when the Mn_{12} molecule is charged. Otherwise, the local electric field is not as strong in our earlier numerical experiment using the isolated
Mn$_{12}$ molecule. It turns out that the decrease in MAE is still 2% with 0.18 additional electrons even though a strong local electric field is present below Mn$_{12}$. Therefore, we exclude the local electric field between Mn$_{12}$ and graphene and the associated electric field across Mn$_{12}$ as a separate reason for the decrease in the MAE of Mn$_{12}$Gr under electron doping. From perturbation theory \[76\], magnetic anisotropy of molecules is closely related to a molecular quadrupole moment, which should change with gate electric field. Since we determine molecular orbitals and thus electron density self-consistently, the change in molecular quadrupole moment and its influence on MAE have been captured implicitly by our calculations. However, the effect of electric field on MAE via spin-orbit coupling amplitude is still unknown.

![Graph showing electron transfer, magnetic moment, and charge density](image)

FIG. 8. Number of electrons transferred from graphene to Mn$_{12}$ (left-hand scale) and magnetic moment of Mn$_{12}$ (right-hand scale) versus electrostatic doping level. A negative charge density means electron doping.

**D. A vertical tunnel junction**

In this section, we propose a vertical tunnel junction for detecting the gate-dependence of MAE discussed in the previous section. The junction is illustrated in Fig. 9a where a Mn$_{12}$ molecule is sandwiched between two graphene layers. The bottom graphene layer should be supported by $n$-type GaAs, which has conducting charge carriers at low temperature (several Kelvins) \[44\] \[45\]. A gate voltage $V_g$ is applied between the bottom graphene layer and the
GaAs and a bias voltage $V_b$ between the bottom and top graphene layers. In the proposed vertical tunnel junction, GaAs is electron-doped to bring the conduction band near the Fermi level. Such a band alignment may change the behavior of the system substantially compared to the results presented in previous sections. Assuming a similar response of MAE to a gate electric field, we argue that the gate-dependence of MAE can be probed by measuring the electron tunneling current $I$ through Mn$_{12}$ as a function of $V_g$ and $V_b$.

![Diagram of a Gr|Mn$_{12}$|Gr|GaAs tunnel junction.](image)

**FIG. 9.** (a) Illustration of a Gr|Mn$_{12}$|Gr|GaAs tunnel junction. $V_g$ is gate voltage, and $V_b$ is bias voltage. The two graphene layers are separated by about 1.42 nm. (b) Calculated plane-averaged electrostatic potential of the junction. The inset shows schematic band alignment between the Mn$_{12}$ molecule and the two graphene layers. (c) Spin excitations with zero gate and with a finite gate. $|m_s\rangle$ are spin states with $m_s = \pm 10, \pm 9, \ldots, 0$. (d) Band alignment when a spin excitation enters the bias window.

First, we construct an atomic structure of the tunnel junction by adding a flat graphene layer above the Mn$_{12}$|Gr|GaAs heterostructure, and calculate from first principles the electronic structure of the junction at zero gate and zero bias. Fig. 9b shows the plane-averaged electrostatic potential (Hartree potential and ionic potential) across the tunnel junction. The electrostatic potential around the bottom graphene layer is similar to that around the top graphene layer. The inset of Fig. 9b depicts a schematic band alignment of the junction. According to our calculations, the Dirac points of either graphene layer are at the Fermi level and the LUMO of Mn$_{12}$ is 0.230 eV above the Fermi level. To estimate the structural change in Mn$_{12}$ caused by a finite bias voltage, we apply static electric fields on a single
isolated Mn$_{12}$ molecule. At 0.2 V/Å (≈ 2.84 V across the junction), the maximal change in Mn-O bonds is 0.032 Å and the change in all other chemical bonds is below 0.003 Å. At 0.1 V/Å, the change in all bond lengths is within 0.018 Å. Because the $S_z$ degeneracy is broken by the spin-orbit interaction, below the LUMO energy there should be spin states of Mn$_{12}$ on an energy scale of 1 meV relative to the ground state energy of Mn$_{12}$. Such spin states are detectable via transport measurements in single-molecule break junctions based on previous studies [77–79].

The mechanism for detecting spin excitations in a tunneling current is similar to the approach for magnetic tunnel junctions [80, 81]. The spin excitations can also be probed in the vertical tunnel junction shown in Fig. 9a. As established in Section III C, the MAE of Mn$_{12}$ can be reduced by electron doping. Consequently, the energy spacings between spin excitations are reduced, as illustrated in Fig. 9c. This is likely the case even though Mn$_{12}$ is fractionally charged and the spin projection $m_s$ is no longer a good quantum index. At finite bias voltages, the Fermi level of the bottom graphene layer $E_F$ is different from that of the top graphene $E'_F$. We call the energy range between $E_F$ and $E'_F$ the bias window. Whenever a spin excitation enters the bias window (see an illustration in Fig. 9d), an additional transmission path through the excitation of the spin state is opened, leading to a sudden increase in the tunneling current $I$. The record of multiple spin excitations allows determination of the energy spacings between these spin excitations, and thus the MAE of Mn$_{12}$. As gate voltage varies, the gate-dependence of MAE can then be probed.

In general, one can expect sensitive change of the tunneling current due to the spin state of the SMM in the junction. Therefore tunneling measurements can be used as a more general probe of the spin state of the SMM than just the MAE. We comment that the usual DFT plus non-equilibrium Green’s function (DFT+NEGF) approach [82] cannot capture the transport signals due to spin excitations. See Appendix C for DFT+NEGF results at zero bias voltage.

IV. CONCLUSION AND DISCUSSION

In conclusion, we have simulated gate field effects on the heterostructures Mn$_{12}$|Gr|GaAs, Gr|GaAs, and Mn$_{12}$|Gr. In the Mn$_{12}$|Gr|GaAs heterostructure, Mn$_{12}$ can gain but not lose electrons at moderate doping levels. The MAE of Mn$_{12}$ adsorbed on graphene decreases
by about 18% at an electron doping level of $-5.00 \times 10^{13} \text{ cm}^{-2}$. Such a decrease in the MAE is due to electron transfer from graphene to Mn$_{12}$ as well as the change in the band alignment between Mn12 and graphene. The band alignment between graphene and GaAs is more sensitive to electron doping than to hole doping. At an electron doping level of $-1.00 \times 10^{13} \text{ cm}^{-2}$, the Dirac point of graphene is lifted by about 0.24 eV relative to the valence band maximum of GaAs. Compared with electrostatic doping, the adsorption of Mn$_{12}$ does not have much effect on the band alignment between graphene and GaAs. The GaAs substrate induces a band gap of about 2.2 meV in graphene due to the interaction between GaAs and graphene. It remains to study gate field effects on similar heterostructures with other ligands around the Mn$_{12}$O$_{12}$(COOR)$_{16}$(H$_2$O)$_4$ molecule.

**ACKNOWLEDGMENTS**

This work was supported by the Center for Molecular Magnetic Quantum Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0019330. Computations were done using the utilities of the National Energy Research Scientific Computing Center and the University of Florida Research Computing.

**Appendix A: Basis set in SIESTA calculations**

Our input specifications for basis set in SIESTA are given below. For accurate description of magnetic properties, we applied DZP basis functions for Mn and O atoms. The remaining atoms (C, H, Ga, and As) employ SZP basis functions. The basis set for C atoms of Mn$_{12}$ is different from those for graphene due to the different chemical environment, and the two basis sets are optimized for Mn$_{12}$ and graphene separately.

%block PAO. Basis

| Element | n | n | Parity | C | H |
|---------|---|---|--------|---|---|
| Mn      | 4 | 2 | P      | 1 |   |
|         |   |   |        | 6.4382730 | 5.1834909 |
|         |   |   |        | 1.000    | 1.000    |
| Mn      | 3 | 2 | P      | 1 |   |
|         |   |   |        | 4.8440717 | 2.8316085 |
|         |   |   |        | 1.000    | 1.000    |
| Mn      | 2 | 2 | P      | 1 |   |
|         |   |   |        | 4.3035057 | 2.9518194 |
|         |   |   |        | 1.000    | 1.000    |
| O       |   | 2 | P      | 1 |   |
|         |   |   |        | 4.3035057 | 2.9518194 |
|         |   |   |        | 1.000    | 1.000    |
Appendix B: Convergence tests

Table B1 shows test results on Mn$_{12}$|Gr for different smearing temperatures. When the smearing temperature is reduced from 400 K to 50 K, the number of electrons on Mn$_{12}$ (Mulliken charge) varies by less than $1 \times 10^{-5}$, the total magnetic moment of the heterostructure varies by less than 0.01 $\mu_B$, and the position (in energy) of the Dirac point varies by less than 0.1 meV. This indicates that a smearing temperature of 200 K yields reliable electronic and magnetic properties. Table B2 shows test results on Mn$_{12}$|Gr for different $k$-point grids. All $k$-point grids contain the K point where the Dirac point lies, and they
yield the same energy of the Dirac point. The variation in both the number of electrons and the total magnetic moment are insignificant when the $k$-point grid is denser than $3 \times 3$. These test results support that a $6 \times 6$ $k$-point grid yields reliable electronic and magnetic properties.

TABLE B1. Convergence test on Mn$_{12}$|Gr with respect to the smearing temperature $T$. The $k$-point grid is fixed at $6 \times 6$. $N_e$ is the number of electrons on Mn$_{12}$ (Mulliken charge). $M$ is total magnetic moment. $E_{\text{Dirac}}$ is the position (in energy) of the Dirac point relative to the Fermi energy.

| $T$ (K) | $N_e$     | $M$ ($\mu_B$) | $E_{\text{Dirac}}$ (meV) |
|---------|-----------|---------------|--------------------------|
| 400     | 460.036436| 19.9992       | 0.1                      |
| 300     | 460.036438| 19.9989       | 0.1                      |
| 200     | 460.036437| 19.9983       | 0.1                      |
| 100     | 460.036434| 19.9964       | 0.1                      |
| 50      | 460.036437| 19.9918       | 0.1                      |

TABLE B2. Convergence test on Mn$_{12}$|Gr with respect to the $k$-point grid. The smearing temperature $T$ is fixed at 200 K. The quantities are the same with those in Table B1.

| $k$-grid | $N_e$     | $M$ ($\mu_B$) | $E_{\text{Dirac}}$ (meV) |
|----------|-----------|---------------|--------------------------|
| $3 \times 3$ | 460.036385| 19.9917       | 0.1                      |
| $6 \times 6$ | 460.036437| 19.9983       | 0.1                      |
| $9 \times 9$ | 460.036448| 19.9994       | 0.1                      |
| $12 \times 12$ | 460.036450| 19.9997       | 0.1                      |

Appendix C: Electron Transmission

We calculated electron transmission for a Gr|Mn$_{12}$|Gr junction under zero bias by Caroli’s formula [83]. The Green’s functions in Caroli’s formula are based on the Kohn-Sham Hamiltonian with spin-orbit coupling. Due to the huge system size (1148 atoms), we included only the $\Gamma$ point for both SCF and transport calculations. Fig. C1 shows the electron transmission as a function of energy above the Fermi level (set at zero). There are four peaks,
corresponding to the LUMO (at 0.2 eV), LUMO+1, LUMO+2, and LUMO+3 orbitals respectively. There are no peaks due to spin excitations, which are a few meV above the Fermi level in Fig. C1. It requires theoretical development beyond the DFT+NEGF method to obtain electron transport signals due to spin excitations. It is noteworthy that both absolute and relative peak positions are tunable by electron doping as well as by spin alignment.

FIG. C1. Electron transmission of a Gr|Mn$_{12}$|Gr junction under (a) zero doping and (b) an electron doping level of $\rho = -5 \times 10^{13}$ cm$^{-2}$. The black (red) line is for the spin aligned in the easy (a hard) direction. The Fermi level is set to zero.

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