

First-principles characterization of spin interfaces between magnetic cobaltocene molecule and the two-dimensional magnets CrI₃ and Fe₃GeTe₂

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In this paper, we examine the properties of spin-polarized interfaces consisting of single-molecule magnet bis(cyclopentadienyl)cobalt(II) (cobaltocene) and two-dimensional magnetic materials, semiconducting CrI₃ and metallic Fe₃GeTe₂, using first-principles density functional theory based calculations. Our calculated adsorption energies indicate the stability of these heterointerfaces with the observation of hybridization of electronic states across the interface. Magnetic properties are characterized using Heisenberg exchange parameters obtained from both total-energy differences and the Liechtenstein-Katsnelson-Antropov-Gubanov formalism in the basis of maximally localized Wannier functions. Analysis of these parameters shows a strong directional anisotropy in the magnetic substrate-molecule interaction in agreement with the nature of orbital hybridization. Additionally, possible exchange mechanisms are proposed based on orbital-resolved exchange and hopping parameters. We also show that the molecular adsorption may enhance the intralayer exchange interactions, with some exchange parameters reaching up to a threefold increase in magnitude compared to the freestanding case. Finally, we observe a 100% spin polarization at the Fermi level in the cobaltocene/CrI₃ interface, which makes it particularly promising for spin-transport applications.

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I. INTRODUCTION

The discovery of giant magnetoresistance effect [1] sparked enormous interest in spin-dependent phenomena that could be exploited in practical applications. Nowadays, a promising alternative to current charge-based devices lies in spintronics [2], which exploits the electron's intrinsic magnetic moment—spin—as an information carrier, which can be effectively manipulated with electric and magnetic fields. While spintronic devices can in principle become faster and more energy efficient than conventional electronics, practical spintronic systems still face challenges such as low spin injection efficiency and short spin diffusion lengths [3,4]. Moreover, the miniaturization of devices may be associated with low switching barriers, which increase the chance of unwanted switching of quantum states due to thermal noise [5]. The successful synthesis of graphene [6] has opened an entirely new route of realizing atomically thin materials, characterized as two-dimensional (2D) materials [7–9] with extraordinary properties tunable by chemical functionalization, strain, and external fields. In recent times, in the realm of spintronics, several magnetic tunnel junctions (MTJs) based

on 2D materials, such as CrI₃ [10,11] or Fe₃GeTe₂ (FGT) [12,13], have been proposed in combination with nonmagnetic 2D materials—graphene, BN, or InSe.

Single-molecule magnets [14] have attracted a lot of interest owing to their potential applications, ranging from quantum computing [15] to high-density data storage [16]. Molecular systems are promising since they are highly tunable via chemical functionalization, and can support longer spin lifetimes owing to weak spin-orbit coupling [3,17], but their magnetic properties on surfaces might be altered or even vanish [18]. A simple example of a molecule with a single magnetic center is metallocenes [19] and their derivatives, commonly used in catalysis of polyolefins [20]. Furthermore, they could find use in quantum circuits with interesting transport properties [21], medicinal chemistry [22], and capacitors [23].

Recently, metallocenes have been used in scanning tunneling microscopy (STM) for the functionalization of the tip that retains their magnetic properties [24]. Using cobaltocene or nickelocene molecules [25–28] as a STM tip may act as an alternative to spin-polarized STM, which is often limited by its reactivity [26]. This approach has recently been applied to 2D materials and thin films to probe local exchange fields [29,30]. Moreover, a previous work has also shown that a surface-molecule tunnel junction for high-performance spin-based devices can provide nearly 100% polarized spin current [27]. Therefore, a fundamental understanding of hybrid interfaces of magnetic molecules and surfaces is necessary.

The interaction between organometallic compounds and metallic substrates or nonmagnetic 2D material has been extensively studied [31–34]. However, when it comes to the

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interfaces with 2D magnetic materials, knowledge is limited to simple and nonmagnetic molecules [35–37]. Only recently, a work on molecular qubits placed on a 2D van der Waals (vdW) ferromagnet [38] has been reported. Unlike surfaces of metallic substrates with chemical bonds, 2D ferromagnets with layers bonded by weak van der Waals forces are fundamentally different in nature, often exhibiting complex physical phenomena. Moreover, their properties can be tuned via the number of layers, stacking, or proximity effects, which provide an extraordinary advantage in achieving novel properties.

Upon adsorption, both the molecule and the substrate are expected to influence each other. Their interaction may result in changes in geometry, charge transfer, or magnetic order and anisotropy, which could potentially lead to modified exchange interactions and the emergence of noncollinear magnetic order. In general, the interaction might be slightly weaker than that with metallic substrates, enabling preservation of unique properties of the molecule.

This work aims to deepen the understanding of the interfaces of magnetic molecules and 2D magnets, mainly focusing on charge transfer, electronic structure, and exchange interactions by first-principles density functional theory based calculations. The paper is organized as follows. In the next section, we describe the computational methods. In the Results and Discussions section, we describe the electronic structure characterization of the isolated molecule followed by the structural properties and stability of the heterointerfaces. The next subsection covers the description of electronic structure followed by the subsection on magnetic properties where we discuss in detail the exchange interaction parameters along with possible exchange pathways. Finally, we present some results on constrained moment calculations for the simulation of the effects of external stimuli, followed by the concluding remarks.

II. COMPUTATIONAL METHODS

Electronic structure calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [39] utilizing projector augmented wave potentials [40,41]. The Perdew-Burke-Ernzerhof (PBE) [42] exchange-correlation functional was employed at the GGA level. Cutoff energy of the plane waves was set to 500 eV with the electronic convergence criterion as 1×10^{-7} eV for electronic structure calculations. For the calculations of magnetocrystalline anisotropy energy (MAE) with the inclusion of spin-orbit interaction, the precision was increased to 1×10^{-8} eV. The Brillouin zone was sampled with a Γ -centered k -point grid. For the CoCp₂/CrI₃ system, a $5 \times 5 \times 1$ k -point grid was used in a 2×2 supercell of CrI₃ for the electronic structure calculations and the determination of MAE. For the FGT-based system, the k -point meshes were $15 \times 15 \times 1$ for MAE calculations, $9 \times 9 \times 1$ for the electronic structure calculations, and $5 \times 5 \times 1$ for the conversion to Wannier functions. In the self-consistent noncollinear calculations, the k -point grids were reduced to $3 \times 3 \times 1$ for CrI₃ and $7 \times 7 \times 1$ for FGT interfaces.

Vacuum of at least 15 Å was included in the unit cells to eliminate interactions along the z axis due to periodic boundary conditions. The geometry optimization criterion was set

to 0.01 eV/Å for the interfaces and 5 meV/Å for freestanding materials. To account for weak van der Waals interaction, the DFT-D3 correction by Grimme *et al.* [43] was included. DFT + U calculations were carried out within the framework of Dudarev's approach as implemented in VASP [44] to account for electron correlations in the d orbitals of Cr and Co ($U_{\text{eff}} = 3$ and 4 eV, respectively). Output data were processed using the VASPKIT tool [45].

The basis change from plane waves to maximally localized Wannier functions (MLWFs) was implemented by the WANNIER90 software [46] with initial projections from the VASP2WANNIER interface. The projections included Co d , C p , and H s states from the molecule; Cr and Fe d states for the magnetic atoms; and additionally p states of I, Ge, and Te atoms to capture relevant bonding character. The convergence tolerance for Wannierization was set to 1×10^{-5} Å². Subsequently, the resulting Hamiltonian in the MLWF basis was used to extract magnetic exchange parameters and even, orbital-decomposed ones with the TB2J code [47], based on the Liechtenstein-Katsnelson-Antropov-Gubanov (LKAG) formalism [48]. The Heisenberg Hamiltonian used in the calculation reads

$$H = - \sum_{i,j} J_{ij} \vec{e}_i \cdot \vec{e}_j. \quad (1)$$

Calculations with constrained local magnetic moment were performed employing the penalty functional approach as implemented in VASP [49], where only the direction of the magnetic moment was fixed. The total energy of the system is given by

$$E = E_0 + \sum_I \lambda [\vec{M}_I - \hat{M}_I^0 (\hat{M}_I^0 \cdot \vec{M}_I)]^2, \quad (2)$$

where E_0 denotes standard self-consistent DFT energy and $\hat{M}_I^0$ is a unit vector in the desired direction of the magnetic moment for a given site I . The local magnetic moment was obtained via the integration inside a sphere of Wigner-Seitz radius centered at a given atomic site. The radii were chosen based on the Bader charge analysis. Since the energy originating from the penalty functional is inversely proportional to λ and vanishes in the limit of $\lambda \rightarrow \infty$ [49], the λ parameter was gradually increased until the value of the energy penalty function was smaller than 5×10^{-8} eV per unit cell. Monte Carlo spin dynamics simulations were performed by the UPPASD code [50,51] using the Metropolis algorithm with 100 000 steps and three ensembles. Several system sizes were tested and periodic boundary conditions were set within the atomic plane.

III. RESULTS AND DISCUSSIONS

To investigate the interaction between the magnetic molecule and the low-dimensional substrate, two 2D magnetic materials with distinct properties, semiconducting CrI₃ and metallic Fe₃GeTe₂, were chosen as substrates. Bis(cyclopentadienyl)cobalt (cobaltocene, CoCp₂) was considered as the magnetic molecule with one unpaired electron.

A. Cobaltocene

The freestanding cobaltocene molecule was first characterized to provide a reference. Cobaltocene consists of a metal center (Co) and two cyclopentadienyl (Cp) rings. It is a structural analog of ferrocene and exists in two conformations with different alignment of the carbon rings, eclipsed conformation (D_{5h} point group), and staggered conformation (D_{5d} group) (see Supplemental Material, Fig. S1 [52]; also see [53]). Experimental measurements suggest that the rotation energy barrier is relatively small and the outcome is strongly dependent on conditions [54]. In accordance with previous theoretical studies [53,55], the eclipsed configuration was found to be more stable (by 20.6 meV at the GGA level) and was used in this work (Fig. S1 [52]). In our calculations, the high-symmetry structure with D_{5h} symmetry changes to C_{2v} due to the Jahn-Teller effect. The magnetic Co atom has the $3d^7$ electronic configuration with electronic levels split due to the presence of the ligand field (Fig. S2 [52]) and one unpaired electron carrying the magnetic moment.

Supercell calculations, which are necessary later in the study, make it impossible to rely on advanced approaches for the description of correlated d electrons (such as hybrid functionals, or DMFT) which are computationally highly demanding. The GGA + U approach is therefore employed in the study using $U_{\text{eff}} = 4$ eV for the Co atom in cobaltocene. This U_{eff} value was selected owing to a close match with the results of hybrid functional (B3LYP) calculations for a freestanding molecule, mainly regarding the hybridization of occupied electronic states. Moreover, the spin magnetic moment per molecule necessarily needs to correspond to the one unpaired electron found in the system. Detailed information on the determination of the Hubbard parameter can be found in the Supplemental Material (SM) (Table S1 [52]).

B. Structural properties

Supercells of different sizes were considered to study different effective molecular coverages on the substrates. Larger supercells represent lower cobaltocene coverage scenarios, leading to enhanced electron delocalization into the monolayer and higher total charge transfer from the molecule to the substrate, which in turn reduces the magnetic moment on Co. The 2×2 supercell was chosen as an appropriate model also taking into account the computational cost. Detailed results across different supercell sizes are provided in the SM (Tables S2–S4 [52]).

The orientation of the molecule on the surface was considered with the main rotation axis (C_5 in high-symmetry conformations) either parallel or perpendicular to the surface. Calculations with the molecule in a parallel (lying) configuration were attempted with various translational and rotational degrees of freedom, but consistently failed to converge to stable geometries. In contrast with previous theoretical studies concerning adsorption on graphene, we did not observe stable parallel orientation [56,57]. Experimentally, cobaltocene deposition on a metallic surface resulted in perpendicular orientation [25]. To identify the most stable adsorption configuration, the molecule was systematically translated in the xy plane by creating a 4×4 spatial grid. After structural

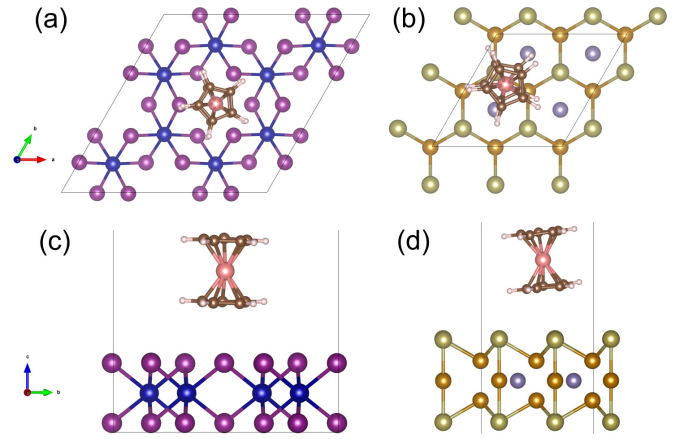


FIG. 1. Final structures after optimization. Top view and side view of CrI_3 (a), (c), and Fe_3GeTe_2 (b), (d) interfaces with cobaltocene. The atoms' colors are Cr (blue), I (purple), Fe (orange), Ge (light purple), Te (green), Co (pink), C (brown), and H (white).

relaxations, the energies were compared and the differences were typically on the order of tens of meV (Fig. S6 [52]).

The average distance between cobaltocene and 2D magnets was similar in both cases, 3.26 Å for CrI_3 , and 3.25 Å for FGT, which can be considered as the typical value of van der Waals distance. However, it should be noted that our value is larger than the previously reported value for a molecule-metal interface (2.59 Å in $\text{CoCp}_2/\text{Cu}(100)$ [25]). While the carbon rings were parallel to the CrI_3 surface, in the FGT case, the molecule became slightly slanted probably due to the surface electron density being highly anisotropic (Fig. 1). More structural information is summarized in Table I.

To assess the stability of the molecule-substrate interfaces, adsorption energies were determined at the GGA level accounting for the dispersion forces. In this work, the adsorption energy is defined as the energy difference between the total energy of the interface and the energies of freestanding substrate and molecule:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{sub}} - E_{\text{mol}}. \quad (3)$$

The resulting values were -0.96 eV for $\text{CoCp}_2/\text{CrI}_3$, and -0.63 eV for CoCp_2/FGT in a 2×2 cell, so both interfaces are expected to be stable.

C. Charge transfer

The surface-molecule interaction is complex, and in general, can also involve charge transfer. Significant changes in electron density were observed at the $\text{CoCp}_2/\text{CrI}_3$

TABLE I. Unit cell lattice parameters a , b , average (d_{avg}), and minimal (d_{min}) van der Waals distances (in Å) and adsorption energy (eV/supercell) for the interfaces in 2×2 supercells, determined using the GGA+ U method.

Substrate	a (Å)	b (Å)	d_{avg} (Å)	d_{min} (Å)
CrI_3	13.88	13.89	3.26	3.16
Fe_3GeTe_2	8.03	8.02	3.25	2.97

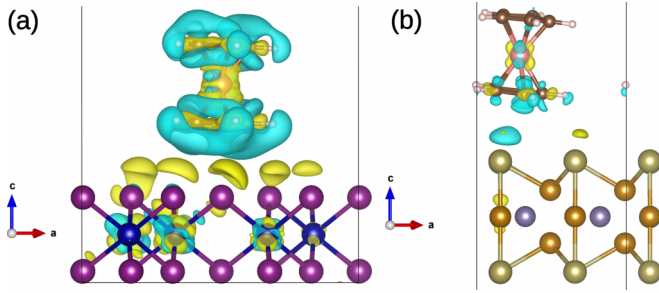


FIG. 2. Charge density differences between the deformed layers and the interface for CrI_3 (a), and Fe_3GeTe_2 (b) highlight large variations in charge density in the CrI_3 -based interface. The isosurface levels were chosen to be $5.5 \times 10^{-4} e/\text{\AA}^3$ for straightforward comparison.

interface with $0.47 e$ transferred to the substrate as predicted by the Bader charge analysis. The additional charge was redistributed mainly between atoms in the top iodine atomic layer. In contrast, for FGT, the transfer of only $0.03 e$ was observed. To resolve the modifications to electronic charge due to molecular adsorption, we calculated the charge density difference ($\Delta\rho$) as

$$\Delta\rho = \rho_{\text{interface}} - (\rho_{\text{molecule}} + \rho_{\text{substrate}}), \quad (4)$$

where $\rho_{\text{interface}}$, ρ_{molecule} , and $\rho_{\text{substrate}}$ represent the charge densities of the whole system and the isolated subsystems, respectively. For the subsystem calculations, the atomic coordinates were kept fixed at their optimized positions within the interface. The resulting redistribution of charge density is visualized in Fig. 2. The cobaltocene molecule is a 19-electron complex and according to the 18-electron rule, it is therefore expected to be an electron donor. The change of the electron density could therefore be related to the stabilization of the molecule by transferring a portion of the charge density onto the substrate atoms. Furthermore, it seems that the behavior of the substrate may facilitate the charge transfer, as the electronegativity of iodine is higher than that of both carbon and tellurium and therefore, a large transfer is observed at the CrI_3 -based interface.

It is important to assess the change in the work function of the substrate due to the molecular adsorption. Work function is a fundamental characteristic feature of surfaces defined as an energy necessary for removing an electron from the material into vacuum:

$$\Phi = -e\phi - E_F, \quad (5)$$

where e is the elementary charge, ϕ is the electrostatic potential in vacuum, and E_F is the Fermi level. For Fe_3GeTe_2 , the work function remained nearly unchanged with a value of 4.12 eV compared to 4.05 eV obtained for the freestanding layer. A significant decrease in the work function was found for the semiconducting substrate CrI_3 where it decreased from 5.65 to 4.79 eV . The line profiles of the electrostatic potential can be found in the SM (Fig. S7 [52]).

D. Electronic properties

Freestanding substrates were first characterized for a reference (Fig. S3 [52]). Afterward, both interfaces were examined for changes in electronic structure due to molecule adsorption.

While freestanding CrI_3 is a semiconductor with a band gap of around 1.1 eV , the Fermi level cuts a finite number of states in the spin-up channel at the interface (Fig. 3).

The numerical integration of density of states for the 2×2 cell of CrI_3 with CoCp_2 between -0.2 eV and the Fermi level showed that 0.98 states are present in the given energy range, which is in agreement with the assumption of one unpaired electron in the system. Therefore, the half-metallic nature of the interface seems to originate from the excess electron density of the molecule, in analogy to n -type doping. The electronic states below the Fermi level mainly consist of hybridized Co d_{xz} , Cr d_{yz} , and C p_z [Fig. 3(c)], which suggests significant electronic interaction between cobalt and chromium atoms. This is also evident in the partial charge density for these states [Fig. 4(a)].

Moreover, there is a strong peak in the majority spin channel just above the Fermi level with hybridized Cr d states, mainly d_{yz} and d_{xz} , and I p states with a smaller contribution of Co d and C p states. This could open new possibilities for electron doping, effectively shifting the Fermi level toward the significant peak.

The density of states at the Fermi level in the CoCp_2/FGT interface (Fig. 3) is higher in the spin-up channel than in the spin-down channel and would lead to a partial spin polarization of the conduction electrons. The intrinsic properties of the substrate are preserved at the interface and the system remains metallic. Based on orbital-resolved density of states, the electronic structure at the Fermi level is mostly determined by Fe d states, particularly d_{z^2} and $d_{x^2-y^2}$, with a small contribution from Te p states [Fig. 3(f)]. The highest occupied molecular orbital (HOMO) of the molecule, which mostly consists of the Co d_{yz} orbital, exhibits a broadened peak centered around -0.25 eV below the Fermi level. It is shifted in comparison with its position in isolated CoCp_2 , most probably due to charge redistribution at the interface.

E. Magnetic properties

The spin magnetic moments were obtained from GGA + U collinear calculations for both interfaces and compared to the corresponding freestanding substrates. In the CrI_3 -based system, Cr atoms show moments between $3.36 \mu_B$ (Cr_4 , Cr_5) and $3.46 \mu_B$ (Cr_6). Induced moments on iodine atoms are smaller in comparison and range from -0.13 to $-0.14 \mu_B$. In freestanding CrI_3 , Cr atoms carry a moment of $3.36 \mu_B$, and I atoms have the same moment of $-0.14 \mu_B$. It was found that the Co atom carries a moment of $0.55 \mu_B$, which is smaller than in the freestanding case, most probably due to charge transfer.

In the FGT system, the Co atom exhibits a moment of $0.92 \mu_B$. For Fe atoms, magnetic moments range from 2.43 to $2.45 \mu_B$ in the first Fe layer, from 2.41 to $2.46 \mu_B$ in the topmost Fe layer (with the largest value on Fe_7), and from 1.40 to $1.49 \mu_B$ in the middle Fe layer (maximum moment found on Fe_9). The moment on Ge atoms is constant throughout the supercell ($-0.10 \mu_B$), and Te atoms carry even smaller moments

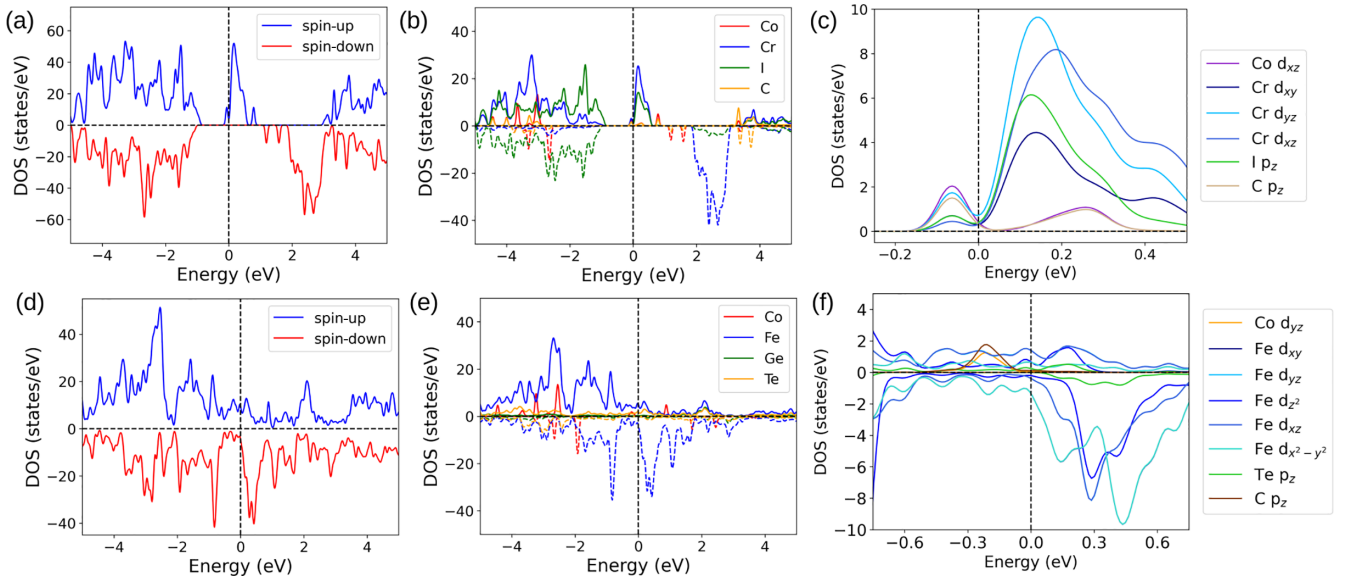


FIG. 3. Spin-polarized total (a), (d), element-projected (b), (e), and orbital-decomposed (c), (f) density of states close to the Fermi level for CoCrP₂/CrI₃ (a)–(c) and CoCrP₂/Fe₃GeTe₂ (d)–(f) interfaces. The (a), (b), (d), (e) plots show a broader interval from -5 to 5 eV around the Fermi level (E_F was set to zero); the (c), (f) part provides a more detailed view of the states close to the Fermi level.

around $-0.04 \mu_B$. In the pristine FGT structure, magnetic moments were $2.45 \mu_B$ for the Fe₁ and Fe₃ sublattices, and $1.44 \mu_B$ for Fe₂, with induced moments of $-0.11 \mu_B$ on Ge and $-0.04 \mu_B$ on Te.

At first, the magnetic ground state of the interfaces was explored at the GGA + U level. The systems were structurally optimized both in FM and AFM surface-molecule coupling and total energies were compared. In all the calculations, the molecular moment was flipped to realize the AFM coupling between the molecule and the magnetic substrate. Our calculations reveal that the ferromagnetic coupling is preferred for both interfaces.

Magnetic exchange interactions contain valuable information about the magnetic order. The magnetic exchange parameters can be obtained via multiple methods. Firstly, a model Hamiltonian can be used to estimate an effective interaction from total energy difference between FM and AFM coupling. Another option is to use LKAG formulation

employing localized basis, such as an atomic orbitals basis or maximally localized Wannier functions.

Using the Wannier basis, highly nondegenerate Heisenberg exchange interactions for the Co-Cr nearest neighbors were found (Fig. 4) despite having the same interatomic distance. This reflects the broken symmetry due to the molecule having a fivefold rotation axis while the substrate's symmetry is sixfold. The strongest interaction of 5.3 meV is found for Co–Cr₆, even higher than the strongest interaction in pristine CrI₃ which has a value of 1.2 meV. GGA calculations confirmed nondegenerate nearest-neighbor Co–Cr interactions with smaller J_{ij} magnitude while the order was preserved. This finding excludes artificial symmetry breaking from incorporating the Hubbard correction.

The direct orbital overlap between Co and Cr atoms is negligible and therefore the magnetic interactions are expected to be indirect. In order to gain insight into the interaction mechanism, the exchange paths for indirect exchange

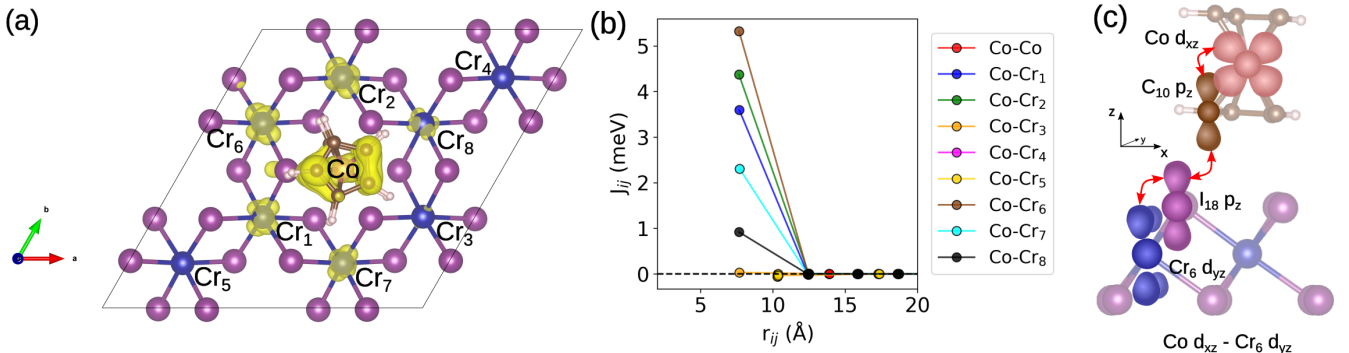


FIG. 4. (a) Top view of the partial charge density for states between -0.2 eV and E_F in the CrI₃ supercell, with isosurface level $10^{-3} e$ and Cr atoms labeled. (b) J_{ij} interaction parameters as a function of distance between atoms i and j obtained from TB2J calculation. (c) Schematic visualization of an indirect exchange mechanism across the interface, where hoppings are denoted by red arrows.

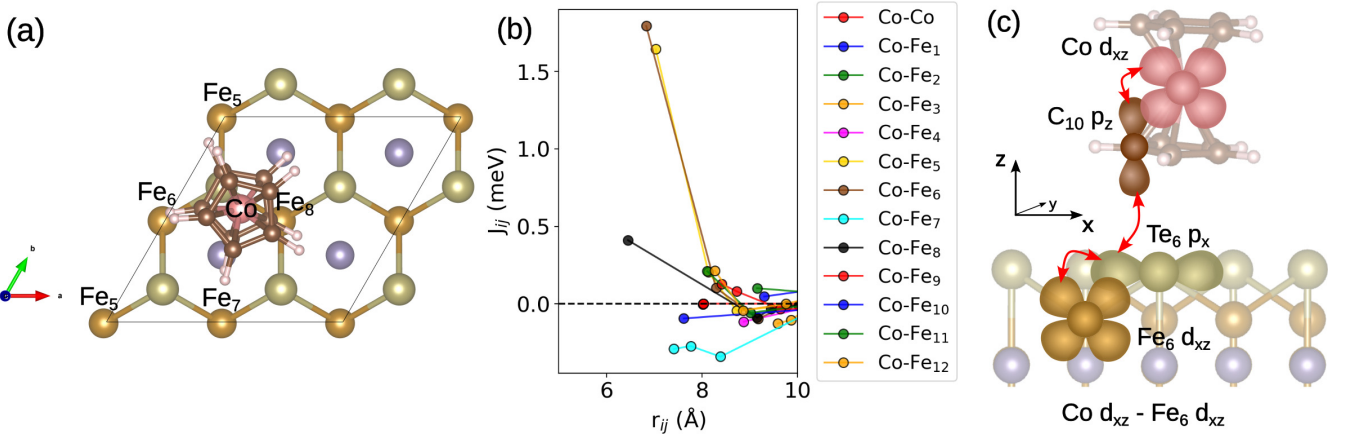


FIG. 5. (a) Top view of the FGT supercell with Fe atoms in the upper Fe layer labeled. (b) J_{ij} interaction parameters as a function of distance between atoms i and j obtained from TB2J calculation. (c) Schematic visualization of an indirect exchange mechanism across the interface, where hoppings are denoted by red arrows.

interaction between Co and the closest Cr atoms with two mediating orbitals of nonmagnetic atoms (Co–C–I–Cr) were analyzed. According to the orbital-decomposed exchange, the strongest contributions to the Co–Cr₆ interaction involve Co d_{xz} with Cr₆ d_{yz} (2.39 meV), $d_{x^2-y^2}$ (0.72 meV), and d_{xy} (1.70 meV). For the Co d_{xz} –Cr₆ d_{yz} interaction, the dominant exchange path is likely to be Co d_{xz} –C₁₀ p_z –I₁₈ p_z –Cr₆ d_{yz} [Fig. 4(c)] based on hopping parameters.

The exchange interactions were also estimated from total energy differences. The placement of CoCp₂ on CrI₃ is symmetric. Nearest-neighbor surface interactions were estimated from total energy differences between ferromagnetic (FM) and antiferromagnetic (AFM) configurations. Collinear calculations yield the energy difference $\Delta E = 98.84$ meV, which indicates a strong exchange coupling between the molecule and the surface.

The Co atom is located nearly at the center of a chromium ring (Fig. 1) with an average Co–Cr distance of 7.67 Å. In this particular case, one can consider six nearest-neighbor interactions. We map this to an Ising model,

$$E_{\text{FM}} - E_{\text{AFM}} = -2 \sum_{i,j} J_{ij} S_i S_j, \quad (6)$$

where i is identified with Co and j runs over the nearest-neighbor chromium atoms. Since both ij and ji are counted, an additional factor of 2 appears:

$$E_{\text{FM}} - E_{\text{AFM}} = -4 \sum_j J_{\text{eff}} e_{\text{Co}} e_j, \quad (7)$$

where $J_{\text{eff}} = J_{ij} S_i S_j$. J_{eff} for the Co–Cr interaction is obtained as 4.12 meV.

In the FGT supercell, there are 12 iron atoms distributed across three atomic layers: atoms Fe₁–Fe₄ are located in the bottom layer (furthest from the molecule), Fe₅–Fe₈ are in the topmost layer (closest to the molecule), and Fe₉–Fe₁₂ lie in the middle layer. The interface lacks symmetry and the J_{ij} parameters are highly nondegenerate. The individual exchange interactions between Co and Fe atoms were calculated from maximally localized Wannier functions (Fig. 5). The strongest interaction was found between Co and Fe₆ (1.79 meV) at a

distance of 6.83 Å, followed by Co–Fe₅ (1.64 meV at 7.03 Å) and Co–Fe₈ (0.41 meV at 6.45 Å). The most negative interaction occurs for the Co–Fe₇ pair, with a value of -0.34 meV at 8.39 Å. The molecule-substrate interaction in this scenario is significantly weaker than the intralayer exchange in pristine FGT (54.5 meV). Since the molecule is not placed symmetrically on the substrate, the distance between Co and Fe atoms varies. However, as in the CoCp₂/CrI₃ case, the distance is not the main factor determining the strength of the interaction. The J_{ij} value for the most significant interaction of each Co–Fe pair can be found in the SM (Table S6 [52]).

For Co–Fe₆, the dominant contributions arise from Co d_{xz} –Fe₆ d_{xz} (0.97 meV) with the main exchange path being likely Co d_{xz} –C₁₀ p_z –Te₆ p_x –Fe₆ d_{xz} [Fig. 5(c)].

In the CoCp₂/FGT interface, the energy difference between AFM and FM collinear configurations was significantly smaller than in the previous case, only 9.416 meV per supercell. The sum of individual contributions was performed in order to compare this result with LKAG formalism:

$$E_{\text{sum}} = -4 \sum_j J_{\text{Co}-j}^{(\text{TB2J})} e_{\text{Co}} e_j, \quad (8)$$

where $J_{\text{Co}-j}$ corresponds to interactions between cobalt and iron atoms. The expression in Eq. (8) should correspond to the energy difference $E_{\text{FM}} - E_{\text{AFM}}$ of 9.42 meV. Unlike in the previous case, the interface is not symmetric and cannot be properly mapped on a simple model. Furthermore, FGT is a metallic magnet, so the interaction between Co of the molecule and Fe atoms of the substrate might not be properly described by just considering the nearest-neighbor interactions.

During the summation the range of the interaction was restricted, as a large number of pairs at longer distances together with computational inaccuracy might lead to higher uncertainty. The summation yielded values of 12.68 meV (10 Å cutoff distance), and 14.20 meV (20 Å cutoff). Both values are slightly higher in comparison with total energy difference.

Modification of intralayer exchange interactions due to molecule adsorption was also analyzed. Pristine CrI₃ contains two Cr atoms in the unit cell, which form a honeycomb lattice

similar to the one in graphene or hexagonal boron nitride. For easier comparison between the unit cell and the supercell, the chromium atoms Cr_1 – Cr_4 in the supercell are considered to belong to the first sublattice (A), while Cr_5 – Cr_8 were assigned to the second sublattice (B) (Fig. 4).

Threefold symmetry in freestanding CrI_3 leads to degenerate nearest-neighbor interactions, but this symmetry is broken upon molecule adsorption. In the case of the Cr_1 atom, two interactions are largely affected (Fig. 6, top): Cr_1 – Cr_6 increases to 3.54 meV, while Cr_1 – Cr_8 becomes significantly negative at -0.54 meV. On the other hand, Cr_4 , which is located further from the molecule, shows only minor changes in exchange interactions (Fig. 6, bottom). As seen in the partial charge density plot [Fig. 4(a)], both Cr_1 and Cr_6 atoms show strong hybridization with the molecule. Heisenberg exchange parameters for all Cr atoms (Cr_1 – Cr_8) in the supercell can be found in the SM (Fig. S9 [52]).

The mean field estimation of critical temperature for pure CrI_3 is 71 K, which increased to 81 K in the presence of the molecule. Metropolis Monte Carlo simulations showed an increase in T_C from 45 K for the monolayer to 50 K for the interface obtained from the Binder cumulant crossing method (Fig. S13 [52]), supported by the divergence of susceptibility and heat capacity. The T_C of 45 K for pristine monolayer CrI_3 is in good agreement with the experimentally measured value [58]. The increase is attributed to enhanced intralayer exchange interactions as seen in Fig. 6. We also conclude that by the inspection of intralayer exchange interactions in the FGT monolayer, T_C is not expected to change significantly.

The magnetocrystalline anisotropy energy (MAE) is defined as the energy difference between the hard and easy magnetization axes. In this study, the MAE is determined as

$$E_{\text{MAE}} = E_{\text{in-plane}} - E_{\text{out-of-plane}}. \quad (9)$$

Total energy calculations were performed for three distinct orientations of the magnetic moments along the Cartesian axes (x, y, z) in 2×2 supercells. Spin-orbit coupling (SOC) was accounted for as a perturbation applied to the collinear charge density. The symmetry was broken at the $\text{CoCp}_2/\text{CrI}_3$ interface, in contrast to the freestanding CrI_3 monolayer, where in-plane orientations are typically degenerate. Consequently, the in-plane MAE values were found to be 4.93 meV/supercell (0.62 meV/f.u.) along the x direction and 1.95 meV/supercell (0.24 meV/f.u.) along the y direction; therefore, the anisotropy is reduced compared to the freestanding case (0.71 meV/f.u.). For the CoCp_2/FGT system, the MAE is significantly larger than that of the $\text{CoCp}_2/\text{CrI}_3$, yielding values of 13.30 meV/supercell (3.33 meV/f.u.) and 13.27 meV/supercell (3.32 meV/f.u.) for the x and y directions, respectively. Similar to the CrI_3 -based system, the MAE decreased upon molecular adsorption relative to the freestanding FGT (3.52 meV/f.u.).

To study possible changes in the magnetization behavior due to external factors such as applied magnetic fields, constrained magnetic moment calculations were performed for five different alignments of the magnetic moments of the substrate and the molecule as detailed in Table II. All these calculations were done fully self-consistently with the inclusion of spin-orbit coupling.

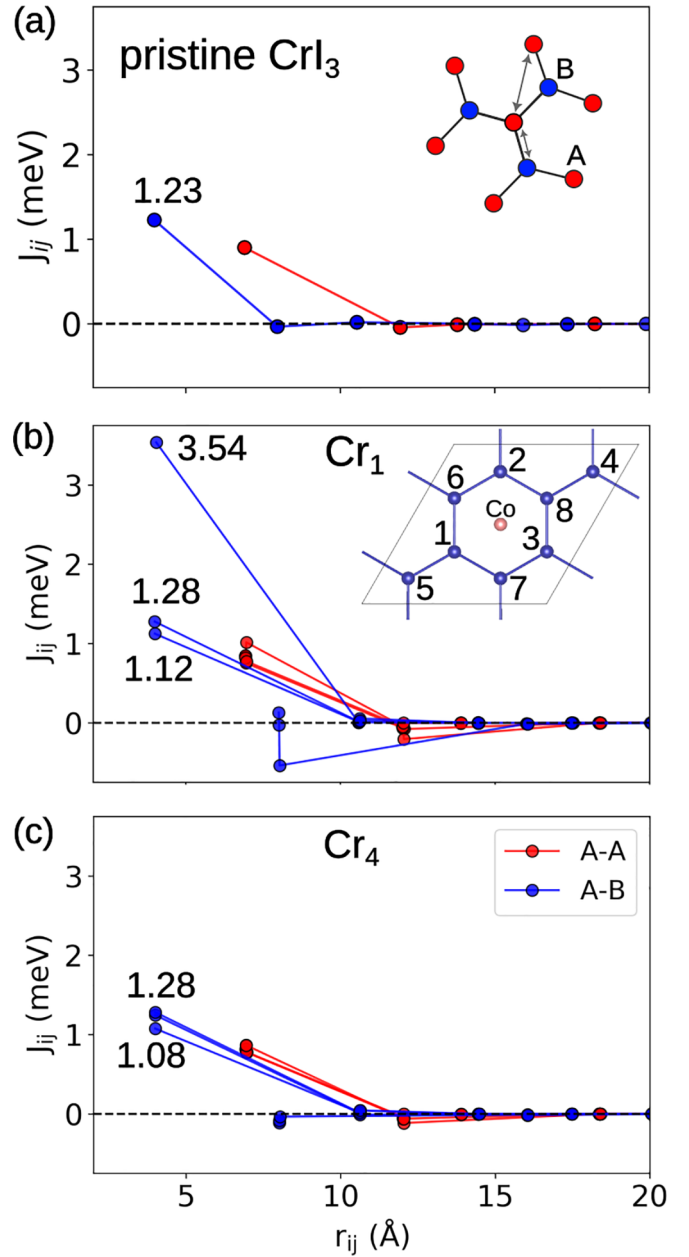


FIG. 6. Comparison of J_{ij} intralayer interactions from TB2J calculation for pristine CrI_3 (a), and Cr_1 (b) and Cr_4 (c) atoms from the $\text{CoCp}_2/\text{CrI}_3$ structure. The labels A and B in the interaction pairs are based on the two sublattices of Cr as shown in the inset in panel (a) with atoms belonging to sublattice A (red) and B (blue), and gray arrows showing the nearest-neighbor (NN) and next-nearest neighbor (NNN) interactions. The identification of Cr atoms within the supercell is shown in the inset in panel (b).

The minimum energy was found for the configuration with both substrate and molecule magnetizations oriented out of plane (configuration 3 in Table II), in line with our previous calculations where SOC effects were treated via the force theorem. The energy difference of 5.0 meV in $\text{CoCp}_2/\text{CrI}_3$, when moments are constrained in the Cartesian x and z axes, is in close agreement to the value found in MAE calculation (4.93 meV). In contrast, the value of 16.4 meV

TABLE II. The total energy differences relative to the most stable configuration for $\text{CoCp}_2/\text{CrI}_3$ and CoCp_2/FGT interfaces from constrained magnetic moment calculations. S is used to denote the magnetization orientation of the substrate while Co corresponds to the molecular magnetic moment on Co in CoCp_2 .

Configuration	Alignment	ΔE (meV)	
		$\text{CoCp}_2/\text{CrI}_3$	CoCp_2/FGT
1	$S\ x, \text{Co}\ x$	5.0	16.4
2	$S\ x, \text{Co}\ z$	40.4	20.3
3	$S\ z, \text{Co}\ z$	0.0	0.0
4	$S\ z, \text{Co}\ x$	35.0	4.9
5	$S\ z, \text{Co}\ y$	36.6	4.8

for CoCp_2/FGT is slightly higher than the MAE value of 13.30 meV.

The highest energy configuration occurs when the substrate magnetization is in plane (x direction) while the molecule maintains out of plane orientation (configuration 2 in Table II), with energy differences of 20.3 meV for FGT/CoCp_2 and 40.4 meV for $\text{CrI}_3/\text{CoCp}_2$. An important distinction between the systems is seen in configurations where the magnetic moments are perpendicular (configurations 2, 4, and 5). The FGT substrate exhibits weaker isotropic exchange coupling with the molecular magnetic moment whereas CrI_3 has a stronger coupling as shown before in Figs. 4(b) and 5(b). The energy differences in mutual perpendicular arrangements of molecular and substrate moments indicate the absence of isotropic exchange and the presence of substantial anisotropic exchange, for which the discussion is beyond the scope of the present paper.

IV. SUMMARY AND OUTLOOK

In this paper, we have studied the interaction between a magnetic molecule, cobaltocene (CoCp_2), and 2D magnetic substrates (CrI_3 , Fe_3GeTe_2 monolayers). The main focus was on the determination of structural, electronic, and magnetic properties using first-principles calculations.

Equilibrium geometry and electronic structure for the isolated CoCp_2 molecule were calculated, including benchmarking the value of the Hubbard U parameter to ensure a reliable description in the plane-wave basis. The ground-state adsorption geometries were obtained by considering various molecule-substrate configurations. The strength of interaction was determined by the nature of the substrate with specific orbital hybridizations across the interfaces.

Isotropic exchange parameters (J_{ij}) obtained using the Green's function method and total energy differences methods were compared. Strong dependence of J_{ij} parameters on the hybridization of individual atoms and orbitals was obtained via the LKAG approach. To further explore modifications of pair exchange interactions, main paths via one or two non-magnetic atoms were analyzed based on hopping parameters from the Wannier Hamiltonian, considering both interfacial and intralayer exchange.

Symmetry breaking also became apparent in the MAE calculations, such as significant inequivalence of in-plane directions in the $\text{CoCp}_2/\text{CrI}_3$ case. Overall, the preference for out of plane magnetization was weakened due to the interfaces. To evaluate possible response to external stimuli, such as magnetic field, constrained magnetic moment calculations were performed for distinct alignments of magnetic moments of both the substrate and the molecule.

The $\text{CoCp}_2/\text{CrI}_3$ interface showed conducting behavior and the possibility of highly spin-polarized current. For practical devices within an all vdW heterostructure setup, 2D NbSe_2 might be suitable for leads due to its good lattice match with CrI_3 . Since Fe_3GeTe_2 exhibits metallic behavior, it could potentially serve as the electrode.

Future work might explore molecules containing multiple magnetic centers that exhibit complex exchange interactions. Moreover, utilizing substrates with various magnetic anisotropies or modulating their properties via doping or external fields might lead to interfaces with desired properties. Lastly, the role of defects or temperature could also be taken into account to mimic realistic experimental conditions.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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