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# Valley spin-splitting in pristine and Cr- and Ni-doped HfN<sub>2</sub> monolayers

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Using first-principles calculations, we systematically studied the spin-orbit coupling (SOC)-induced valley spin splitting in a pristine HfN<sub>2</sub> monolayer (HfN<sub>2</sub>-ML) and in Cr- and Ni-doped systems. The pristine HfN<sub>2</sub>-ML is revealed to host a direct band gap at the K and K' points of the Brillouin zone. The valley spin splitting reaches 350 meV for the conduction bands and 83.5 meV for the valence bands. Furthermore, the exciton binding energy of the HfN<sub>2</sub>-ML is estimated to be approximately 0.90 eV. The exciton ground states belong to the Wannier-Mott type, which are governed by the electron and hole band edge states. More importantly, the valley spin at the K and K' points could substantially change the effects when Cr or Ni is doped into the HfN<sub>2</sub>-ML. Consequently, the Cr-doped HfN<sub>2</sub> monolayer exhibits a pronounced Zeeman splitting of approximately 300 meV. These findings highlight the promise of the HfN<sub>2</sub>-ML and related two-dimensional (2D) materials for prospective applications in valleytronic and spintronic devices.

## 1. Introduction

Nowadays, valleytronics focuses on exploiting and manipulating the valley degree of freedom in electronic materials, offering promising opportunities for future electronic, optoelectronic, and spintronic applications.<sup>1–4</sup> Unlike conventional electronic materials, valleytronic materials offer advantages, such as high speed and low power consumption.<sup>1</sup> This is attributed to the presence of two or more local energy extremes in the occupied and unoccupied states, offering opportunities for encoding, storing, or processing diverse information.<sup>5</sup> Recently, the transition metal dichalcogenides (TMDs), such as MoS<sub>2</sub> and WSe<sub>2</sub> monolayers, have garnered attention for their prominent valley properties<sup>6–8</sup> and have been the subject of extensive study for valleytronic applications.

Beyond TMDs, other 2D materials have also emerged as promising candidates for valleytronic and spintronic applications, owing to their rich electronic structures, tunable interlayer couplings, and the possibility of engineering symmetry breaking through external fields or selective doping.<sup>9</sup> Like TMDs, transition metal nitride semiconductors have garnered considerable interest<sup>10–12</sup> owing to their exceptional properties.<sup>13–16</sup> Moreover, extensive efforts have been devoted to doping in 2D systems as an effective strategy to tailor their electronic and magnetic

properties, thereby opening avenues for prospective applications in spintronics and valleytronic devices.<sup>17</sup>

Hafnium dinitride (HfN<sub>2</sub>) represents one of the materials attracting substantial interest. Bulk HfN<sub>2</sub> has been reported to exhibit remarkable ductility, and thin films of HfN<sub>x</sub> have been successfully fabricated using the through-silicon-*via* technology.<sup>18</sup> Although experimental efforts toward the synthesis of 2D HfN<sub>2</sub> are still ongoing, the stability of the HfN<sub>2</sub>-ML has been established theoretically.<sup>19</sup> It's generating significant interest due to its unique properties, such as optical, electronic, and structural characteristics.<sup>19–21</sup> In particular, the HfN<sub>2</sub>-ML is emerging as a candidate for exploring new possibilities in valleytronics.<sup>22,23</sup> Using first-principles calculations, substrate-induced excellent electronic properties in HfN<sub>2</sub>-ML have been observed in the literature, such as CrS<sub>2</sub>/HfN<sub>2</sub><sup>24</sup> and MoTe<sub>2</sub>/HfN<sub>2</sub>.<sup>25</sup> However, there has been a scarcity of comprehensive investigations into HfN<sub>2</sub>-ML up to now, encompassing both theoretical calculations and experimental measurements related to the properties of valley electronics and excitonic properties. Additionally, the effects of doping transition metal elements on the HfN<sub>2</sub>-ML-induced enriched valley properties have not yet been explored.

In this work, we systematically investigate the intrinsic electronic and excitonic properties of pristine HfN<sub>2</sub>-ML, along with the remarkable electronic modifications induced by chromium (Cr) and nickel (Ni) doping, using first-principles calculations. The HfN<sub>2</sub>-ML exhibits several key characteristics: (i) a moderate direct band gap of 4.20 eV at the K and K' valleys, accompanied by distinct conduction- and valence-band splittings; (ii) strong excitonic effects arising from its unique band dispersion and non-uniform dielectric screening; and (iii)

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pronounced valley–spin polarization at the K and K' points upon Cr and Ni doping, leading to a significant Zeeman-type splitting. These results highlight HfN<sub>2</sub>-ML as a promising 2D material for next-generation spintronic, valleytronic, and optoelectronic applications. Moreover, Cr dopants introduce net magnetic moments into the otherwise nonmagnetic HfN<sub>2</sub>-ML, offering an effective route to realize spin-polarized functionalities for practical spintronic device applications.

## 2. Computational methods

This work was performed on the investigated materials using first-principles calculations.<sup>26,27</sup> The projector augmented-wave (PAW)

method was employed to represent the ionic potential.<sup>28</sup> For the description of exchange–correlation interactions, the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) was used.<sup>29,30</sup> The calculations utilized a plane wave cut-off energy of 500 eV,<sup>31</sup> ensuring convergence with energy precision of 10<sup>−8</sup> eV<sup>32</sup> and a force precision of 2 × 10<sup>−3</sup> eV Å<sup>−1</sup>. A vacuum slab with a thickness of 20 Å was implemented to prevent spurious interactions along the z-direction. A sampling of the Brillouin zone was achieved using a  $\Gamma$ -centered *k*-mesh grid of 25 × 25 × 1. The SOC<sup>33,34</sup> was considered to calculate the electronic band structure and optical properties due to the heavy Hf element.<sup>35</sup> We have employed the single-shot *G*<sub>0</sub>*W*<sub>0</sub> method applied to Kohn–Sham wave functions<sup>36</sup> to obtain quasi-electronic band structures utilizing a *k*-point grid of 15 × 15 × 1 and a

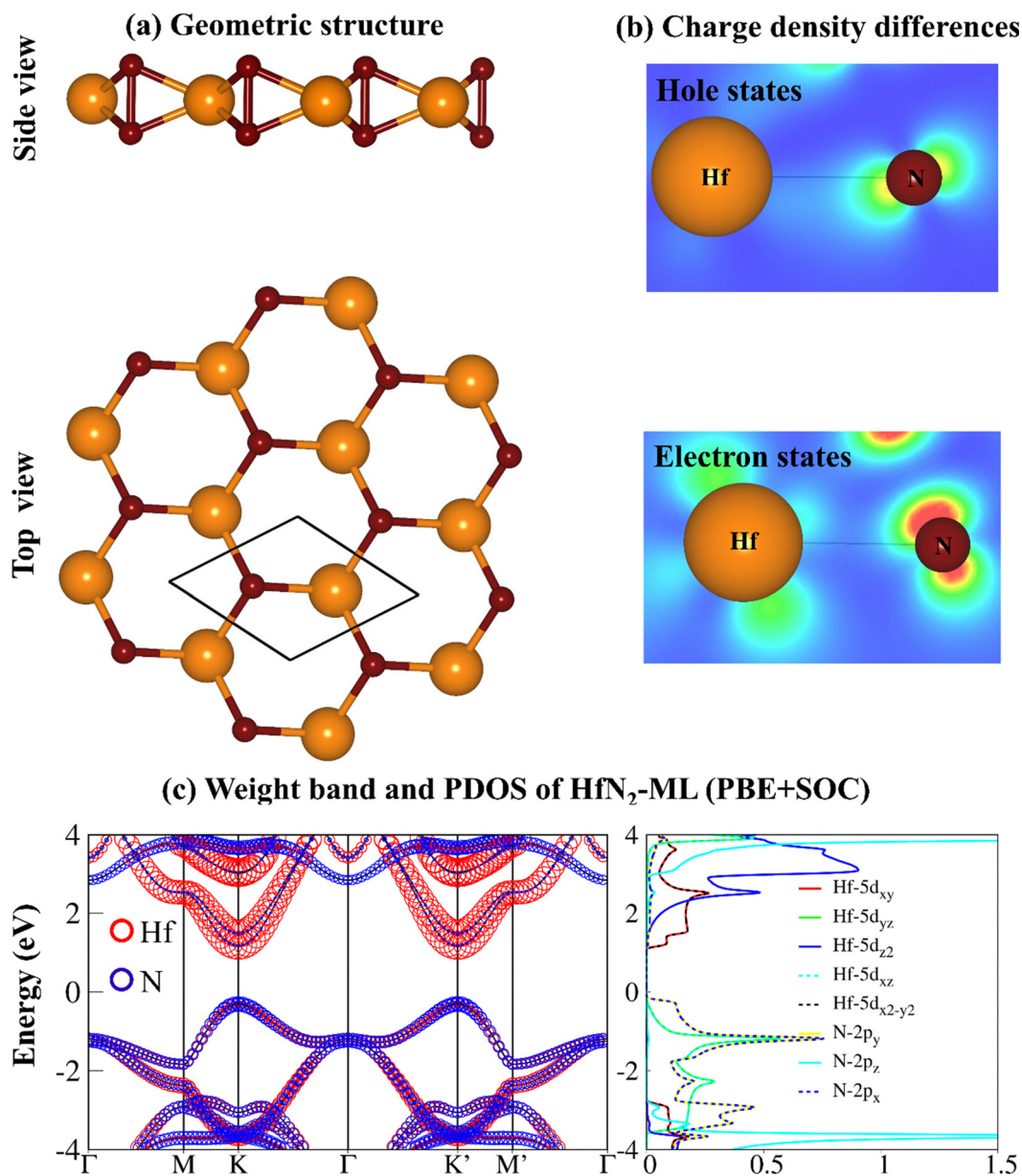


Fig. 1 (a) Optimized structure of 2D HfN<sub>2</sub>-ML (side and top views), (b) band-decomposed charge densities at the valence-band maximum and conduction-band minimum, and (c) band weights and projected density of states (PDOS) obtained from PBE + SOC.



response function cutoff energy of 120 eV. To accurately determine the exciton spectrum, we systematically explored the convergence behavior of the Bethe–Salpeter equation (BSE),<sup>37</sup> focusing on parameters such as the number of  $k$ -points and the electron–hole pairs involved. Our findings suggest that achieving convergence involves utilizing a  $k$ -point grid of  $25 \times 25 \times 1$  and accounting for the four highest occupied and the three lowest unoccupied states for pristine HfN<sub>2</sub>.

On the other hand, the Berry curvature<sup>38,39</sup> is defined as  $\Omega_n(k) = i \left\langle \frac{\partial}{\partial k} u_{n,k} \middle| \times \middle| \frac{\partial}{\partial k} u_{n,k} \right\rangle$ , where  $u_{n,k}$  and  $k$  represent the Bloch function and wave vector, respectively. For an applied in-plane electric field, this Berry curvature gives rise to an anomalous velocity  $v_{\perp} = -\frac{e}{\hbar} E \times \Omega(k)$ , which drives the charge carriers at the K and K' points in opposite directions. The Berry curvature is calculated from the wave functions *via* WANNIER90;<sup>40</sup>

$$\Omega_n(k) = - \sum_{(n' \neq n)} \frac{2\text{Im} \langle \psi_{n,k} | v_x | \psi_{n',k} \rangle \langle \psi_{n',k} | v_y | \psi_{n,k} \rangle}{(E_{n'} - E_n)^2}$$

where  $v_{x,y}$  are the velocity operators, and the summation is over all the occupied states. By applying an in-plane electric field and optical selection rule, charge, spin, and valley Hall current can be effectively manipulated, which has great potential for valleytronic applications.

### 3. Results and discussion

Fig. 1a presents the top and side views of the HfN<sub>2</sub>-ML. The optimized lattice parameters are  $a = b = 3.38 \text{ \AA}$ , in good agreement with previously reported values.<sup>20,21,23</sup> According to prior publications,<sup>19,41</sup> HfN<sub>2</sub>-ML exhibits excellent thermal, dynamical, and mechanical stability, as confirmed by *ab initio* molecular-dynamics simulations, phonon dispersion, and elastic-constant analyses. These results indicate that the HfN<sub>2</sub>-ML is structurally stable and suitable for further doping studies.

The electronic band structures, calculated at the GW level including spin–orbit coupling (SOC), reveal a direct band gap of 4.20 eV located at the K and K' points, as shown in Fig. 2a. The blue and red curves represent the spin-up and spin-down states, respectively. The band dispersion of the HfN<sub>2</sub>-ML

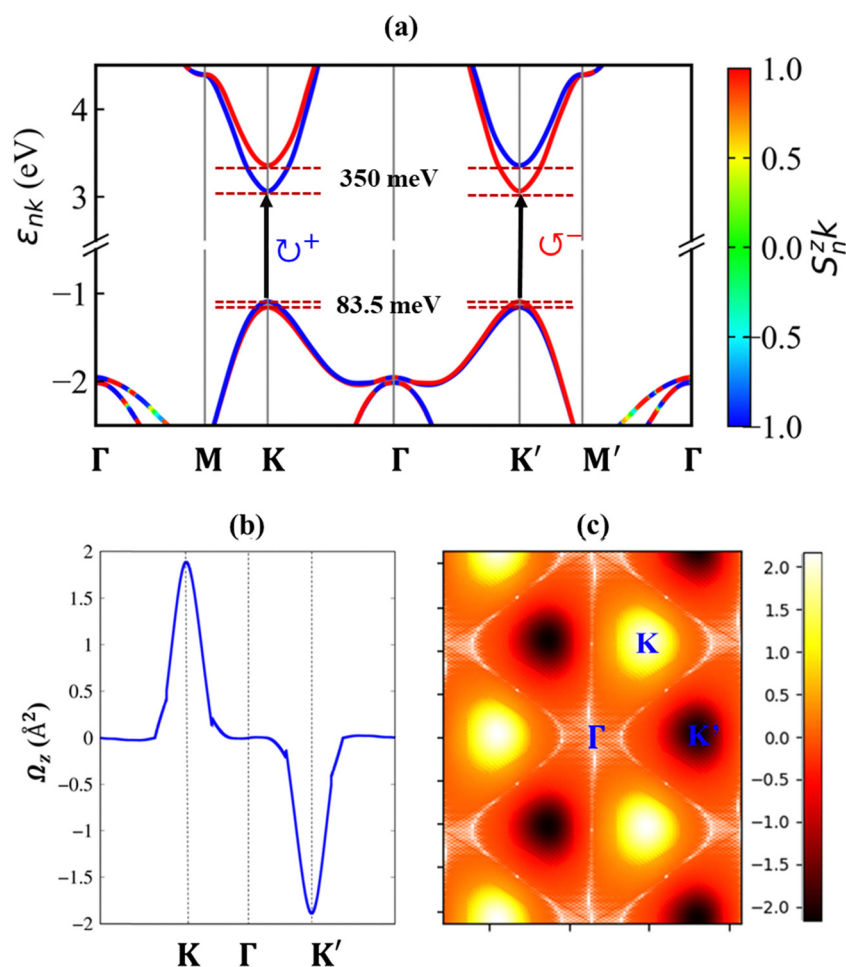


Fig. 2 (a) Energy band structure of HfN<sub>2</sub>-ML calculated at the GW level including spin–orbit coupling (SOC), showing the spin-resolved (spin-projected) bands. The black arrows indicate the optical transitions corresponding to left- and right-handed circularly polarized light ( $\sigma^+$  and  $\sigma^-$ ), (b) Berry curvature of HfN<sub>2</sub>-ML plotted along the high-symmetry path in the Brillouin zone, and (c) 2D distribution of Berry curvature in momentum space.

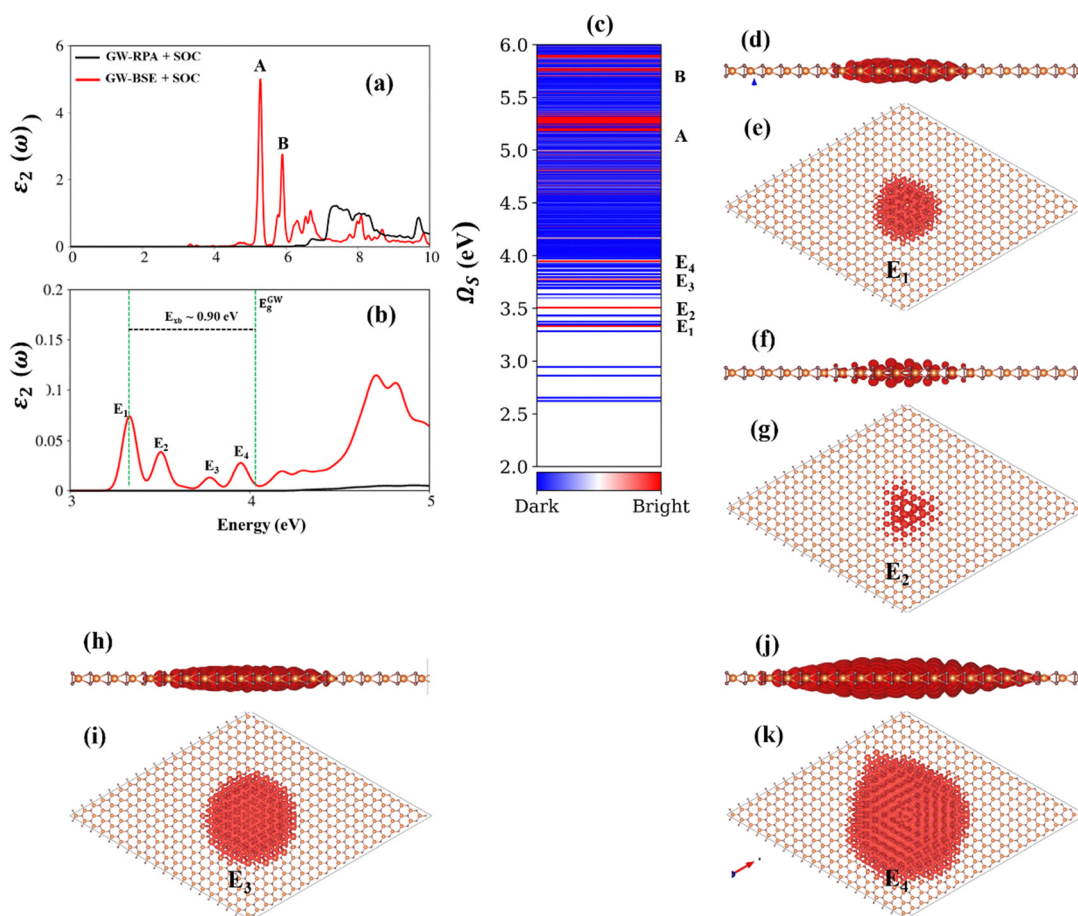


exhibits a pronounced valley spin splitting (VSS) of approximately 350 meV in the conduction band and a smaller VSS of about 83.5 meV in the valence band. Interestingly, this trend is opposite to that observed in conventional transition-metal dichalcogenides (TMDs), where the valence-band VSS dominates. For comparison, the VSS in monolayer MoS<sub>2</sub> and WSe<sub>2</sub> is about 150 meV and 430 meV, respectively, while the corresponding conduction-band splitting is nearly negligible.<sup>42</sup> The distinct SOC-induced splittings in the valence and conduction bands originate from the different orbital characters of the underlying Bloch states. Specifically, the valence band is primarily derived from the N-(2p<sub>x</sub>, 2p<sub>y</sub>) orbitals, whereas the conduction band is dominated by the Hf-(5d<sub>xy</sub>, 5d<sub>x<sup>2</sup>-y<sup>2</sup>) orbitals. These orbital contributions are clearly reflected in the band-decomposed charge densities and the orbital-resolved projected density of states (PDOS), as shown in Fig. 1b and c.</sub>

The spin ordering at the K and K' valleys is opposite; consequently, carriers in these valleys can be selectively excited by circularly polarized light following opposite optical selection rules, as indicated by the black arrows in Fig. 2a. It is worth

noting that the spin-split states at the K and K' valleys remain energetically degenerate rather than significantly lifted. This subtle degeneracy stems from the underlying time-reversal symmetry that intrinsically connects the two valleys. Nevertheless, the absence of inversion symmetry in HfN<sub>2</sub>-ML leads to opposite Berry curvatures for charge carriers at the K and K' points, as clearly shown in Fig. 2b and c. This valley-contrasting Berry curvature not only reveals the nontrivial topological nature of the electronic bands, but also offers a promising route for manipulating valley-dependent charge transport and optical selection in this system.

Fig. 3 shows the optical absorption spectra of HfN<sub>2</sub>-ML obtained from GW and GW-BSE calculations including SOC. In Fig. 3a, the imaginary part of the dielectric function,  $\epsilon_2(\omega)$ , computed within the GW-RPA framework (black), is compared with that obtained from the GW-BSE approach (red), which explicitly incorporates electron-hole interactions. Two pronounced absorption peaks, labeled A and B and located near 5.8 and 6.0 eV, respectively, correspond to bright resonant excitons that dominate the optical response above the



**Fig. 3** (a) and (b) The imaginary part of the dielectric functions, depicting the impact of excitonic effects (GW-BSE, represented by the solid red line) and without excitonic effects (GW-RPA, shown by the solid black line), covering the energy range from 0.0 eV to 10.0 eV, including an enlarged view within the 3.0 eV to 5.0 eV energy range, (c) exciton energy levels of HfN<sub>2</sub>-ML, derived by the GW-BSE method. Optically bright exciton states are highlighted in red, while dark exciton states are depicted in blue. (d)–(k) Representation of exciton amplitudes in real space, showcasing iso-value surfaces of the amplitude square, with the value set at 0.0003 of the maximum value. The upper panel provides a side view, while the lower panel offers a top view. Specific representations include (d)–(k) exciton E<sub>1</sub>–E<sub>4</sub>.



quasiparticle band gap. The inclusion of electron–hole interactions markedly enhances these features, highlighting the strong excitonic effects in this material. Fig. 3b focuses on the low-energy region, where four bound excitonic states ( $E_1$ – $E_4$ ) are identified below the GW quasiparticle band gap with a large binding energy of approximately 0.90 eV, primarily arising from transitions at the K and K' valleys. This value exceeds those reported for typical transition-metal dichalcogenides (TMDs), such as MoS<sub>2</sub> (0.54 eV)<sup>43</sup> and WS<sub>2</sub> (0.71 eV),<sup>44</sup> indicating enhanced Coulomb interactions and reduced dielectric screening in HfN<sub>2</sub>-ML. The excitons  $E_1$ – $E_4$  exhibit relatively small but finite oscillator strengths, as shown in Fig. 3c, suggesting that they are weakly bright (quasi-dark) due to spin–orbit-induced mixing and the lack of inversion symmetry. Fig. 3d–k illustrates the real-space exciton wavefunctions of these four lowest bound states from both side and top views. The excitonic wavefunctions are spatially well confined within a few unit cells, confirming their Wannier–Mott character, consistent with the exciton localization observed in monolayer TMDs.<sup>45,46</sup>

To investigate the influence of doping on the valleytronic properties of HfN<sub>2</sub>-ML, we substitute transition-metal atoms into the pristine system. Specifically, Cr and Ni atoms are selected as dopants, with a single Cr or Ni atom replacing one Hf atom in a  $4 \times 4 \times 1$  supercell of HfN<sub>2</sub>-ML to model the doping effect. The choice of Cr and Ni is motivated by their partially filled 3d orbitals, which can introduce localized magnetic moments and significantly enhance SOC. These characteristics are crucial for valleytronics, as they enable the

breaking of time-reversal and inversion symmetries, leading to valley splitting and spin–valley polarization. Upon doping, the Cr-doped HfN<sub>2</sub>-ML becomes spin-polarized, whereas the Ni-doped system remains non-spin polarized. The calculated total magnetic moments are  $-1.937\mu_B$  for Cr-doped HfN<sub>2</sub>-1L and  $0.000\mu_B$  for Ni-doped HfN<sub>2</sub>-ML, respectively. This contrasting behavior originates from their distinct electronic configurations: the Cr-3d orbitals lie near the Fermi level and strongly hybridize with Hf-d and N-p states, resulting in exchange splitting and stabilization of a ferromagnetic ground state. In contrast, the Ni-3d orbitals are positioned deeper in the valence region, exhibiting weak hybridization near the band edges, which suppresses spin polarization and leads to a nonmagnetic ground state.

The charge density difference ( $\Delta\rho$ ) is plotted in Fig. 4a, and defined as  $\Delta\rho = \rho_{\text{Cr-/Ni-HfN}_2} - \rho_{\text{Cr/Ni}} - \rho_{\text{HfN}_2}$ , where  $\rho_{\text{Cr-/Ni-HfN}_2}$ ,  $\rho_{\text{HfN}_2}$ , and  $\rho_{\text{Cr/Ni}}$  represent the charge densities of the Cr- or Ni-doped HfN<sub>2</sub>-ML, the pristine HfN<sub>2</sub>-ML, and the isolated Cr or Ni atoms, respectively, in the same spatial configuration. The resulting maps reveal pronounced charge accumulation and depletion regions primarily localized at the doping interface, confirming strong orbital hybridization between the dopant and the host lattice. Bader charge analysis further shows that approximately 2.50 (2.40) electrons are transferred from Cr (Ni) to the HfN<sub>2</sub>-ML, indicating significant charge redistribution and covalent bonding characteristics. To gain deeper insight into the magnetic behavior, the spin density distribution of the Cr-doped HfN<sub>2</sub>-ML is presented in Fig. 4b. The spin density is

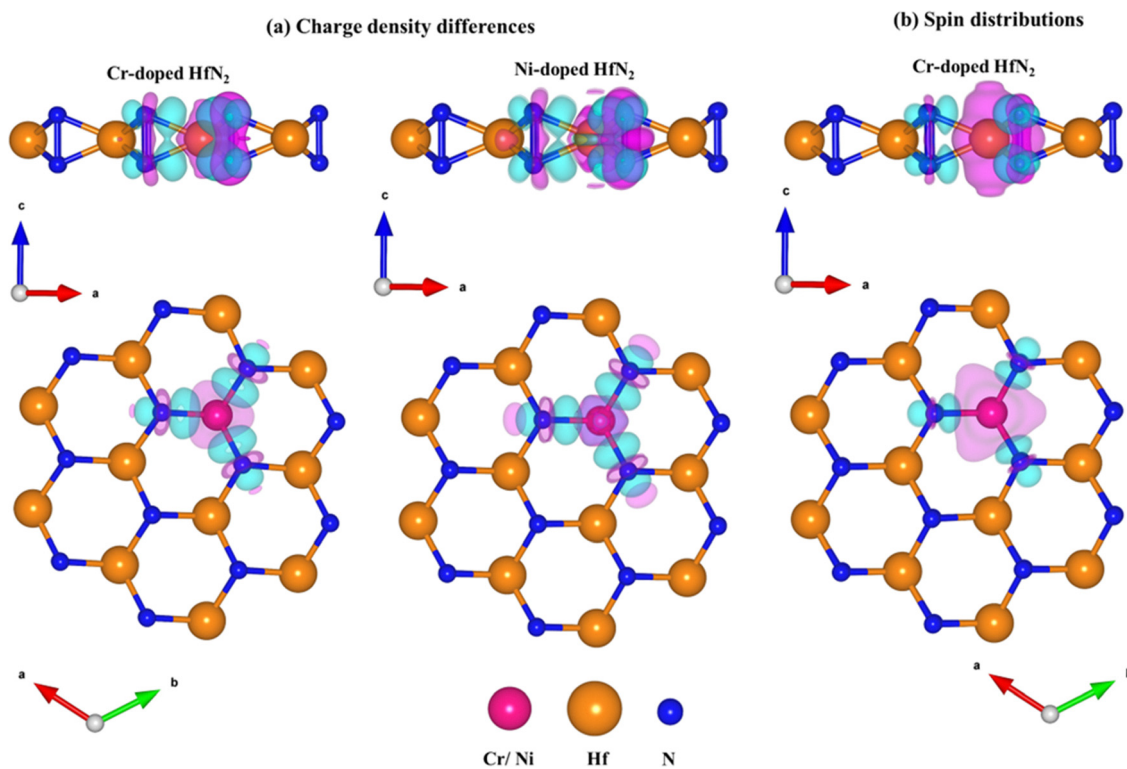


Fig. 4 (a) Side view and top view of the charge density differences of Cr-/Ni-doped HfN<sub>2</sub>-1L, and (b) spin distributions of Cr-doped HfN<sub>2</sub>, respectively. Note: the pink and cyan iso-surfaces are 0.002.



mainly concentrated around the Cr dopant site, while contributions from the surrounding Hf and N atoms are relatively minor, confirming that the magnetic moment predominantly originates from the localized Cr-3d states.

Fig. 5a presents the density of states (DOS) of the pristine  $\text{HfN}_2$ -ML, calculated at the PBE level without SOC. For comparison, Fig. 5b and c display the DOS of the Cr- and Ni-doped  $\text{HfN}_2$ -ML, respectively, obtained using the same theoretical level of theory. Upon Cr doping (Fig. 5b), a ferromagnetic ground state emerges, as indicated by the distinct spin-resolved orbital contributions of Cr, Hf, and N atoms in both

the valence and conduction regions. This behavior aligns with the spin-density distributions in Fig. 4b, where a clear asymmetry between spin-up and spin-down channels is evident. The induced magnetism originates from spin-dependent splitting of the valence states and the localization of Cr-3d orbitals near the Fermi level ( $E_F$ ), which enhances exchange interactions and mediates spin polarization among neighboring Hf and N atoms. Such orbital hybridization and energy-level rearrangement reveal that Cr doping not only stabilizes long-range ferromagnetic order but also substantially modifies the electronic structure near  $E_F$ , thereby offering a mechanism to tailor

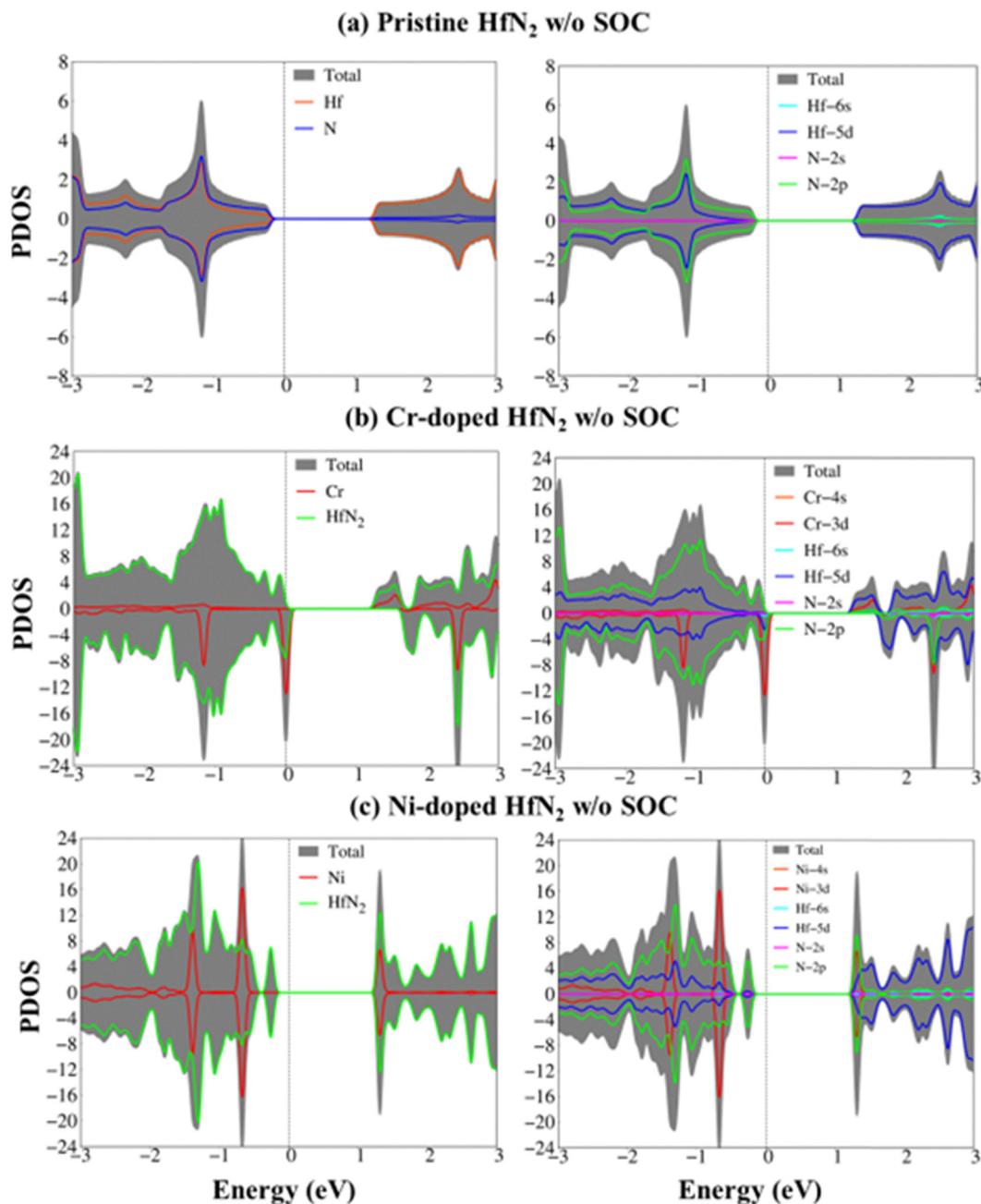


Fig. 5 (a) The van Hove singularities in the density of states (DOS) without (w/o) SOC of pristine  $\text{HfN}_2$ , corresponding to (b) and (c) doping Cr, and Ni atoms in  $\text{HfN}_2$ -ML, respectively.



the spintronic functionality of HfN<sub>2</sub>-ML. Specifically, the adsorption of Cr introduces an n-type character, as Cr-3d orbitals donate additional electrons close to the conduction-band edge, shifting the Fermi level upward and producing a metallic response in the spin-polarized DOS. Ni-doped HfN<sub>2</sub>-ML in Fig. 5c, on the other hand, retains nonmagnetic and semiconducting characteristics. The nearly symmetric van Hove singularities in the spin-up and spin-down DOS closely mirror those of the pristine HfN<sub>2</sub>-ML, confirming the absence of exchange splitting and net magnetic moment. The electronic structure thus remains dominated by the host Hf-d and N-p states. Consequently, while Cr incorporation enables the formation of spin-polarized states and magnetic ordering, Ni doping primarily alters the band dispersion, serving instead as an effective route to tune the electronic transport properties without breaking time-reversal symmetry.

Fig. 6a–c present the PBE + SOC band structures of the pristine, Cr-doped, and Ni-doped HfN<sub>2</sub>-ML. The corresponding magnified views focusing on the valence band dispersions near the Fermi level are shown in Fig. 6d–f. As illustrated in Fig. 6a, the pristine HfN<sub>2</sub>-ML exhibits distinct band-edge features

around the K and K' valley points. The calculated parameters, including the valley Zeeman splitting ( $E_z$ ), valley splitting ( $\Delta_v$ ), and spin splitting ( $\Delta_{spin,c/v}^\pm$ ) at the K and K' valleys for the pristine, Cr-doped, and Ni-doped HfN<sub>2</sub>-ML are summarized in Table 1. The valley Zeeman splitting is given by  $E_z = \Delta_{opt}^+ - \Delta_{opt}^-$ , where  $\Delta_{opt}^+$  and  $\Delta_{opt}^-$  correspond to the optical transition energies under left- and right-circularly polarized light ( $\sigma^+$  and  $\sigma^-$ ), respectively. Notably, in the Cr-doped HfN<sub>2</sub>-ML, the emergence of magnetic ordering breaks time-reversal symmetry and lifts the valley degeneracy, resulting in a pronounced Zeeman splitting of  $E_z = 300$  meV. In contrast, the Ni-doped system, being nonmagnetic, preserves the valley degeneracy, consistent with its absence of spin polarization.

## 4. Conclusions

In summary, based on first-principles calculations, we have investigated the valley properties and excitonic states of monolayer HfN<sub>2</sub>, as well as the effects of Cr and Ni doping on its electronic structure. The pristine HfN<sub>2</sub>-ML exhibits a direct

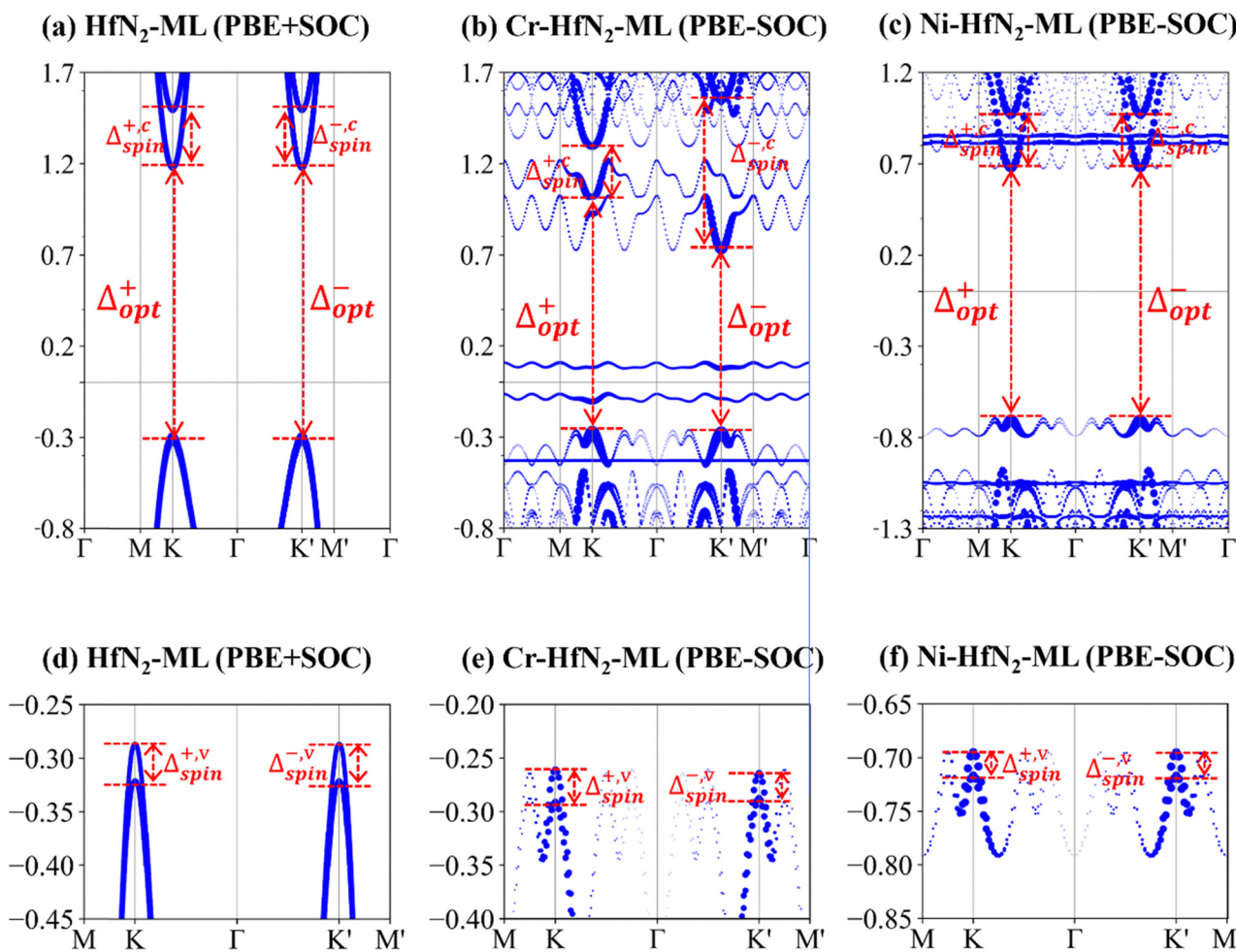


Fig. 6 (a) Energy band structure of the pristine HfN<sub>2</sub>-ML obtained with PBE + SOC; (b) and (c) unfolded electronic band structures of the Cr- and Ni-doped HfN<sub>2</sub>-ML, respectively, obtained using the vaspkit code.<sup>47</sup> Panels (d)–(f) show the corresponding enlarged band structures in the valence bands.



**Table 1** Calculated optical and spin–valley parameters of HfN<sub>2</sub>-ML under Cr and Ni doping, obtained under the DFT + SOC level of theory. Listed are the energies of the  $\sigma^+$  ( $\sigma^-$ ) circularly polarized absorption edges corresponding to the excitonic transitions  $\Delta_{\text{opt}}^+$  ( $\Delta_{\text{opt}}^-$ ), the spin splittings of the conduction and valence bands ( $\Delta_{\text{spin,c}}^{\pm}$  and  $\Delta_{\text{spin,v}}^{\pm}$ ), and the valley Zeeman splitting ( $E_z$ ). The symbols “+” and “-” represent quantities at the K and K' valleys, respectively, while “c” and “v” denote the conduction and valence bands. All energies are expressed in meV

System	$\Delta_{\text{spin}}^{+,c}$	$\Delta_{\text{spin}}^{-,c}$	$\Delta_{\text{spin}}^{+,v}$	$\Delta_{\text{spin}}^{-,v}$	$\Delta_{\text{opt}}^+$	$\Delta_{\text{opt}}^-$	$E_z$
Pristine HfN <sub>2</sub>	40.0	40.0	400	400	1450	1450	0
Cr-doped HfN <sub>2</sub>	35.0	30.0	300	800	1150	850	300
Ni-doped HfN <sub>2</sub>	25.0	25.0	350	350	1350	1350	0

band gap located at the K and K' valleys. Remarkably, pronounced VSSs of 350 meV and 83.5 meV are obtained in the conduction and valence bands, respectively, primarily originating from strong SOC. Two bright resonant excitons (A and B) appear near 5.8 and 6.0 eV, while four bound excitonic states ( $E_1$ – $E_4$ ) are identified below the quasiparticle gap with a large binding energy of approximately 0.90 eV, indicating strong Coulomb interactions and reduced dielectric screening. Furthermore, Cr and Ni doping significantly modify the valley–spin characteristics at the K and K' valleys through SOC-induced interactions. These results deepen the theoretical understanding of valleytronic and excitonic phenomena in 2D materials and underscore the potential of doped HfN<sub>2</sub>-MLs for next-generation electronic, spintronic, and valleytronic applications.

## Conflicts of interest

The authors declare no competing interests.

## Data availability

All data supporting the findings of this study are available within the article. This includes numerical data underlying all figures and tables, structural models, and representative input files used in the calculations. Additional details regarding computational parameters and analysis procedures are fully described in the Computational details section.

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