A simple electron-counting rule to determine the interlayer magnetic coupling of the van der Waals materials

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Magnetic van der Waals materials have received considerable attention, inspired by the successful exfoliation of magnetic monolayers and few layers in experiments, such as semiconducting CrI$_3$ and metallic Fe$_3$GeTe$_2$ [1–7]. Besides intriguing 2D magnetism, these layers can further form magnetic multiple layers and heterostructures as novel spintronic devices [8–11] and topological materials [12, 13]. Inside the van der Waals layer, most materials are ferromagnetic (FM) and can be understood by the conventional superexchange [14] and the itinerant exchange [15] mechanisms. In contrast, the interlayer magnetic coupling across the van der Waals gap is less explored, although it is essential to design magnetic junctions.

However, the interlayer interaction is found to be subtle. For example, in the representative material CrI$_3$, the interlayer magnetic order, FM or antiferromagnetic (AFM), depends sensitively on the stacking order and the external pressure [16, 17]. The interlayer exchange is believed to be weak because of the van der Waals gap, usually leading to low magnetic ordering temperature, e.g., 61 K for the FM CrI$_3$ [18] and 24 K for the AFM MnBi$_2$Te$_4$ [19]. Surprisingly, it is found very recently that the CrI$_3$ monolayer couples to the MnBi$_2$Te$_4$ layer in a FM way with the large exchange energy of 40 meV [20]. As separated by the van der Waals gap, interlayer magnetic exchange originates from indirect exchange pathways, referred to the super-supercexchange effect [16]. This is different from the conventional superexchange where single anion serves as an intermediate to bridge two magnetic cations [14].

I. INTRODUCTION

Magnetic van der Waals materials have received considerable attention, inspired by the successful exfoliation of magnetic monolayers and few layers in experiments, such as semiconducting CrI$_3$ and metallic Fe$_3$GeTe$_2$ [1–7]. Besides intriguing 2D magnetism, these layers can further form magnetic multiple layers and heterostructures as novel spintronic devices [8–11] and topological materials [12, 13]. Inside the van der Waals layer, most materials are ferromagnetic (FM) and can be understood by the conventional superexchange [14] and the itinerant exchange [15] mechanisms. In contrast, the interlayer magnetic coupling across the van der Waals gap is less explored, although it is essential to design magnetic junctions.

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II. COMPUTATIONAL METHODS

But challenging to clarify the microscopic mechanism of interlayer magnetic coupling and provide a generic but simple understanding that is applicable to a wide range of van der Waals magnets. In the present work, we aim to build up a general rule to determine interlayer magnetic coupling for van der Waals materials. This rule defines two basic exchange pathways that cross the van der Waals gap (see Figure 1): The AFM exchange between two occupied $d$ orbitals and the FM exchange between one occupied and the other empty $d$ orbital, which can be regarded as generalizing the 180-degree superexchange pathway to the van der Waals layers. Only through counting the occupation of $d$ orbitals with different exchange effects, without requiring sophisticated calculations, interlayer magnetic order can be anticipated with the satisfactory accuracy for both semiconducting and metallic materials. With this rule, monolayers are classified into type-I ($d^n$, $n < 5$) and type-II ($d^n$, $n \geq 5$), where $n$ is the $d$-orbital occupation number of the magnetic cation. Subsequently, three types of bilayer-interfaces are identified. Bilayers as type I-II, II-II and I-I display FM, AFM and competing magnetic orders, respectively. In addition, for metallic bilayers, the extra itinerant exchange effect via the interlayer free carrier hopping requires a minor correction to the above rule. Our proposed rule is further verified by first-principles computations. By revealing the interlayer magnetic exchange, our work serves a simple guidance for the experiment and theory on layered magnetic structures.
monolayers, are investigated. They all display the intralayer FM order except MnY$_2$ (Y = Cl/Br) and CrS$_2$ monolayer phase with the stripy AFM order. Furthermore, van der Waals magnets considered here include I-T phase, CrI$_3$ phase, CrGeTe$_3$ phase. Their coordination environments all belong to the distorted octahedral field (Figure S1). Therefore, the d-orbital crystal field is of the $t_{2g}$-$e_g$ type. Regarding the experimental progress, we restrict our discussions to materials with 3$d$ transitional elements and the colinear intralayer FM coupling in this work. Therefore, the strong 3$d$ onsite Coulomb repulsion ($U$) is usually much larger than the crystal field splitting ($\Delta$). Thus, magnetic cation is assumed to be high spin state while low spin state can also be incorporated as discussed in the following text.

First-principles calculations have been performed in the framework of density functional theory using the Vienna Ab initio Simulation Package (VASP) [26, 27]. Perder-Burke-Ernzerhof (PBE) formulation was applied to describe the exchange-correlation under the generalized gradient approximation (GGA) [28]. Van der Waals corrections are included by the DFT+D3 method [29] in the bilayer structural optimization. Considering the localized nature of 3$d$ electrons for transition metals, the GGA+U method was adopted [30], where the effective $U - J$ value was set to 3 eV, a typical value for 3$d$ transitional elements. Spin-orbit coupling (SOC) is not considered here, which is generally weak compared to the exchange coupling in 3$d$ systems.

III. RESULTS AND DISCUSSIONS

A. The rule for the interlayer exchange coupling

Interlayer magnetic coupling between van der Waals layers originates from the indirect exchange interaction, where $p$ orbitals in adjacent layers intermediates intralayer $d$ orbitals, as presented in Figure 1(a). Here we concentrate on interlayer magnetic coupling and intralayer magnetic order is assumed to be FM. To understand the interlayer interaction, we classify two basic exchange pathways, as shown in Figure 1(b): (i) AFM exchange interaction between two occupied $d$ orbitals, (ii) FM exchange interaction between one occupied and the other empty $d$ orbital.

Two basic exchange pathways can be further rationalized by two elementary process: intralayer $d$-$p$ hopping and interlayer $p$-$p$ interaction. The former one is stronger and spin selective based on the occupation of $d$ orbitals. Given the average exchange pathway is along the out-of-plane direction, the $d$-$p$ coupling is approximately equivalent to that of the 180° superexchange. However, the latter one is subtle. For the weak interlayer $p$-$p$ interaction, we postulate that it favors the anti-parallel alignment of $p$ electrons that are separated by van der Waals gap, since this alignment allows interlayer electron hopping and has the stronger kinetic energy contribution.

To determine the interlayer magnetic order, we need to count all the basic exchange pathways based on the $d$ orbital occupation and evaluate the total exchange interaction. To further proceed, we categorize two kinds of monolayers as type-I and type-II, with electronic states as $d^n$ ($n < 5$) and $d^n$ ($n \geq 5$). Since van der Waals magnets considered here belong to the distorted octahedral ligand filed with the high spin state (Figure S1), electronic configurations can be denoted as type-I $t_{2g}^x e_g^y$ ($x+y < 5$) and type-II $t_{2g}^x e_g^y$ ($x+y \geq 5$). Compared to type-I monolayer, all $d$ orbitals in type-II layer are occupied with no empty $d$ orbitals available. Therefore, two types of monolayers construct three types of bilayers: type-I-I, II-II and I-II. With this classification, we can intuitively predict that the type II-II bilayer exhibits the interlayer AFM order, since only occupied to occupied exchange, i.e. the AFM coupling, pathways exist. In contrast, both the type I-I and type I-II bilayers display competing FM and AFM orders, since two types of pathways (occupied to occupied, and occupied to empty) coexist. But, for the type I-II, we further find that the FM coupling is usually more favorable because of the orbital orientation and large on-site $U$, as discussed in the following text.

FIG. 1. Schematics of the interlayer exchange coupling. a. The exchange coupling between two layers via the ligand atoms crossing the van der Waals gap. M1, M2 and L1, L2 denote magnetic cations and ligands, respectively. Red arrows represent spins on magnetic cations. The blue dumbbell shapes represent the $p$ orbitals of ligands. b. Two basic exchange pathways with the AFM and FM exchange effects.
### B. Insulating magnetic layers

To verify the above scenario, we first investigated insulating bilayers with varied electronic configurations and stacking orders. First-principles results are presented in Table I and the corresponding energy differences between interlayer FM and AFM order against stacking orders are shown in Section SII. Firstly, for type I-I bilayer composed of MS₂ (M = V, Mn), VI₃, CrI₃, and CrGeTe₃ layers, as what we predicted, they show competing magnetic orders, which originate from both the existence of FM and AFM exchange pathways. For instance, bilayer phase of VS₂ possess interlayer FM order, in accordance with experiments and their corresponding bulk phases [21]. CrGeTe₃-MnS₂ heterostructure and CrGeTe₃ bilayers display the interlayer AFM order. However, most bilayers and heterostructures display the stacking-dependent magnetism, as denoted by FM/AFM in the green box in Table I. Such a stacking-dependent magnetic order is a manifestation of the competing exchange pathways.

For type II-II bilayers and heterostructures composed of MX₂ (M = Mn, Co, Ni, X = Cl/Br), they always favor the AFM coupling since only the AFM exchange pathway between occupied d orbitals is available. This type of bilayer also incorporates few layer phases of MnBi₂Te₄, whose electronic state of magnetic cation Mn²⁺ is t₃₂g e₃g². For type I-II bilayers, all tested heterostructures exhibit FM order, for instance CrI₃-MBr₂ (M = Mn, Co, Ni). Therefore, the FM exchange pathway is always more favorable than the AFM one. Our previous work also identified the interlayer FM coupling for CrI₃-MnBi₂Te₄ heterostructure [20], which can be incorporated into this type I-II system.

To understand Table I in detail, we elaborated exchange pathways for different bilayers based on d-orbital occupation. Figure 2(a) presents a typical electronic configuration as t₂₃g e₀₂g⁻t₃₂g e₀g² for type I-I bilayer. On the one hand, the AFM coupling results in two exchange pathways: (1) magnetic interaction between two occupied t₂g orbitals (t₂g-p-p-t₂g); (2) magnetic interaction between two empty e₉ orbitals (e₉-p-p-e₉). On the other hand, there also exists two FM exchange pathways between one empty e₉ and one occupied t₂g orbital (e₉-p-p-t₂g and t₂g-p-p-e₉). In Figure 2(a), the basic hopping process further indicates that the t₂g-p hopping involves the onsite U energy with the π-bonding between the t₂g and p orbitals. On the other hand, the e₉-p hopping is related to the crystal field splitting energy Δ with the σ-bonding. Because of U > Δ and the stronger σ-bonding compared to the π-bonding, e₉-p hopping is generally more favorable than the t₂g-p process.

However, the stronger e₉-p hopping exists in both AFM e₉-p-p-e₉ and FM e₉-p-p-t₂g and t₂g-p-p-e₉, and their combined effect is the uncertain interlayer magnetic order. While for the weak interlayer p-p interaction, it can be further tuned by stacking orders and affects AFM e₉-p-p-e₉ and t₂g-p-p-t₂g and FM e₉-p-p-t₂g and t₂g-p-p-e₉ to different extent, thus leading to the stacking dependent magnetism. For other electronic configurations of type I-I bilayer, both the empty and occupied d orbitals generally exist, whose interaction scenario is similar to the t₂g³-e₉⁰-t₂g²-e₉² system, as presented in Figure S4.

However, the situation is simpler for the type I-II interface. In Figure 2(c), AFM effect is from the interaction between two occupied t₂g orbitals in type I and type II layer (t₂g-p-p-t₂g), and FM effect is produced by the interaction between one empty e₉ in type I and one occupied t₂g in type II (e₉-p-p-t₂g). Comparing AFM and FM pathways, the σ-type e₉-p hopping with the Δ gap is much stronger than the corresponding π type t₂g-p hopping with the U gap. Thus, we obtain the FM order in the end. Finally, for type II-II bilayer in Figure 2(b), it is not surprising that interlayer interaction always favors AFM order, since only AFM pathways exist.

To summarize, type I-I, type II-II and type I-II bi-
layer exhibit competing, AFM and FM orders, and we further validate this rule from model Hamiltonian approaches (see the Supplementary Materials). Generally, when multiple \( d \) orbitals exist, through listing exchange pathways based on \( d \) orbital occupation, we can determine the interlayer magnetic order by considering their competitions. This procedure is also applicable to the low spin state of magnetic cations once their electronic configurations are clarified.

C. Metallic magnetic layers

The above interlayer exchange coupling applies to both insulating and metallic systems. For metallic bilayers, however, the additional interlayer exchange from itinerant carriers modifies the interaction. To understand this correction, bilayers composed of intrinsic metallic monolayers, including VSe\(_2\), CrS\(_2\), MnSe\(_2\), FeCl\(_2\) and FeBr\(_2\), are investigated. The former three candidates belong to type I and FeCl\(_2\) and FeBr\(_2\) belong to type II. Results are presented in Table II. The interlayer magnetic order for type I-I, type II-II and type I-II bilayer basically follows the above scenario. But some deviations indeed appear: type I-I bilayers mainly adopt interlayer FM order; some candidates in type II-II and type I-II region even exhibit stacking dependent magnetism, like type II-II FeCl\(_2\)-FeBr\(_2\) and type I-II VSe\(_2\)-FeCl\(_2\).

To understand this behavior, the interlayer exchange effect from intralayer itinerant carriers need to be incorporated. Similar to the itinerant magnetism [15], the spin configuration that allows interlayer electron hopping among free carriers is favored, since it contributes to the kinetic energy. Figure 3(a) presents the typical electronic configuration for FM metals. It shows that interlayer carrier hopping is allowed for FM state but impeded for AFM order, since, in AFM order, conducting carriers in

| TABLE II. Interlayer magnetic orders for metallic bilayers with varied electronic states. |
|---------------------------------------------|------------------|------------------|
| Type I                                             | Type II                                              |
| VSe\(_2\)                                       | FM               | FM               | FM/AFM                     | FM/AFM                     | FM               |
| CrS\(_2\)                                       | FM/AFM          | FM               | FM/AFM                     | FM               | FM               |
| MnSe\(_2\)                                      | FM/AFM          | FM               | FM/AFM                     | FM               | FM               |
| Type II                                           | FM/AFM          | FM/AFM           | FM/AFM                     | FM/AFM           |
| FeCl\(_2\)                                      | FM/AFM          | FM/AFM           | FM/AFM                     | FM/AFM           |
| FeBr\(_2\)                                      | FM/AFM          | FM/AFM           | FM/AFM                     | FM/AFM           |

FIG. 2. Exchange pathways for a. type I-I, b. type II-II and c. type I-II bilayer. \( \Delta \) and \( U \) represents the \( t_{2g} - e_g \) crystal field splitting and the onsite Hubbard energy, respectively. \( \pi \) and \( \sigma \) represent the \( d - p \) atomic bonding type.
the top layer can only hop into gapped states in the lower layer and vice versa. Therefore, free carriers bring additional FM exchange effect, and this is applicable to both type I-I and type II-II bilayers. For the former, the FM coupling is enhanced. For the latter, the itinerant FM interaction induces the competition with the AFM coupling, resulting in the stacking dependent magnetism in type II-II, as seen in Table II.

However, the type I-II bilayer possesses special electronic configuration, where itinerant electrons in different layers have different spin components. Spin up electrons in type I and spin down electrons in type II, as shown in Figure 3(b). Therefore, for AFM order, conducting electrons in type I and type II can hop into each others partially occupied states rather than gapped states in the less favorable FM order. As a result, free carriers in type I-II bilayer bring AFM exchange effect that competes with the dominant FM superexchange, and lead to the stacking dependent magnetism in type I-II VSe\textsubscript{2}-FeCl\textsubscript{2} and CrS\textsubscript{2}-FeCl\textsubscript{2}.

Besides intrinsic metallic phases, carrier doped insulating bilayers also has the itinerant exchange effect. As illustrated in Figure 3(c) and S5, for both electron and hole doping, type I-I MnS\textsubscript{2}-MnS\textsubscript{2} and CrI\textsubscript{3}-CrI\textsubscript{3} and type II-II MnCl\textsubscript{2}-MnCl\textsubscript{2} and NiCl\textsubscript{2}-NiCl\textsubscript{2} all manifest the enhanced FM or weakened AFM coupling, with the increasing concentration of free carriers. It can be understood that, FM effect introduced by free carriers gradually modify the insulating exchange. Interestingly, the phase transition for CrI\textsubscript{3}-CrI\textsubscript{3}, MnCl\textsubscript{2}-MnCl\textsubscript{2}, and NiCl\textsubscript{2}-NiCl\textsubscript{2} can even be observed as increasing the carrier doping. This is consistent with the experimental electrostatic doping control of 2D magnetism in CrI\textsubscript{3} bilayer [31]. Furthermore, for type I-I and type II-II bilayers with the intrinsic AFM order, electrostatic doping introduces FM effect and can be regarded as a general strategy to effectively tune the phase transition from AFM to FM order. While for type I-II bilayer, we have tested MnS\textsubscript{2}-NiBr\textsubscript{2} and MnS\textsubscript{2}-MnBr\textsubscript{2} heterostructure and results in Figure 3(c) and Figure S5 show that electron doping weakens the intrinsic FM coupling since free carriers in type I and type II layer possess different spin components, as predicted. On the other hand, due to the special alignment of electronic states (Figure S6), doped holes possess the same spin components, and still lead to the FM exchange effect.

To summarize, metallic bilayers basically follow the prediction of superexchange. The additional itinerant FM effect for type I-I and type II-II and itinerant AFM effect for type I-II need to be considered to understand some deviations. Even for insulating layers, carrier doping can display the similar itinerant exchange interactions.

IV. CONCLUSION

To conclude, we proposed a simple rule to determine the interlayer magnetic coupling between van der Waals materials based on the $d$-orbital occupation. Through elaborating exchange pathways and identifying their combined effects, the general competing, AFM and FM interlayer magnetic orders for type I-I, type II-II and type I-II bilayers are predicted and verified by first-principles computations and model Hamiltonian calculations. While for metallic bilayer, the additional exchange correction by free carriers is revealed. Our work clarifies the interlayer exchange mechanism and provides guiding principles to design and tailor 2D magnetic materials.
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