

Electronic Supplementary Information for
Intrinsic Ferromagnetism and Valley Polarization in Hydrogenated Group V
Transition-metal Dinitride (MN_2H_2 , $M = V/Nb/Ta$) Nanosheets: Insights from
First-principles

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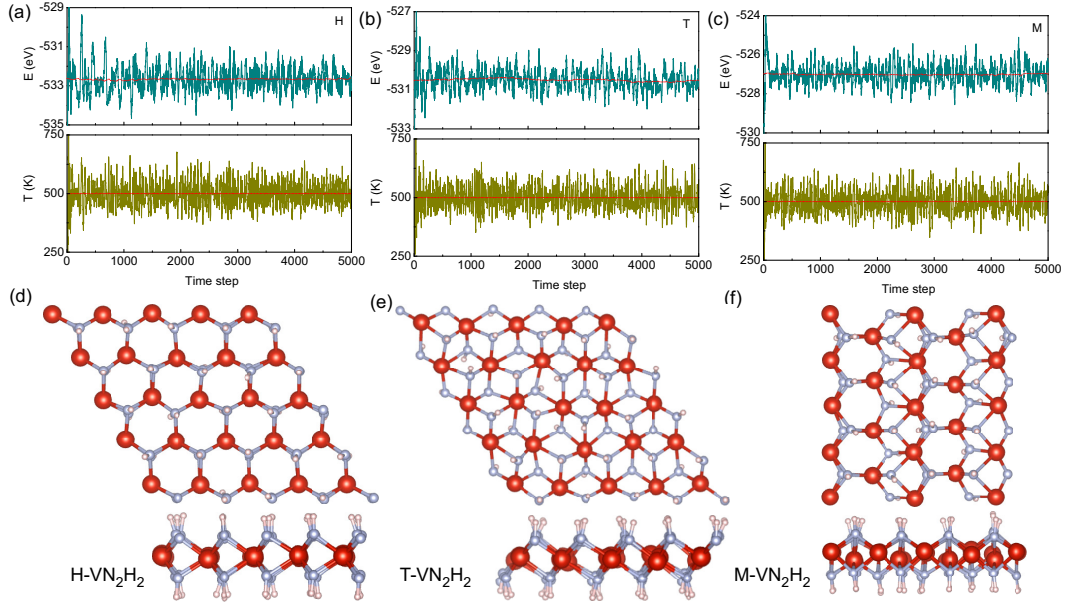


FIG. 1. [(a)-(c)] The total energy and temperature versus time steps for the H-, T-, and M-VN₂H₂ nanosheets during the AIMD simulations. The dotted lines represent the average values of adjacent data in 1 ps. [(d)-(f)] The snapshots for the final configurations after AIMD simulations.

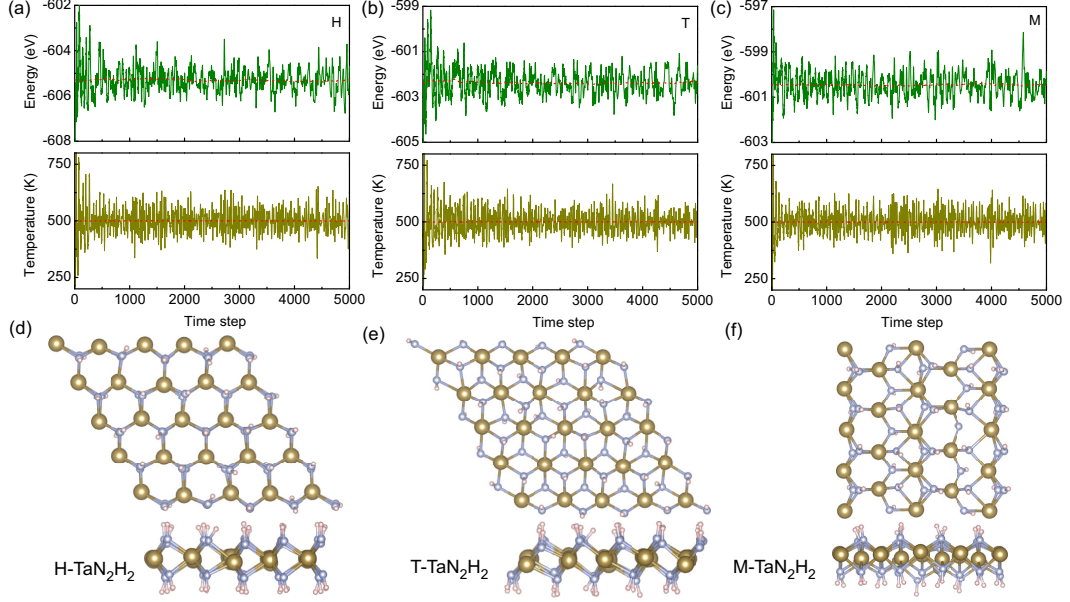


FIG. 2. [(a)-(c)] The total energy and temperature versus time steps for the H-, T-, and M-TaN₂H₂ nanosheets during the AIMD simulations. The dotted lines represent the average values of adjacent data in 1 ps. [(d)-(f)] The snapshots for the final configurations after AIMD simulations.

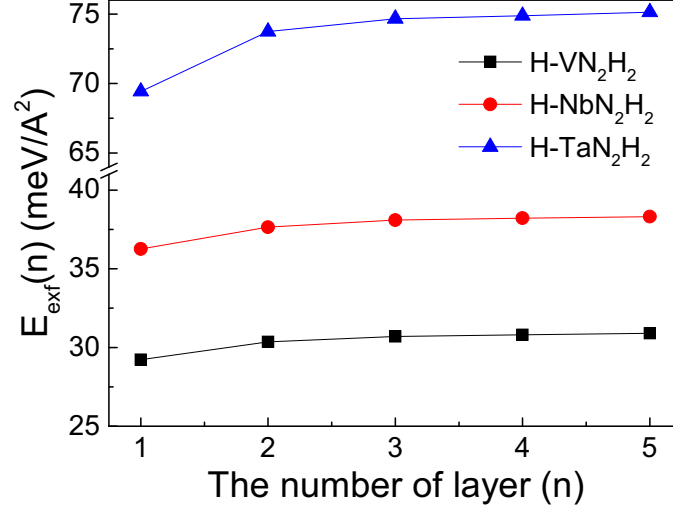


FIG. 3. The n -layer exfoliation energies ($E_{exf}(n)$) of H-MN₂H₂ (M=V/Nb/Ta) nanosheets. Here, $E_{exf}(n)$ is calculated as $(E_{iso}(n) - E_{bulk} \times n/m)/A$. $E_{iso}(n)$ is the unit cell energy of an isolated n -layer slab structure, E_{bulk} is the unit cell energy of a bulk material with m layers, and A is the in-plane area of the bulk unit cell. For these H-MN₂H₂ systems, a $2H$ -NbS₂-like structure is adopted as their bulk references.

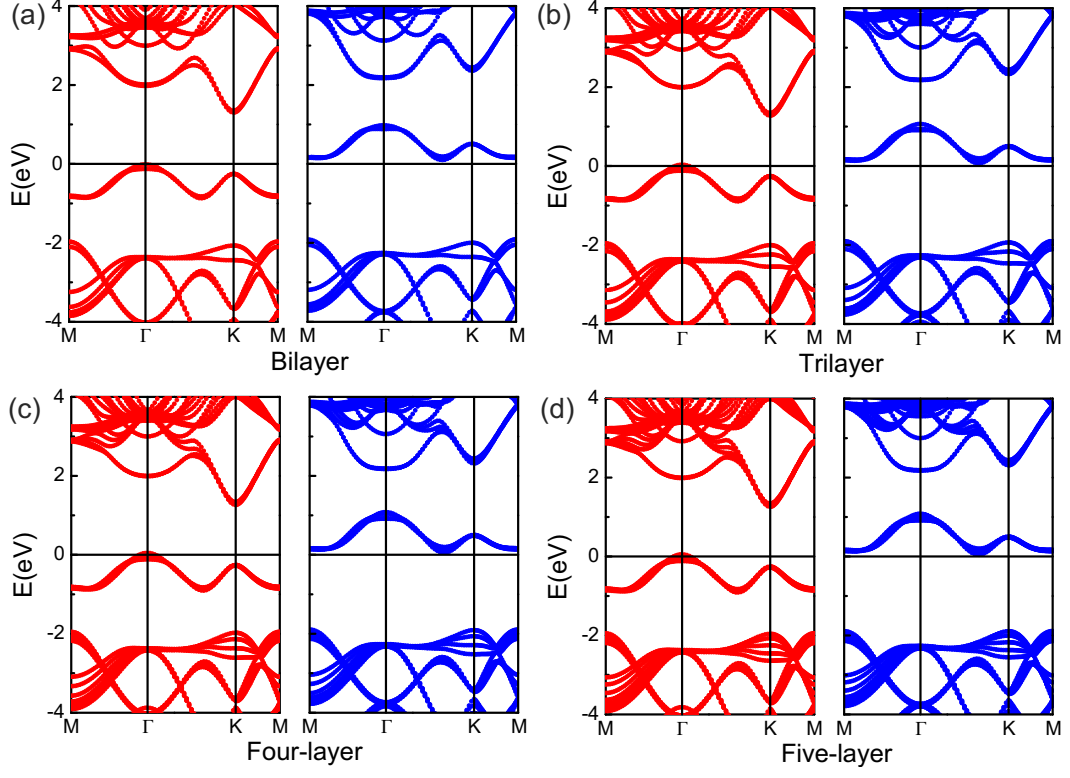


FIG. 4. The PBE band structures of H-NbN₂H₂ (a) bilayer, (b) trilayer, (c) four-layer, and (d) five-layer systems at the FM state. The corresponding PBE band gaps are 0.12, 0.035 and ~ 0 eV for the bilayer, trilayer, and four-/five-layer ones, which are all smaller than the monolayer case (0.29 eV).

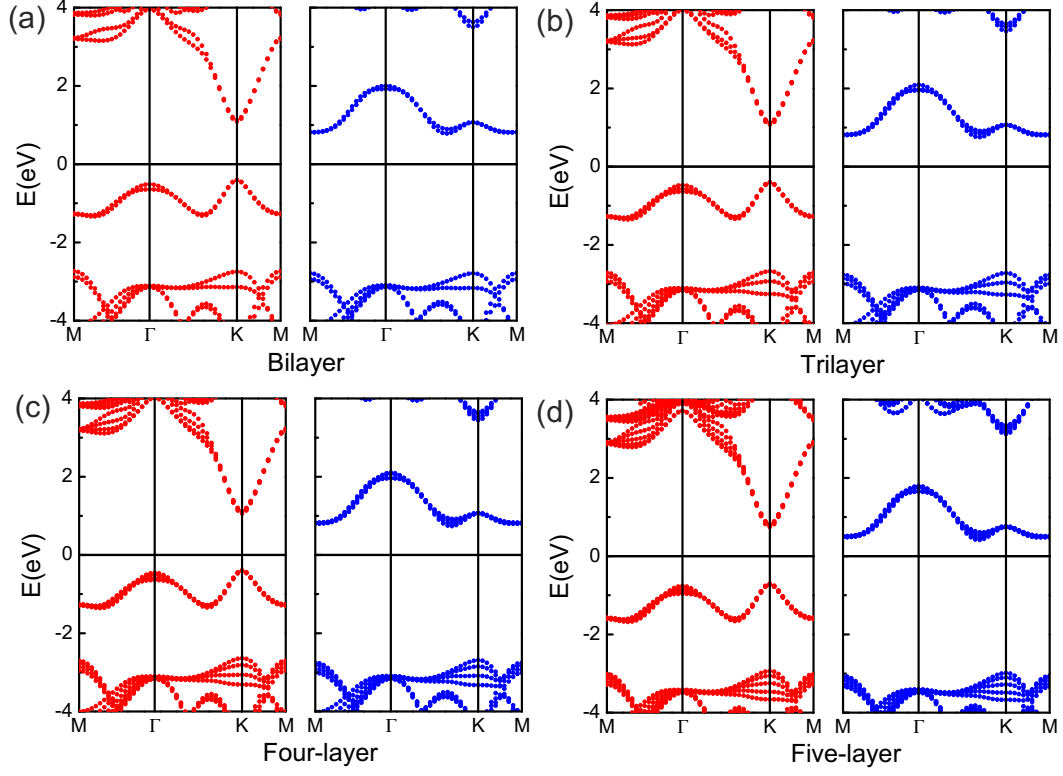


FIG. 5. The HSE band structures of the $\text{H-NbN}_2\text{H}_2$ (a) bilayer, (b) trilayer, (c) four-layer, and (d) five-layer systems at the FM state. The corresponding HSE band gaps are 1.20, 1.15, 1.14 and 1.12 eV for the bilayer, trilayer, four-layer and five-layer ones, which are also smaller than the monolayer case (1.22 eV).

H-NbN ₂ H ₂											
Raman	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	IR	ω'_1	ω'_2	ω'_3	ω'_4
modes	E''	E'	A'_1	E''	E'	A'_1	modes	E'	A_2''	E'	A_2''
(cm ⁻¹)	335	410	653	660	695	3392		410	592	695	3393

TABLE I. The frequencies of the Raman and IR active vibrational modes in the H-NbN₂H₂ nanosheet.

T-NbN ₂ H ₂									
Raman	ω_1	ω_2	ω_3	ω_4	IR	ω'_1	ω'_2	ω'_3	ω'_4
modes	E_g	E_g	A_{1g}	A_{1g}	modes	E_u	E_u	A_{2u}	A_{2u}
(cm ⁻¹)	379	533	572	3392		210	533	580	3394

TABLE II. The frequencies of Raman and IR active vibrational modes in the T-NbN₂H₂ nanosheet.

M-NbN ₂ H ₂									
Raman+IR	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	ω_9
modes	A'	A''	A''	A'	A'	A''	A'	A''	A'
(cm ⁻¹)	124	153	235	240	320	368	382	408	430
	ω_{10}	ω_{11}	ω_{12}	ω_{13}	ω_{14}	ω_{15}	ω_{16}	ω_{17}	ω_{18}
	A''	A'	A''	A'	A'	A''	A'	A'	A''
	470	475	521	524	580	607	617	652	658
	ω_{19}	ω_{20}	ω_{21}	ω_{22}	ω_{23}	ω_{24}	ω_{25}	ω_{26}	ω_{27}
	A'	A'	A''	A'	A'	A'	A'	A'	A'
	670	691	715	783	799	3325	3412	3422	3442

TABLE III. The frequencies of Raman and IR active vibrational modes in the M-NbN₂H₂ nanosheet.

$\theta_D(\text{K})$	H-phase	T-phase	M-phase
VN_2H_2	376	248	262
NbN_2H_2	261	173	198
TaN_2H_2	199	139	155

TABLE IV. The Debye temperature of MN_2H_2 nanosheets. Here, the Debye temperature (θ_D) is estimated from the phonon bands as $\frac{1}{\theta_D^3} = \frac{1}{3}(\frac{1}{\theta_{FA}^3} + \frac{1}{\theta_{TA}^3} + \frac{1}{\theta_{LA}^3})$, where $\theta_{FA}/\theta_{TA}/\theta_{LA}$ is obtained from the highest frequency of flexural acoustic (FA)/transverse acoustic (TA)/longitudinal acoustic (LA) phonon branches as $\theta = \hbar\omega_{max}/k_B$ ($\hbar$ and k_B are the Planck constant and Boltzmann constant, respectively).

	VN ₂ H ₂			NbN ₂ H ₂			TaN ₂ H ₂		
(eV)	H	T	M	H	T	M	H	T	M
PBE	0.73	0.09	metal	0.32	metal	0.12	0.15	metal	0.21
PBE+ <i>soc</i>	0.72	0.07	metal	0.27	metal	0.09	0.05	metal	0.13
HSE	2.01	1.50	metal	1.22	0.39	0.91	0.96	metal	0.97
HSE+ <i>soc</i>	1.99	1.50	metal	1.17	0.39	0.89	0.88	metal	0.86

TABLE V. The band gaps of H-, T- and M-MN₂H₂ (M=V/Nb/Ta) nanosheets by the PBE, PBE+*soc*, HSE and HSE+*soc* calculations.