Giant proximity exchange and valley splitting in transition metal dichalcogenide/hBN/(Co, Ni) heterostructures

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We investigate the proximity-induced exchange coupling in transition-metal dichalcogenides (TMDCs), originating from spin injector geometries composed of hexagonal boron-nitride (hBN) and ferromagnetic (FM) cobalt (Co) or nickel (Ni), from first principles. We employ a minimal tight-binding Hamiltonian that captures the low energy bands of the TMDCs around $K$ and $K'$ valleys, to extract orbital, spin-orbit, and exchange parameters. The TMDC/hBN/FM heterostructure calculations show that due to the hBN buffer layer, the band structure of the TMDC is preserved, with an additional proximity-induced exchange splitting in the bands. We extract proximity exchange parameters in the 1–10 meV range, depending on the FM. The combination of proximity-induced exchange and intrinsic spin-orbit coupling (SOC) of the TMDCs, leads to a valley polarization, translating into magnetic exchange fields of tens of Tesla. The extracted parameters are useful for subsequent exciton calculations of TMDCs in the presence of a hBN/FM spin injector. Our calculated absorption spectra show large splittings for the exciton peaks; in the case of MoS$_2$/hBN/Co we find a value of about 8 meV, corresponding to about 50 T external magnetic field in bare TMDCs. The reason lies in the band structure, where a hybridization with Co $d$ orbitals causes a giant valence band exchange splitting of more than 10 meV. Structures with Ni do not show any $d$ level hybridization features, but still sizable proximity exchange and exciton peak splittings of around 2 meV are present in the TMDCs.

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I. INTRODUCTION

Spintronics is based on the efficient injection, transport, manipulation, and detection of spins in a material [1–3]. The current generation of spintronics devices employ hybrid geometries consisting of several two-dimensional (2D) materials [4,5] in order to overcome intrinsic limitations of the transport medium. A new branch of physics has emerged, which is solely dedicated to the interface engineering [6,7] of those ultrathin layers, including semiconductors, ferromagnets, and superconductors, leading to new device technologies.

The most prominent example in this field is graphene, which has intrinsically outstanding spin and charge transport properties. For several years now, physicists have studied graphene based spintronics devices [2] and have found an efficient way to inject spins via FM/insulator tunnel junctions into graphene [8–13]. Nonlocal measurement geometries reveal the spin transport properties of graphene, which can be modified by the presence of various 2D materials in van der Waals heterostructures. Currently, state of the art spin transport geometries are based on hBN encapsulated graphene [10,12,14,15], where spins are injected by FMs, with giant mobilities up to $10^6$ cm$^2$/Vs [16–18] and spin lifetimes exceeding 10 ns [10]. The insulating hBN is ideal to reduce the contact resistance to the FM and helps to preserve the linear dispersion of graphene, which is desired for spin transport [19]. Also oxide insulators are used, such as MgO and SiO$_2$, resulting in less efficient spin injection [14]. The manipulation of spins can be achieved by inducing SOC or exchange coupling from proximity. For example, a TMDC in proximity to graphene induces strong valley Zeeman spin-orbit fields on the order of 1 meV [20–22], significantly reducing spin lifetimes in graphene to about 10 ps [23–25], but leading to giant spin relaxation anisotropies (the ratio of out-of-plane to in-plane spin lifetime) of about 10 [22–27]. Additionally, it has been demonstrated that a TMDC can be utilized for optical spin injection in graphene [21,25,28], relevant for the field of optospintronics.

Recently, there has been a lot of effort to use also other 2D materials such as phosphorene or TMDCs as the transport medium. The advantage is that they are already semiconducting, making them suitable for electronic and spintronic devices [1,3], such as spin diodes and field effect transistors [29–32]. In the case of phosphorene, very little is known about its spin transport properties [33–35]; the electronic ones are highly anisotropic and show large mobilities [36,37]. Furthermore, measurements combined with first-principles calculations show that hBN is also an ideal tunnel barrier, when injecting spin polarized carriers from Co into phosphorene [35].

Monolayer TMDCs have a band gap in the optical range and the valley degree of freedom plays a major role [38–43] in their (opto-) electronic properties. The helicity selective excitation of carriers with certain spin in a certain valley at the same excitation energy, makes those materials very attractive for the field of valleytronics [44–48]. By an exchange field one can break the time-reversal symmetry of the TMDC, the degeneracy of the valleys, and introduce valley polarization.
In an external magnetic field, the valley splitting rises roughly linear with 0.1–0.2 meV/T [49–52], such that large fields are required to get a sizable effect. A much better perspective to achieve large valley polarization in TMDCs is by the proximity exchange effect. Indeed, placing the TMDC on a magnetic substrate, giant valley splittings can be achieved, ranging from a few to hundreds of meV [47,48,53–61], which can additionally be tuned by gating and twisting [62].

For spin injection, one can either contact the TMDC with metal or metal/insulator interfaces or inject them optically [63,64]. In the former case, studying the dependence of the Schottky barrier on the used electrode is crucial [65–72]. It turns out that a BN tunnel barrier is also a good choice here, preserving the intrinsic properties of the TMDC while enormously reducing the contact resistance [66,73–75]. Also other insulating barriers, such as TiO₂, MgO, or Al₂O₃ [76–80], are promising candidates, where the thickness of the barrier plays an important role for the efficiency of spin injection. The contact resistance can also be decreased by strong electron doping [81] or using graphene electrodes [82].

Electronic and spin transport [83–86] in TMDCs is becoming an important topic. It has been shown that the carrier mobility increases (1–3 meV) for both TMDCs. Our investigations are reduced to the CB and VB. The Hamiltonian $H_{\text{soc}}$ describes a gapped spectrum with spin-degenerate parabolic CB and VB. In addition, the bands are spin split due to SOC which is captured by the term $H_{\text{soc}}$ with the parameters $\lambda_c$ and $\lambda_s$ describing the spin splitting of the CB and VB. The Hamiltonian $H_0 + H_\Delta + H_{\text{soc}}$ is already suitable to describe the spectrum of intrinsic TMDCs around the band edges at $K$ and $K'$. In the case when we have a ferromagnetic substrate, proximity exchange effects are present and we introduce the term $H_{\text{ex}}$ with $B_c$ and $B_s$ describing the proximity induced exchange splittings. Note that this term explicitly breaks time-reversal symmetry and thus the valley degeneracy. Finally, a Rashba term $H_{\text{Rash}}$ with $\lambda_R$ being the Rashba parameter, can be present since a substrate breaks the inversion symmetry of the TMDC.

III. COMPUTATIONAL DETAILS

A. First-principles calculations

The electronic structure calculations and structural relaxation of our geometries are performed with density functional theory (DFT) [92] using QUANTUM ESPRESSO [93]. Self-consistent calculations are performed with the $k$-point sampling of $18 \times 18 \times 1$ for the TMDC/hBN/FM heterostructures. We perform open shell calculations that provide the spin polarized ground state, when a FM substrate is present. We use an energy cutoff for charge density of 550 Ry, and the kinetic energy cutoff for wave functions is 65 Ry for the scalar relativistic pseudopotential with the projector augmented wave method [94] with the Perdew-Burke-Ernzerhof exchange correlation functional [95]. When SOC is included, the fully relativistic versions of the pseudopotentials are used. In addition we include the Hubbard correction for the FMs Co and Ni with $U = 1$ eV [96]. For this value of the Hubbard

II. MODEL HAMILTONIAN

As basis states for our model we use $|\Psi_{\text{CB}}\rangle = |d_{z^2}\rangle$ and $|\Psi_{\text{VB}}\rangle = \frac{1}{\sqrt{2}}(|d_{x^2-y^2}\rangle + i\tau |d_{xy}\rangle)$, corresponding to conduction band (CB) and valence band (VB) at $K$ ($\tau = 1$) and $K'$ ($\tau = -1$), since the band edges of bare TMDC monolayers are formed by different $d$ orbitals from the transition metal [38]. The model Hamiltonian, in the basis which includes electron spin $|\Psi_{\text{CB}}, \uparrow\rangle$, $|\Psi_{\text{VB}}, \uparrow\rangle$, $|\Psi_{\text{CB}}, \downarrow\rangle$, and $|\Psi_{\text{VB}}, \downarrow\rangle$, to describe the band structure of the TMDC close to $K$ and $K'$, in the presence of proximity exchange [55,62] is

$$H = H_0 + H_\Delta + H_{\text{soc}} + H_{\text{ex}} + H_R,$$

$$H_0 = \hbar v_F s_0 \langle \tau x | k_x + \tau y | k_y \rangle,$$

$$H_\Delta = \frac{\Delta}{2} s_0 \otimes \sigma_z,$$

$$H_{\text{soc}} = \tau s_z \otimes (\lambda_c \sigma_x + \lambda_s \sigma_\uparrow),$$

$$H_{\text{ex}} = -s_z \otimes (B_c \sigma_+ + B_s \sigma_-),$$

$$H_R = \lambda_R (\tau s_y \otimes \sigma_y - s_x \otimes \sigma_x).$$

Here $v_F$ is the Fermi velocity. The Cartesian components $k_x$ and $k_y$ of the electron wave vector are measured from $K (K')$. The pseudospin Pauli matrices are $\sigma_i$ acting on the (CB,VB) subspace and spin Pauli matrices are $s_i$ acting on the ($\uparrow$, $\downarrow$) subspace, with $i = \{0, x, y, z\}$. For shorter notation we introduce $\sigma_\pm = \{\sigma_0 \pm \sigma_i\}$. TMDCs are semiconductors, and thus $H_\Delta$ introduces a gap, represented by parameter $\Delta$, in the band structure such that $H_0 + H_\Delta$ describes a gapped spectrum with spin-degenerate parabolic CB and VB. In addition, the bands are spin split due to SOC which is captured by the term $H_{\text{soc}}$ with the parameters $\lambda_c$ and $\lambda_s$ describing the spin splitting of the CB and VB. The Hamiltonian $H_0 + H_\Delta + H_{\text{soc}}$ is already suitable to describe the spectrum of intrinsic TMDCs around the band edges at $K$ and $K'$. In the case when we have a ferromagnetic substrate, proximity exchange effects are present and we introduce the term $H_{\text{ex}}$ with $B_c$ and $B_s$ describing the proximity induced exchange splittings. Note that this term explicitly breaks time-reversal symmetry and thus the valley degeneracy. Finally, a Rashba term $H_{\text{Rash}}$ with $\lambda_R$ being the Rashba parameter, can be present since a substrate breaks the inversion symmetry of the TMDC.
to simulate quasi-2D systems, a vacuum of at least 16 Å is used to avoid interactions between periodic images in our slab geometries. Dipole corrections [101] are included for heterostructure calculations to get correct band offsets and internal electric fields. Structural relaxations are performed until all components of all forces were reduced below 10^{-3} (Ry/a₀), where a₀ is the Bohr radius.

B. Absorption spectra calculations for excitons

To compute the excitonic spectra, we employ the effective Bethe-Salpeter equation (BSE) [62,102–107] focusing on direct intralayer excitons at zero temperature and without doping effects. The specific form of the BSE we use is given in the Supplemental Material of Ref. [62]. The single-particle spectra is obtained using the model Hamiltonian of Eq. (1) fitted to the first-principles band structures. Because of the coupling between conduction and valence bands (due to the Fermi velocity term), the direct term of the electron-hole interaction is given by

\[ \text{D}^\text{eh}_{\vec{k} \vec{k}'} = -\Delta^\text{eh}_{\vec{k} \vec{k}'} \text{V}(\vec{k} - \vec{k}'), \]  

(7)

with V(\vec{k} - \vec{k}') being the electrostatic potential and the mixing term \( \Delta^\text{eh}_{\vec{k} \vec{k}'} \) can be written in a very general way as

\[ \Delta^\text{eh}_{\vec{k} \vec{k}'} = \left[ \sum_m \beta m c,\ell(\vec{k}) \beta_{\ell',m}(\vec{k}') \right] \left[ \sum_l \beta m c',\ell(\vec{k}) \beta_{\ell',l}(\vec{k}') \right], \]  

(8)

in which \( M \) is the size of the effective Hamiltonian, \( c, c' \) (\( v, v' \)) are the conduction (valence) bands, and \( \beta_{m,l}(\vec{k}) \) is the \( l \)th coefficient (\( l = 1, \ldots, M \)) of the band \( m \) at point \( \vec{k} \). We point out that for decoupled models, for instance parabolic dispersions described by effective masses, the mixing term (8) would not be present and the BSE is reduced to the Wannier equation in \( k \) space [108].

We model the electron-hole electrostatic potential \( \text{V}(\vec{k} - \vec{k}') \) that appears in Eq. (7) by the widely used Rytova-Keldysh potential [109,114]. Such potential essentially describes the electrostatics of a thin slab, i.e., the 2D material, with different top and bottom dielectric environments. In \( k \) space the Rytova-Keldysh potential is given by

\[ \text{V}(\vec{k}) = \frac{1}{A} \frac{e^2}{2\varepsilon_0} \frac{1}{\varepsilon K + r_0 K^2}, \]  

(9)

with \( K = \vec{k} - \vec{k}' \), \( A \) is the 2D unit area, \( e \) is the electron charge, \( \varepsilon_0 \) is the vacuum permittivity, \( r_0 \) is the screening length of the 2D material, and \( \varepsilon \) is the effective dielectric constant given by the average of the top and bottom dielectric constants, i.e., \( \varepsilon = (\varepsilon_t + \varepsilon_b)/2 \). For the screening lengths of the TMDCs we used the values provided in Ref. [112].

The BSE is solved on a 2D \( k \) grid from -0.5 to 0.5 Å⁻¹ in \( k_x \) and \( k_y \) directions with total discretization of 101×101 points (leading to a spacing of \( \Delta k = 10^{-2} \) Å⁻¹). To improve convergence, the Coulomb potential is averaged around each \( k \) point in a square region of -\( \Delta k/2 \) to \( \Delta k/2 \) discretized with 101×101 points [62,105].

The absorption spectra for a photon with energy \( \hbar \omega \), incorporating excitonic effects, is given by [105,106]

\[ \alpha^a(\hbar \omega) = \frac{4\pi^2 e^2}{\varepsilon_0 c^2 \hbar^2} \sum_{c'v} \sum_{c'v} A_{c'v}(N) p_{c'v}^a(\vec{k}) \left| \delta(\Omega_{c'v} - \hbar \omega) \right|^2, \]  

(10)

with the superindex \( a \) indicating the polarization of the light, \( e \) is the electron charge, \( \varepsilon_0 \) is the vacuum permittivity, \( c \) is the speed of light (the subindex \( l \) was added to not be confused with the conduction band index \( c \) ), \( A \) is the 2D unit area, the summation indices \( c \) and \( v \) label the conduction and valence bands, respectively, \( \vec{k} \) is the wave vector, \( N \) labels the excitonic states, \( A_{c'v}(N) \) is the exciton envelope function, \( \Omega_{c'v} \) is the exciton energy, and the single-particle dipole matrix element is \( p_{c'v}^a(\vec{k}) = \frac{\hbar}{2\varepsilon_0} \left( n, \vec{k} \varepsilon_{c'} \cdot \vec{p}[c,\ell] \right) \) (computed using the eigenstates of the model Hamiltonian). Finally, to the calculated absorption spectra we apply a Lorentzian broadening with energy dependent full width at half-maximum [106,115]

\[ \Gamma(\hbar \omega) = \Gamma_1 + \frac{\Gamma_2}{1 + e^{(\hbar \omega - \hbar \omega_0)/\Gamma_3}} \]  

(11)

using \( \Gamma_1 = \Gamma_2 = \Gamma_3 = 10 \) meV. \( E_0 \) is the single-particle energy at the \( K \) point for the first allowed optical transition.

IV. TMDC/hBN/FM HETEROSTRUCTURES

A. Geometry

In order to calculate the proximity exchange in a TMDC/hBN/FM heterostructure, we have to find a common unit cell for all compounds minimizing strain effects. In Fig. 1 we show the geometry for MoS₂/hBN/Co as an exemplary structure. Initial atomic structures are set up with the atomic simulation environment (ASE) [116], as follows. We choose a 4×4 supercell of the TMDC (MoS₂, WS₂), a 5×5 cell of hBN, and a 5×5 cell of the FMs (Co, Ni). For the FM we take three monolayers of hcp Co or fcc(111) Ni. The hBN is placed above the FM, such that the nitrogen sits above the topmost Co/Ni atom, and the boron above the fcc position above the FM slab, as found by previous studies [19]. The TMDC is placed above the hBN/FM slab, that a transition metal atom (Mo, W) sits above a nitrogen atom. By choosing the heterostructure as explained, our unit cell contains 173 atoms, with a lattice constant of 12.637 Å, for all of our considered hybrid geometries. For that we have to modify the lattice constants of the subsystem layers (TMDC, hBN, FM). In Table I we give an overview on the original experimental and the new modified lattice constants used for the heterostructures, as well as the introduced strain. We can see that a maximum strain of about 1.5% is present for Ni, being still acceptable for our purposes.

To determine the interlayer distances, the atoms of the TMDC, hBN, and the top two Co/Ni layer atoms were...
allowed to relax only in their z positions (vertical to the layers). The average distances between the layers \(d_{FM/ABN}\) and \(d_{ABN/TMDC}\), as defined in Fig. 1, are listed in Table III for all considered geometries. The distances are measured from the average position of the top Co/Ni (bottom S) atoms, with respect to the average position of the N atoms of the hBN layer. The corrugation of the hBN is on average 0.12 Å, independent of the heterostructure. The distances \(d_{FM/ABN}\) between the FMs and hBN are around 2.1 Å, indicating strong bonding. The distances \(d_{ABN/TMDC}\) between the hBN and the TMDCs are roughly 3.15 Å, being in the range of typical van der Waals distances. All these observations are in agreement with previous calculations of fcc(111) Ni and hcp Co, the hybridization of FM d orbitals and hBN p orbitals and the resulting proximity exchange strength are not completely the same in the two cases. Finally, the Mo atoms have a magnetic moment of about 0.004 \(\mu_B\), which is responsible for the exchange splitting in the TMDC bands, which we analyze in the following.

B. Band structure analysis and fit results

In the following we analyze the results for MoS\(_2\)/hBN/Co, shown in Fig. 2, as a representative example. Similar to Fig. 2, we show the DFT results for the other TMDC/hBN/FM heterostructures in the Appendix.

In Fig. 2(a) we show the calculated band structure without SOC of the MoS\(_2\)/hBN/Co heterostructure. Since a lot of bands are involved, originating from the hBN/FM substrate, the orbital gap of the spectrum, the Fermi velocity \(v_F\), and \(B_{c}\) and \(B_{e}\) are the proximity exchange parameters, respectively. The dipole of the structures is given in debye and \(d_{ABN/TMDC}\) is the distance between hBN and the TMDC, and \(d_{FM/ABN}\) is the distance between the FM and hBN, as defined in Fig. 1.

### TABLE I. Overview of the lattice constants and strains for the subsystems used in the TMDC/hBN/FM heterostructures.

|          | Co | Ni | hBN | MoS\(_2\) | WS\(_2\) |
|----------|----|----|-----|----------|---------|
| \(a\) (expt) (Å) | 2.507 | 2.492 | 2.504 | 3.150 | 3.153 |
| \(a\) (het) (Å) | 2.527 | 2.527 | 2.527 | 3.159 | 3.159 |
| Strain (%) | 0.8 | 1.4 | 0.9 | 0.3 | 0.2 |

### TABLE II. Calculated atomic magnetic moments of the TMDC/hBN/FM systems given in \(\mu_B\). The values are obtained by averaging the magnetic moments of the individual atomic species. For Co/Ni atoms we distinguish the three layers of the FM slab by the numbers in brackets (1–3) ordered from vacuum to hBN-interface side.

| System | MoS\(_2\) | MoS\(_2\) | WS\(_2\) | WS\(_2\) |
|--------|----------|----------|----------|----------|
|        | hBN      | hBN      | hBN      | hBN      |
| Mo\(_0\)/W | 0.004  | 0.003  | 0.002  | 0.002  |
| B      | −0.010   | −0.004  | −0.010  | −0.004  |
| N      | 0.003    | 0.014   | 0.003   | 0.014   |
| Co/Ni (3) | 1.60   | 0.61    | 1.60    | 0.61    |
| Co/Ni (2) | 1.71   | 0.76    | 1.71    | 0.76    |
| Co/Ni (1) | 1.77   | 0.75    | 1.77    | 0.75    |

1.60 \(\mu_B\), ordered from vacuum to the hBN interface. The FM metal layer induces a small negative (positive) magnetic moment in the B (N) atoms of about −0.010 (0.003) \(\mu_B\). In the case of Ni, the magnitude of proximity induced magnetic moments in the hBN layer are different compared to Co. Due to the different lattices and magnetic moments of fcc(111) Ni and hcp Co, the hybridization of FM d orbitals and hBN p orbitals and the resulting proximity exchange strength are not completely the same in the two cases. Finally, the Mo atoms have a magnetic moment of about 0.004 \(\mu_B\), which is responsible for the exchange splitting in the TMDC bands, which we analyze in the following.

### TABLE III. Summary of the fit parameters, calculated dipoles, and distances for TMDC/hBN/FM systems without SOC. The Hamiltonian used to fit these systems is \(H_0 + H_D + H_{ex}\), with \(\Delta\) as the orbital gap of the spectrum, the Fermi velocity \(v_F\), and \(B_{c}\) and \(B_{e}\) are the proximity exchange parameters, respectively. The dipole of the structures is given in debye and \(d_{ABN/TMDC}\) is the distance between hBN and the TMDC, and \(d_{FM/ABN}\) is the distance between the FM and hBN, as defined in Fig. 1.

| System | MoS\(_2\) | MoS\(_2\) | WS\(_2\) | WS\(_2\) |
|--------|----------|----------|----------|----------|
|        | hBN      | hBN      | hBN      | hBN      |
| \(\Delta\) (eV) | 1.761 | 1.769 | 1.910 | 1.910 |
| \(v_F\) (10^\(5\) m/s) | 5.303 | 5.475 | 6.907 | 6.908 |
| \(B_{c}\) (meV) | 1.964 | 0.75 | 1.60 | 0.61 |
| \(B_{e}\) (meV) | 6.365 | 1.964 | 1.080 | 1.077 |
| Dipole (Debye) | 1.940 | 2.871 | 2.386 | 3.713 |
| \(d_{FM/ABN}\) (Å) | 2.089 | 2.085 | 2.089 | 2.084 |
| \(d_{ABN/TMDC}\) (Å) | 3.157 | 3.217 | 3.151 | 3.137 |
we only show a projection of the bands originating from the TMDC. We find that the band structure closely resembles the bands of pristine MoS$_2$. The Fermi level is located below the CB edge originating from MoS$_2$ around the $K$ point. Symbols are DFT data and solid lines are the fit to the model Hamiltonian. (d) Same as (b), but for VB edge.

Co $d$ orbitals hybridize with the $p$ orbitals of the hBN layer and mediate the exchange coupling. The band edges of the MoS$_2$ layer can also be identified in the density of states at about 0 and $-1.7 \text{ eV}$. Especially near the VB edge of MoS$_2$ at $-1.7 \text{ eV}$, there is a significant contribution from B and N atoms in the spin-down channel. Thus, the Co $d$ orbitals hybridize, via the hBN buffer layer, with the VB spin-down states of MoS$_2$.

If we zoom to the fine structure around the $K$ point, we find that the bands of the TMDC are spin split due to proximity exchange coupling, see Figs. 2(c) and 2(d). The splitting of the CB is smaller than that of the VB, both being in the few meV range. Since SOC effects are turned off, we can fit the band structure around the $K$ point to our model Hamiltonian, neglecting for now $H_{\text{soc}}+H_{\text{K}}$. In Figs. 2(c) and 2(d) we can see that the bands are nicely reproduced by the model with the fit parameters given in Table III. However, we can see that there is a discrepancy between the model and the calculation, especially for the spin-down VB away from the $K$ point. The case of MoS$_2$/hBN/Co is the only one, where this happens. The origin of this, is the hybridization of the VB spin-down states of MoS$_2$ with Co $d$ states, as one can see in Figs. 2(a) and 2(b).

In Table III we summarize our fit parameters for all considered heterostructures. We notice that especially the parameter $B_\epsilon$ for the MoS$_2$/hBN/Co case is very large, which is caused by the previously explained effect of hybridization. In a similar way, an earlier study has shown that the hybridization with Co $d$ orbitals can strongly enhance the proximity exchange splitting in graphene on a hBN/Co substrate [19]. Note that
TABLE IV. Summary of the fit parameters, calculated dipoles, and distances for TMDC/hBN systems with SOC. The Hamiltonian used to fit these systems is $H_0 + H_{ss} + H_{soc} + H_R$, with $\Delta$ as the orbital gap of the spectrum, the Fermi velocity $v_F$, and $\lambda_s$ and $\lambda_c$ are the SOC parameters. The distances are given as defined in Fig. 1.

| System       | MoS$_2$ hBN | WS$_2$ hBN |
|--------------|-------------|------------|
| $\Delta$ (eV) | 1.756       | 1.872      |
| $v_F$ ($10^3$ m/s) | 5.432       | 6.786      |
| $\lambda_s$ (meV) | −1.361      | 17.03      |
| $\lambda_c$ (meV) | 72.96       | 208.6      |
| Dipole (Debye) | −0.701      | −0.703     |
| $d_{hBN/TMDC}$ (Å) | 3.330       | 3.252      |

the value of the Hubbard $U$, which shifts the Co $d$ levels in energy, affects the hybridization and the spin splitting, as shown in Ref. [19]. Since we have considered $U = 1$ eV only, we can only predict that such a hybridization is present in experiments, which leads to an enhanced spin splitting.

Unfortunately, we were not able to properly converge the calculations of the TMDC/hBN/FM heterostructures including SOC effects. The spin-orbit splitting in the TMDC VB is large [38,124] and may shift the corresponding bands too much in energy to spoil the hybridization. Therefore, we cannot be completely sure whether the mentioned hybridization effect in the MoS$_2$/hBN/Co structure will remain. However, a similar work of proximity exchange in TMDC/GeI$_3$ heterostructures has shown that inclusion of SOC barely affects the proximity exchange parameters [62]. Thus, we believe that proximity exchange on the order of 1–5 meV would still be present when including SOC for our TMDC/hBN/FM structures.

Similar to graphene/hBN/FM stacks [19], we expect that the proximity exchange in the TMDCs also decreases with increasing number of hBN layers between the FM and the TMDC. Unfortunately, due to computational limitations (number of atoms in the supercell), we cannot study more than one hBN layer.

**C. TMDC/hBN subsystems**

Experimentally it is also interesting to consider the bare MoS$_2$/hBN and WS$_2$/hBN heterostructures, without any influence from the FM. For that we take the TMDC/hBN/FM geometries, but remove the FM layers. After subsequent relaxation, similar as described above, we calculate the electronic band structures for the subsystems, including SOC effects. The corrugation of the hBN reduces to about 20 pm on average, and the distances $d_{hBN/TMDC}$ between hBN and the TMDC are given in Table IV for the TMDC/hBN stacks. The FM is responsible for the corrugation of the hBN layer, as already pointed out in an earlier work [19]. Our model Hamiltonian is also suitable to describe this situation, when neglecting $H_{ex}$.

The calculated band structure for MoS$_2$/hBN is shown in Fig. 3. We find that we can perfectly reproduce the band structure around $K$ and $K'$ valleys, with the fit parameters given in Table IV. The fit parameters for the TMDC/hBN heterostructures are nearly identical to the ones obtained for the bare TMDC monolayers [38,124]. We conclude that the hBN has effectively no impact on the TMDC dispersion and SOC. In principle, one would also expect Rashba SOC due to inversion symmetry breaking, but from previous calculations of graphene/hBN/FM structures [19], we conclude that the proximity induced SOC due to the hBN/FM substrate is negligible, compared to the proximity induced exchange and the giant intrinsic SOC of the bare TMDCs [38,124]. Indeed, we find by fitting the model Hamiltonian to the band structure of the TMDC/hBN systems, that $H_{ex}$ can be neglected, as the $s_z$ spin expectation values of the bands near the $K$ and $K'$ points almost do not differ from $\pm 0.5$, as we can see in Fig. 3.

FIG. 3. Calculated band structure of MoS$_2$/hBN including SOC effects. (a) Band structure along high symmetry lines. The bands corresponding to MoS$_2$ (hBN) are plotted in black (green). (b) Zoom to the CB edge. The color corresponds to the $s_z$-expectation value. Symbols are DFT data and solid lines are fits to the model Hamiltonian. (c) Same as (b), but for VB edge.

In conclusion, the extracted proximity exchange (intrinsic SOC) parameters from the calculations of the TMDC/hBN/FM (TMDC/hBN) systems, together with the Hamiltonian, can be used for further studies.

**V. PROXIMITY EXCHANGE INDUCED VALLEY SPLITTING**

The individually extracted parameters for proximity exchange and SOC, see Tables III and IV, in combination with our model Hamiltonian, can be used to calculate the low energy bands around $K$ and $K'$ point with both effects present. We average the parameters for $v_F$ and $\Delta$ from Tables III
and IV, for the MoS$_2$ and WS$_2$ based structures. We take the the orbital gap parameter $\Delta$, the Fermi velocity $v_F$, $B_z$ and $B_c$ are the proximity exchange parameters, and $\lambda_c$ and $\lambda_\sigma$ are the SOC parameters. The valley splitting calculated from the single particle picture (s. part.) and from the absorption spectra of the $A_{1u}$ exciton peak.

| System          | MoS$_2$   | MoS$_2$ | WS$_2$   | WS$_2$   |
|-----------------|-----------|---------|----------|----------|
|                 | Co Ni Co Ni | hBN hBN | hBN hBN |
| $\Delta$ (eV)   | 1.759     | 1.763   | 1.891    | 1.891    |
| $v_F$ (10$^3$ m/s) | 5.368     | 5.454   | 6.847    | 6.847    |
| $\lambda_c$ (meV) | -1.361    | -1.361  | 17.03    | 17.03    |
| $\lambda_\sigma$ (meV) | 72.96     | 72.96   | 208.6    | 208.6    |
| $B_z$ (meV)     | 1.964     | 1.697   | 1.080    | 1.077    |
| $B_c$ (meV)     | 6.365     | 2.185   | 3.629    | 2.308    |
| s. p. at $K, K'$ (meV) | 8.80      | 0.98    | 5.10     | 2.46     |
| $A_{1u}$ ($\varepsilon = 2.75$) (meV) | 8.20      | 0.91    | 4.76     | 2.30     |
| $A_{1u}$ ($\varepsilon = 4.5$) (meV) | 8.31      | 0.93    | 4.84     | 2.34     |

and proximity exchange, time-reversal symmetry is broken and the valley degeneracy is lifted, as can be seen when comparing the spin-split CB at $K$ and $K'$, see Figs. 4(a) and 4(c). Remarkably, the order of the spin bands in the CB is the same for the two valleys. For bare TMDCs, the spin splitting in the CB is determined by the corresponding SOC parameter $\lambda_c$. For the case of MoS$_2$, we find that the SOC parameter is comparable in magnitude with the proximity exchange parameter $\lambda_c \approx B_c$, due to the hBN/FM substrate. When the proximity exchange is larger than the SOC, the band ordering of the spin-split CB is the same for both valleys, as can be seen in Figs. 4(a) and 4(c). In contrast, the VB SOC parameter is much larger than the corresponding proximity exchange parameter $\lambda_v \gg B_c$, and the VB splitting is dominated by SOC.

For a more realistic assessment of the proximity exchange in the optical spectra, we investigate the valley splitting of the excitonic levels, employing the parameters summarized in Table V for the model Hamiltonian and the effective BSE. Let us first look at the absorption spectra assuming an effective dielectric constant of $\varepsilon = 2.75$ as a model case of a TMDC placed on hBN ($\varepsilon_h = 4.5$ [125]) and vacuum on top ($\varepsilon_v = 1$), as suggested by the geometry shown in Fig. 1. The calculated absorption spectra for the TMDC intralayer excitons is shown in Fig. 5 as function of the photon energy $E_{ph}$ relative to the optical energy gap at the $K$ point, $E_K$ (the energy of the first allowed optical transition). With this $x$-axis convention, the energy of the first absorption peak is roughly the $A_{1u}$ exciton binding energy. Because we are assuming a TMDC embedded in a dielectric environment with effective $\varepsilon = 2.75$, the exciton binding energy is smaller than in the freestanding case (with $\varepsilon = 1$ the binding energies are typically 0.5–0.6 eV for TMDCs [112,126]). Due to the induced proximity exchange, $K$ and $K'$ valleys have now different transition energies and this is directly reflected in the absorption spectra as a splitting of the excitation energies with $\sigma_+$ and $\sigma_-$ polarizations. The extracted values for the valley splitting of the $A_{1u}$ exciton peak and for the single-particle picture at the $K, K'$ points are summarized in Table V. Along with the visible excited excitonic states $A_{2u}$ and $A_{3u}$, the $B$ excitons are also visible for the MoS$_2$-based systems. For instance, $B_{1g}$ excitons show large peaks around $-150$ meV and have a valley splitting with the same value as the $A_{1u}$ exciton but with opposite sign.

What about the valley splitting of other exciton peaks and the effect of stronger dielectric surroundings? In Figs. 6(a)–6(d) we show the valley splittings of the $A$ excitons (1$s$, 2$s$, and 3$s$) visible in Fig. 5 for effective dielectric constants of $\varepsilon = 2.75$ and $\varepsilon = 4.5$ (resembling a case for hBN encapsulated TMDC or assuming a stronger screening due to the presence of Co/Ni below the hBN layer [127]). Essentially, excited excitonic states and larger values of $\varepsilon$ provide larger valley splittings which tend to converge to the single-particle values obtained directly at the $K, K'$ points. In order to grasp the physics behind this behavior, we can look at the expectation value of the exciton valley splitting given by $|A_{1u}^K| E_{K} (\hat{k}) |A_{1u}^K \rangle - |A_{1u}^{K'}| E_{K'} (\hat{k}) |A_{1u}^{K'} \rangle$. Since the exciton wave functions are nearly identical for $K$ and $K'$ points (due to same effective masses) we can simply write the expectation...
value of the valley splitting as \(\langle \hat{A}_k | \Delta(\hat{k}) | \hat{A}_k \rangle\), in which \(\Delta(\hat{k}) = E_K(\hat{k}) - E_K(\hat{k})\) is the single-particle valley splitting in momentum space. The spreading of \(\Delta(\hat{k})\) (calculated with the model Hamiltonian) and the exciton envelope functions are shown in Figs. 6(e)–6(h). Since \(\Delta(\hat{k})\) has a maximum value at \(\hat{k} = 0\), the largest exciton valley splitting in this case is achieved for excitons more localized at \(\hat{k} = 0\), which is precisely the effect of looking at excited exciton states or increasing the effective dielectric constant as shown in Figs. 6(a)–6(d). This intuitive picture of looking at the expectation value within the exciton framework has been recently employed to successfully explain the evolution of the g factor in excited exciton states [128]. Furthermore, our analysis suggests that one possibility to engineer larger exciton valley splittings is to look for proximity exchange effects that increase as one moves away of the \(K, K'\) edges.

As a final remark, we point out that the optical excitation energy difference between \(K\) and \(K'\) valleys for MoS\(_2\)/hBN/Co is giant, around 8 meV, translating into about 50 T magnetic field for bare TMDCs, if assuming 0.15 meV/T valley splitting [49–52]. A similar giant valley splitting of about 5 meV is achieved in the case of WS\(_2\)/hBN/Co, translating to about 30 T magnetic field. Remarkably, in the case of MoS\(_2\)/hBN/Co, we have seen that proximity exchange together with band hybridization to d orbitals causes a large VB splitting, leading to the giant valley splitting. In the case of WS\(_2\)/hBN/Co, the valley splitting is also giant, but without any band hybridization effects. When Ni is considered as the FM, we find smaller valley splittings, \(~1\) meV (7 T) for MoS\(_2\)/hBN/Ni and 2.3 meV (15 T) for WS\(_2\)/hBN/Ni, but still the corresponding magnetic fields are quite large, compared to the valley splittings achieved without proximity exchange. Furthermore, our exciton calculations show that the valley splitting increases for excited exciton states, which could be observed experimentally in reflectance/transmittance measurements [113,125]. Besides a direct observation of the exciton valley splitting, recent studies have shown that the induced proximity exchange has visible signatures in the magneto-optical Kerr response of excitons [129,130].
FIG. 7. Same as Fig. 2, but for the MoS$_2$/hBN/Ni system.

VI. SUMMARY

We have calculated the band structures of TMDC/hBN/FM heterostructures and extracted valuable proximity exchange and SOC parameters, using a minimal low energy Hamiltonian. Due to the hBN buffer layer, the TMDC preserves a great degree of autonomy of its electronic structure. Proximity exchange is found to be on the order of 1–10 meV, depending on the specific FM. Especially in MoS$_2$/hBN/Co, the spin splitting is giant, about 10 meV, due to proximity exchange and hybridization of Co $d$ states with the spin-down VB of the TMDC. The excitonic absorption spectra, shows a giant valley splitting for the exciton peaks, translating into a valley polarization corresponding to tens of Tesla exchange field for bare TMDC monolayers. The Ni-based heterostructures show less strong proximity exchange. We believe our

FIG. 8. Same as Fig. 2, but for the WS$_2$/hBN/Co system.
calculations provide useful insight to interpret experimental properties of TMDC/hBN/(Co, Ni) devices, for instance related to spin injection, spin tunneling, and optics. Finally, our extracted parameters can be used as input for transport simulations and additional studies of excitonic effects.

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APPENDIX: FURTHER DFT RESULTS

For completeness, in Figs. 7, 8, and 9 we show the calculated band structure, density of states, and low energy model fits for the MoS2/hBN/Ni, WS2/hBN/Co, and WS2/hBN/Ni heterostructures.

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