

Supporting Information

An electron counting formula to explain and to predict hydrogenated and metallated borophenes

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S1. ELECTRON COUNT FORMULA IN BOROPHENES

The most prominent way of removing excess electrons from a 2D boron layer is found to be the formation of hexagonal holes. The number of hexagonal holes in a triangular lattice of boron is described by a parameter called hole density (h), which is defined as follows,

$$h = \frac{\text{number of hexagonal holes}}{\text{total boron atoms in the sheet without holes}} = \frac{x}{n} \quad (\text{S1})$$

The numerator in the above equation gives the number of atoms removed from the unit cell (x) and the denominator shows the total number of atoms in the sheet before the hole formation (n). To address the problem of excess/deficient electron in a borophene sheet with hole density h , we construct the parent borophene sheet with n number of boron atoms (prior to the hole formation) as a multiple of triangular units B–B₂. As B–B₂ unit has one extra electron compared to MgB₂ or graphene, the number of excess electrons in the newly constructed triangular lattice is directly proportional to the multiple of B–B₂ units present in the lattice. Now, removal of x number of boron atoms from the triangular framework of n atoms would give a borophene with HD, h . However, a mismatch of electrons arises from the number of excess electrons in the triangular framework versus the number of actual electrons eliminated from the framework through the removal of boron atoms to form hexagonal holes.

To determine this mismatch of electrons, first, we calculate the minimum number of atoms required (N_{B-B_2}) to construct a triangular lattice made up of B–B₂ units for a given hole density (h). This can be obtained by taking the least common multiple of 3 (as there are three atoms in B–B₂) and n , $LCM[3, n]$. Here, we formulate another parameter $f = (\frac{LCM[3, n]}{3})$, which stands for the multiples of B–B₂ units in the newly constructed triangular lattice.

$$N_{B-B_2} = LCM[3, n] \quad (\text{S2})$$

$$f = \frac{LCM[3, n]}{3} \quad (\text{S3})$$

Now, to obtain the hole density (h), x_{B-B_2} number of atoms have to be removed from the N_{B-B_2} triangular lattice, which is given as,

$$x_{B-B_2} = N_{B-B_2} * \frac{x}{n} \quad (\text{S4})$$

As each B-B₂ unit contains one excess electron, for f number of B-B₂ units there will be f excess electrons. On the other hand, we are removing x_{B-B_2} number of boron atoms from the lattice, where each boron contributes 3 electrons. In other words, we are eliminating $3 * x_{B-B_2}$ electrons from a triangular lattice of f excess electrons. Therefore, the number of mismatched electrons can be written as,

$$N_{B-B_2}^e = f - 3 * x_{B-B_2} \quad (\text{S5})$$

Further,

$$N_{B-B_2}^e = (f - 3x_{B-B_2}) * \frac{N_{B-B_2}}{N_{B-B_2}} \quad (\text{S6})$$

$$= \left(\frac{f}{N_{B-B_2}} - \frac{3x_{B-B_2}}{N_{B-B_2}} \right) * N_{B-B_2} \quad (\text{S7})$$

$$= \left(\frac{1}{3} - 3h \right) * N_{B-B_2} \quad (\text{S8})$$

The above equation stands for the number of mismatched electrons, in a triangular framework of N_{B-B_2} atoms. This can be applied to any borophene with hole density h ($=\frac{x}{n}$), where n is the number of atoms in the parent triangular lattice without holes.

$$N^e = \left(\frac{1}{3} - 3h \right) n \quad (\text{S9})$$

$$= \left(\frac{1}{3} - 3h \right) * \text{Denomantor of the hole density} \quad (\text{S10})$$

Borophene	δ'_6	α_8	α	β_{12}	χ_3
Hole density $(h = \frac{x}{n})$	$\frac{0}{3}$	$\frac{1}{12}$	$\frac{1}{9}$	$\frac{1}{6}$	$\frac{1}{5}$
Number of mismatching electrons per unit cell (N_e)	+1	+1	0	-1	$-\frac{4}{3}$
Fractional electron count at each boron (f_e)	$+\frac{1}{3}$	$+\frac{1}{11}$	$\frac{0}{8}$	$-\frac{1}{5}$	$-\frac{1}{3}$

TABLE S1: Electronic requirement in borophene sheets with varying HD.

	β_{12}	B_5H_2	B_5H_3	LiB_5	$\text{LiB}_{10}\dagger$	$\text{MgB}_{10}\dagger$
a (Å)	5.06	5.13	5.16	5.11	5.08	5.08
b (Å)	2.93	2.81	2.89	2.95	2.93	2.94
I.E. (eV/atom)	-0.27	-0.46	-0.22	-0.18	-0.12	-0.11

TABLE S2: The lattice parameters (a, b) for the standalone sheets and their respective interaction energy (eV/atom) with $\text{Ag}(111)$. † indicates a bilayer.

S2. COMPUTATIONAL DETAILS

All the electronic structure calculations are performed using VASP program.[1–3] PBE functional and the plane-wave basis set (with a cut off of 600 eV) clubbed with the projector augmented wave (PAW) potentials are employed for optimizing the structures.[4] Van der Waals correction is incorporated using the DFT-D3 method. [5] A k-mesh of 0.2 \AA^{-1} is used during optimization. For band structure, Density of States (DOS), and Lobster calculations for projected Crystal Orbital Overlap Population (pCOOP) and Mulliken gross orbital population analysis [6], a Monkhorst-Pack mesh of 0.01 \AA^{-1} is considered. To determine the dynamic stability of the systems we performed phonon calculations using the phonopy software. [7]

For Borophane systems, the formation energy (E_f) is calculated using the following formula,

$$E_f = \frac{(E_{BH} - E_{Borophene} - n * E_H)}{N} \quad (S11)$$

where E_{BH} , $E_{Borophene}$ and E_H are the energies of the boron-hydrogen sheet, isolated borophene and the isolated hydrogen atom respectively; n and N are the number of H atoms and total number of atoms in the system.

Further, 2D layers are optimized on $Ag(111)$ surface, which contains four layers of Ag with each layer containing four Ag atoms. During optimization, the first two layers are relaxed while the rest two layers are kept fixed. We choose the 2D lattices of boron such a way that the percentage of lattice mismatched with the $Ag(111)$ surface doesn't exceed 3%. The interaction energy of the 2D layers on $Ag(111)$ is calculated using the following formula,

$$E_{Int} = \frac{(E_{total} - E_{2D-Surface} - E_{Ag-Surface})}{N} \quad (S12)$$

In the above equation, E_{Int} is the interaction energy per atom, E_{total} is the energy of the system, $E_{2D-Surface}$ is the energy of free standing 2D layer, $E_{Ag-Surface}$ is the energy of the $Ag(111)$ surface and N is the total number of atoms in the free standing borophene sheet/borophane sheet/metal encapsulated monolayer or bilayer borophene.

We also performed *ab-initio* molecular dynamic simulations at Gamma point using a Nose-Hoover thermostat under NVE ensemble to check the thermal stability of the metal encapsulated borophene systems.

S3. HYDROGENATION OF β_{12} BOROPHENE

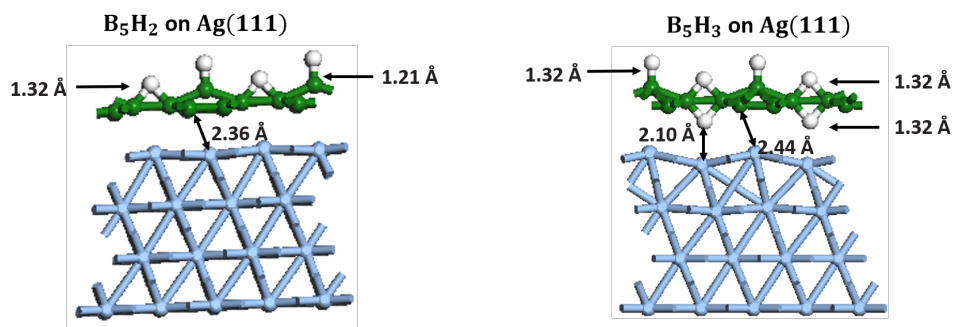


FIG. S1: (a) B_5H_2 and (b) B_5H_3 optimized on $Ag(111)$.

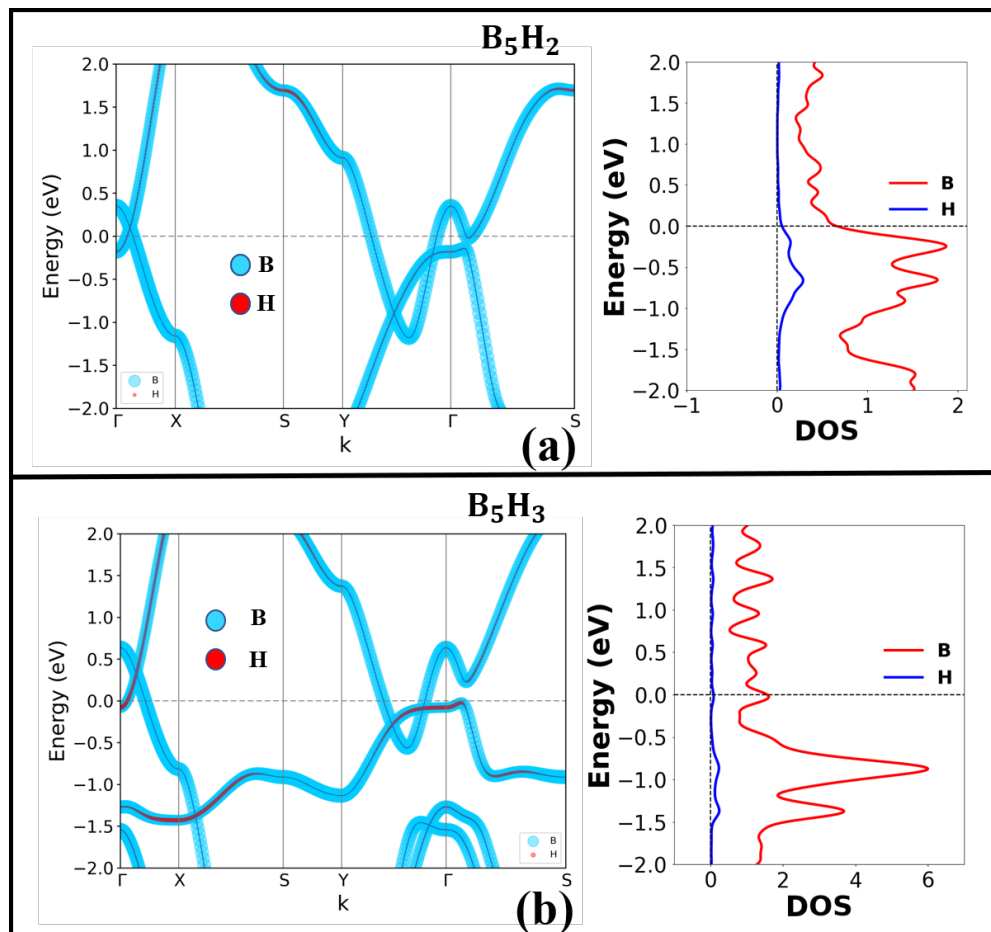


FIG. S2: Band structure and DOS of the standalone (a) B_5H_2 and (b) B_5H_3 sheets.

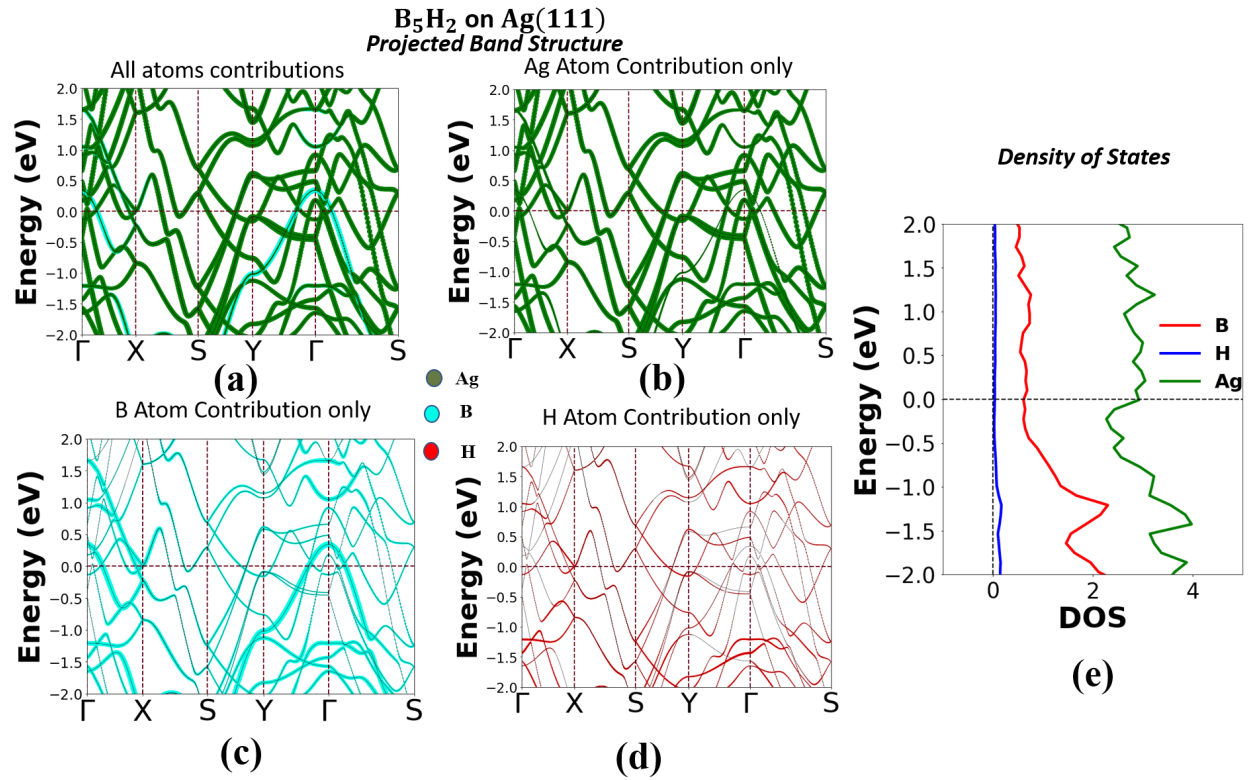


FIG. S3: Projected band structure for B₅H₂ on Ag(111) showing contribution from (a) all atoms (b) Ag atoms only (c) B atoms only (d) H atoms only. The projected DOS for the same is shown in (e).

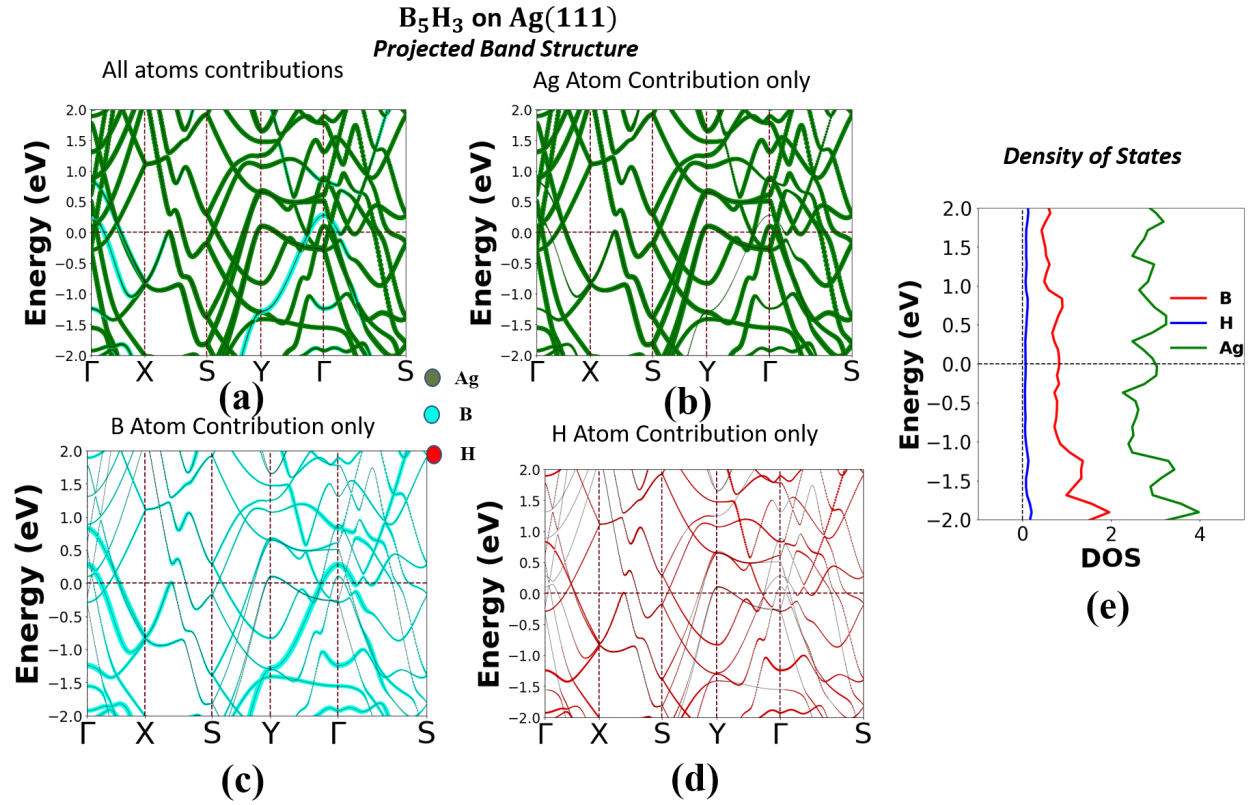


FIG. S4: Projected band structure for B₅H₃ on Ag(111) showing contribution from (a) all atoms (b) Ag atoms only (c) B atoms only (d) H atoms only. The projected DOS for the same is shown in (e).

Mulliken Gross Population of <i>Ag</i> atoms in β_{12} - <i>Ag</i> (111)							
Atom		5 <i>s</i>	<i>d</i> _{<i>xy</i>}	<i>d</i> _{<i>yz</i>}	<i>d</i> _{<i>xz</i>}	<i>d</i> _{<i>x²-y²</i>}	<i>d</i> _{<i>z²</i>}
First Layer	1	0.18	1.95	1.95	1.95	1.94	1.94
	2	0.17	1.95	1.95	1.95	1.94	1.94
	3	0.18	1.95	1.95	1.95	1.95	1.94
	4	0.18	1.95	1.95	1.95	1.95	1.94
Second Layer	1	0.18	1.95	1.95	1.95	1.95	1.94
	2	0.18	1.95	1.95	1.95	1.95	1.94
	3	0.19	1.94	1.95	1.95	1.94	1.94
	4	0.18	1.95	1.95	1.95	1.94	1.94
Third Layer	1	0.14	1.95	1.95	1.95	1.95	1.92
	2	0.13	1.95	1.95	1.95	1.95	1.92
	3	0.13	1.95	1.95	1.95	1.95	1.91
	4	0.13	1.95	1.95	1.95	1.95	1.91
Fourth Layer	1	0.43	1.94	1.97	1.97	1.94	1.96
	2	0.43	1.94	1.97	1.97	1.94	1.96
	3	0.43	1.94	1.97	1.97	1.94	1.96
	4	0.43	1.94	1.97	1.97	1.94	1.96

TABLE S3: Mulliken Gross Population of the 5*s* and 4*d* orbitals of *Ag* atoms in the *Ag*(111) surface containing β_{12} borophene. The first layer corresponds to the nearest *Ag*(111) layer to the β_{12} borophene. The second layer corresponds to the second nearest *Ag*(111) layer and so on.

Mulliken Gross Population of Ag atoms in $B_5H_2-Ag(111)$							
Atom		$5s$	d_{xy}	d_{yz}	d_{xz}	$d_{x^2-y^2}$	d_{z^2}
First Layer	1	0.16	1.94	1.91	1.96	1.94	1.89
	2	0.16	1.94	1.91	1.96	1.94	1.89
	3	0.13	1.94	1.89	1.97	1.94	1.89
	4	0.13	1.94	1.89	1.97	1.94	1.89
Second Layer	1	0.18	1.93	1.94	1.94	1.94	1.93
	2	0.18	1.93	1.94	1.94	1.94	1.93
	3	0.19	1.94	1.94	1.94	1.93	1.93
	4	0.19	1.94	1.94	1.94	1.93	1.93
Third Layer	1	0.18	1.94	1.95	1.95	1.94	1.93
	2	0.18	1.94	1.95	1.95	1.94	1.93
	3	0.18	1.94	1.95	1.95	1.94	1.93
	4	0.18	1.94	1.95	1.95	1.94	1.93
Fourth Layer	1	0.42	1.94	1.96	1.96	1.93	1.96
	2	0.41	1.94	1.96	1.96	1.93	1.96
	3	0.42	1.94	1.97	1.96	1.94	1.96
	4	0.41	1.94	1.97	1.96	1.94	1.96

TABLE S4: Mulliken Gross Population of the $5s$ and $4d$ orbitals of Ag atoms in the $Ag(111)$ surface containing B_5H_2 borophane. The first layer corresponds to the nearest $Ag(111)$ layer to the B_5H_2 borophane. The second layer corresponds to the second nearest $Ag(111)$ layer and so on.

Mulliken Gross Population of Ag atoms in $B_5H_3-Ag(111)$							
Atom		$5s$	d_{xy}	d_{yz}	d_{xz}	$d_{x^2-y^2}$	d_{z^2}
First Layer	1	0.39	1.95	1.93	1.97	1.95	1.90
	2	0.39	1.95	1.93	1.97	1.95	1.90
	3	0.43	1.95	1.96	1.96	1.94	1.94
	4	0.43	1.95	1.96	1.96	1.94	1.94
Second Layer	1	0.42	1.94	1.95	1.95	1.94	1.93
	2	0.42	1.94	1.95	1.95	1.94	1.93
	3	0.43	1.94	1.95	1.95	1.94	1.93
	4	0.43	1.94	1.95	1.95	1.94	1.93
Third Layer	1	0.42	1.94	1.95	1.96	1.94	1.93
	2	0.42	1.94	1.95	1.96	1.94	1.93
	3	0.43	1.94	1.95	1.95	1.94	1.93
	4	0.43	1.94	1.95	1.95	1.94	1.93
Fourth Layer	1	0.60	1.94	1.96	1.96	1.94	1.95
	2	0.60	1.94	1.96	1.96	1.94	1.95
	3	0.61	1.94	1.96	1.96	1.94	1.95
	4	0.61	1.94	1.96	1.96	1.94	1.95

TABLE S5: Mulliken Gross Population of the $5s$ and $4d$ orbitals of Ag atoms in the $Ag(111)$ surface containing B_5H_3 borophane. The first layer corresponds to the nearest $Ag(111)$ layer to the B_5H_3 borophane. The second layer corresponds to the second nearest $Ag(111)$ layer and so on.

Area from -0.5 eV to 0.0 eV			Area from 0.0 eV to 0.05 eV		
β_{12}	B_5H_2	B_5H_3	β_{12}	B_5H_2	B_5H_3
1.37	1.25	1.38	1.44	1.46	1.42

TABLE S6: Integrated Density of States numbers for Ag atoms in the three $Ag(111)$ surfaces containing β_{12} , B_5H_2 , and B_5H_3 sheets, in the range -0.5 eV to 0.0 eV (valence region, below the Fermi level) and 0.0 eV to 0.5 eV (conduction region, above the Fermi level). The unit for the integrated DOS is number of states.

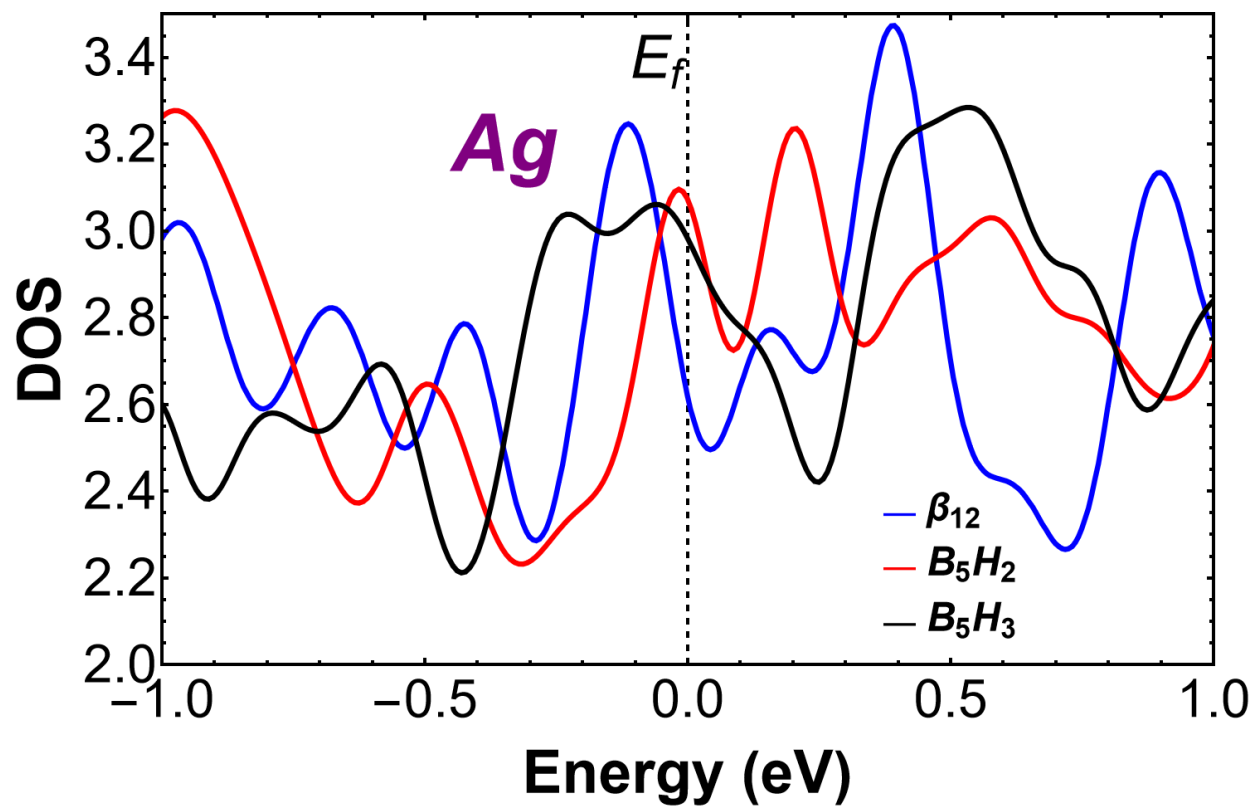
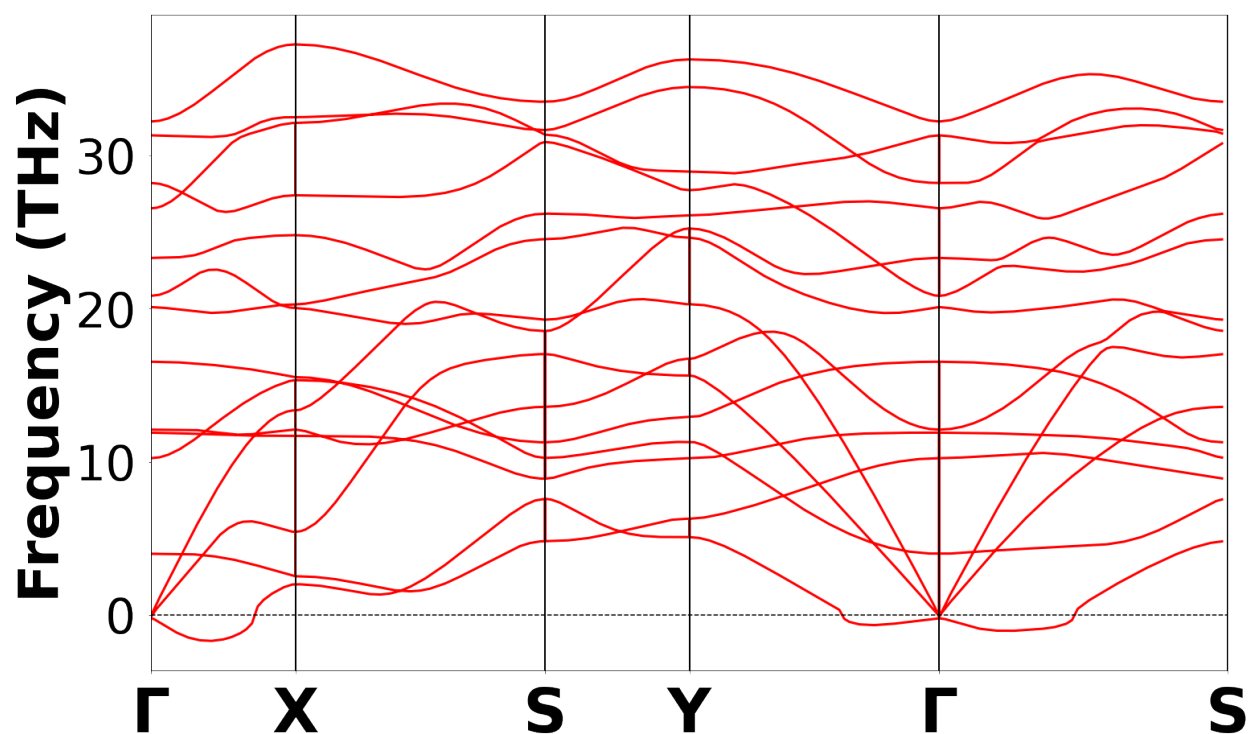
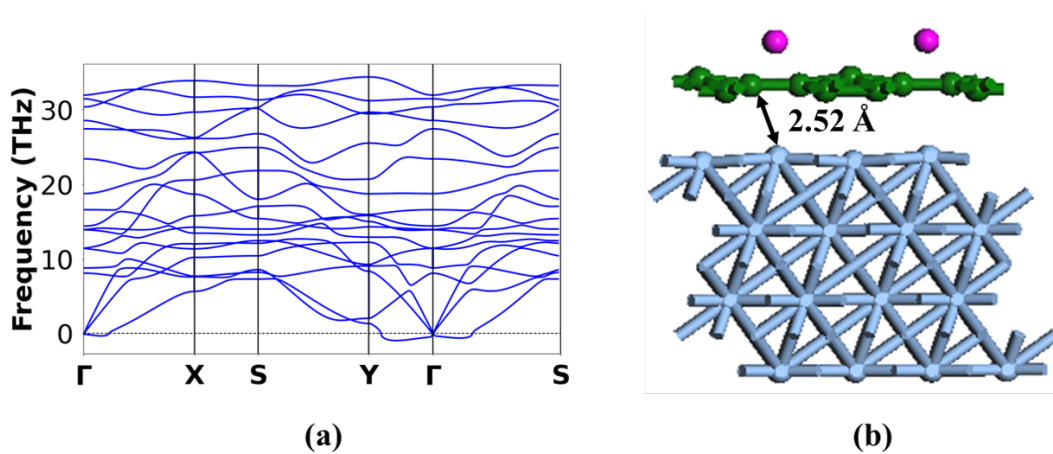


FIG. S5: The Density of states for *Ag* atoms in the *Ag*(111) surfaces below β_{12} (shown in blue), B_5H_2 (red), and B_5H_3 (black) sheets. E_f represents Fermi energy and lies at 0.0 eV.

S4. METAL ENCAPSULATION IN β_{12} BOROPHENEFIG. S6: Phonon Dispersion Diagram for β_{12} .FIG. S7: (a) Phonon dispersion diagram for LiB_5 showing small negative frequencies around Gamma (b) LiB_5 on Ag(111).

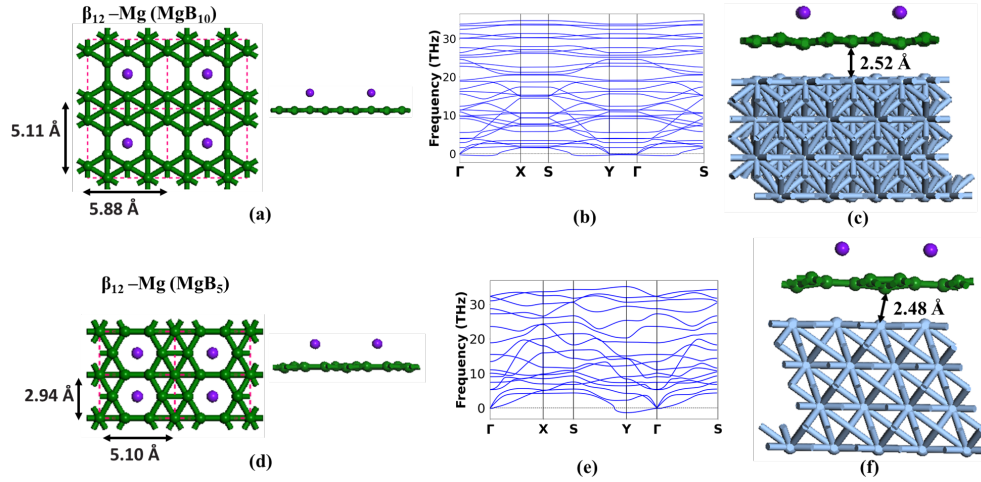


FIG. S8: (a) Monolayer MgB_{10} (b) phonon dispersion diagram of monolayer MgB_{10} (c) monolayer MgB_{10} on $\text{Ag}(111)$ (d) monolayer MgB_5 (e) phonon dispersion diagram of monolayer MgB_5 (f) monolayer MgB_5 on $\text{Ag}(111)$.

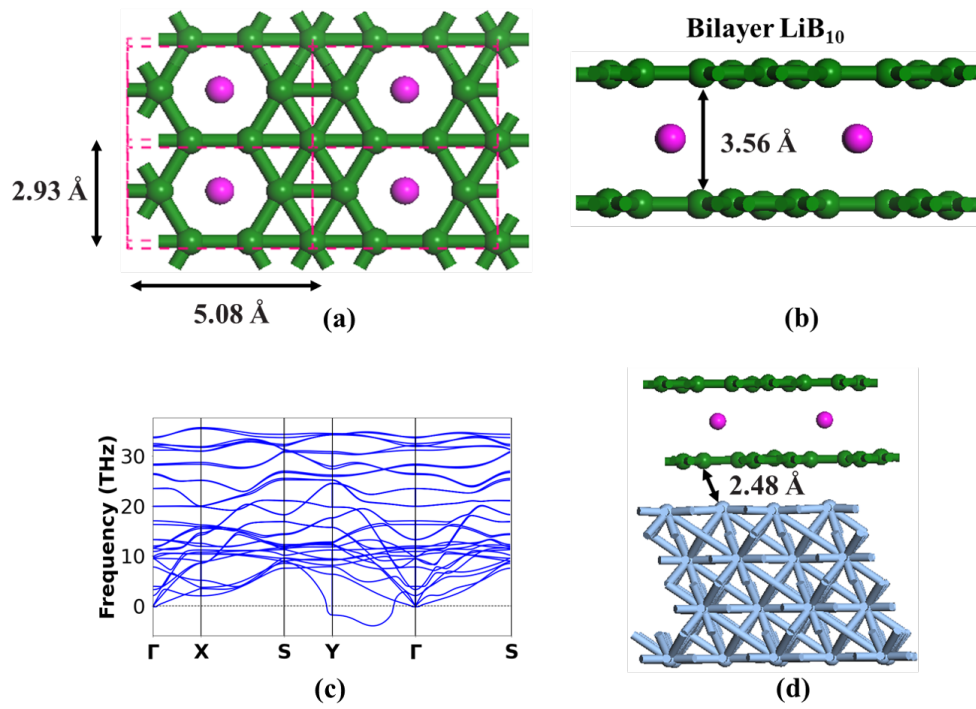


FIG. S9: (a) Top (b) side view of bilayer LiB_{10} (c) phonon dispersion diagram of bilayer LiB_{10} (d) bilayer LiB_{10} on $\text{Ag}(111)$.

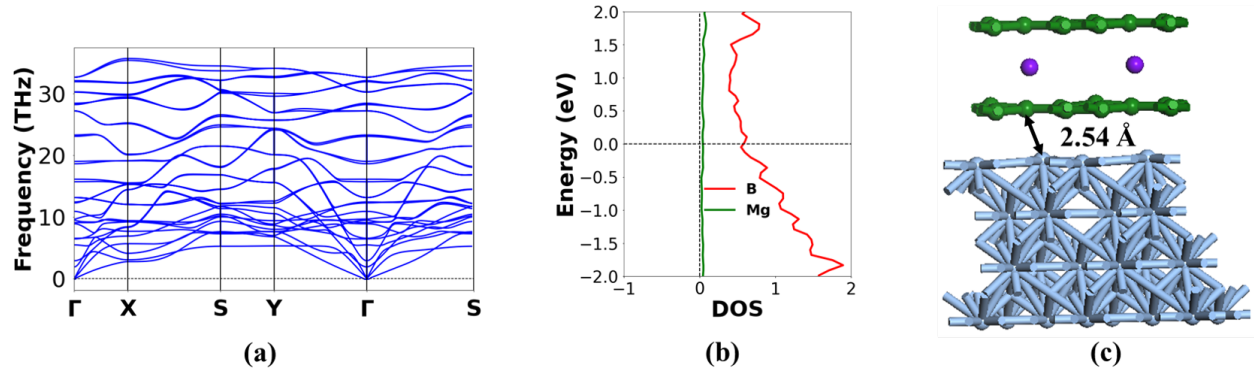


FIG. S10: Bilayer MgB_{10} : (a) phonon dispersion diagram with no negative frequency (b) partial DOS (c) optimized structure on $\text{Ag}(111)$.

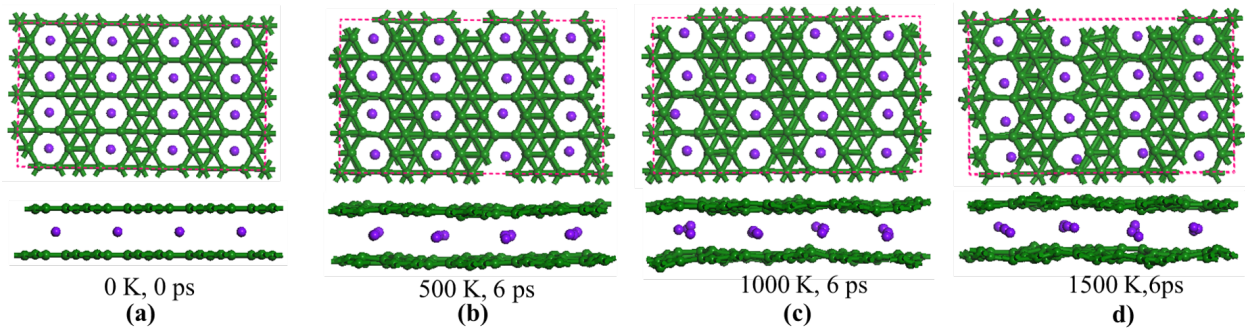


FIG. S11: Molecular dynamic simulation for $(4 \times 4 \times 1)$ supercell of MgB_{10} at different temperatures for 6 ps.

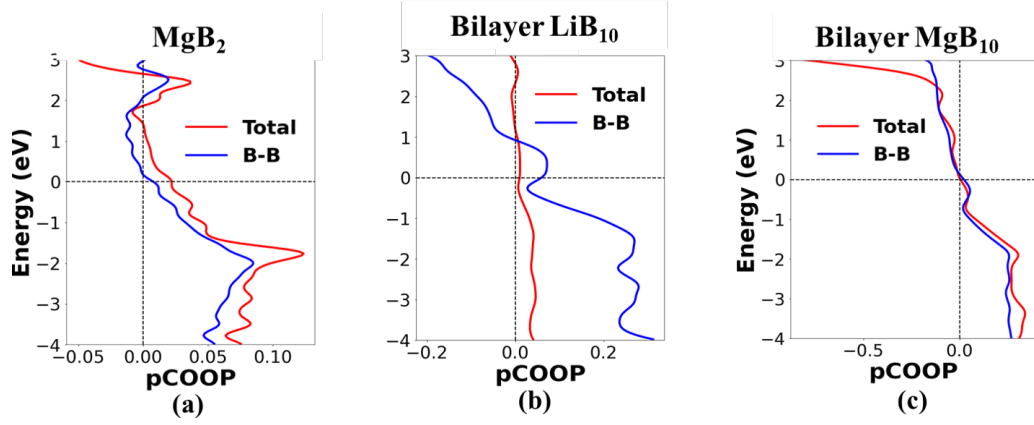


FIG. S12: Partial crystal orbital overlap population (pCOOP) curves for (a) MgB₂ (b) bilayer LiB₁₀ (c) bilayer MgB₁₀. A direct comparison shows similarity between MgB₂ and bilayer MgB₁₀, where the B-B bonding region is occupied near the Fermi level. Bilayer LiB₁₀ shows unoccupied B-B bonding levels above the Fermi level. The x axis scale depends on the number of boron atoms per unit cell.

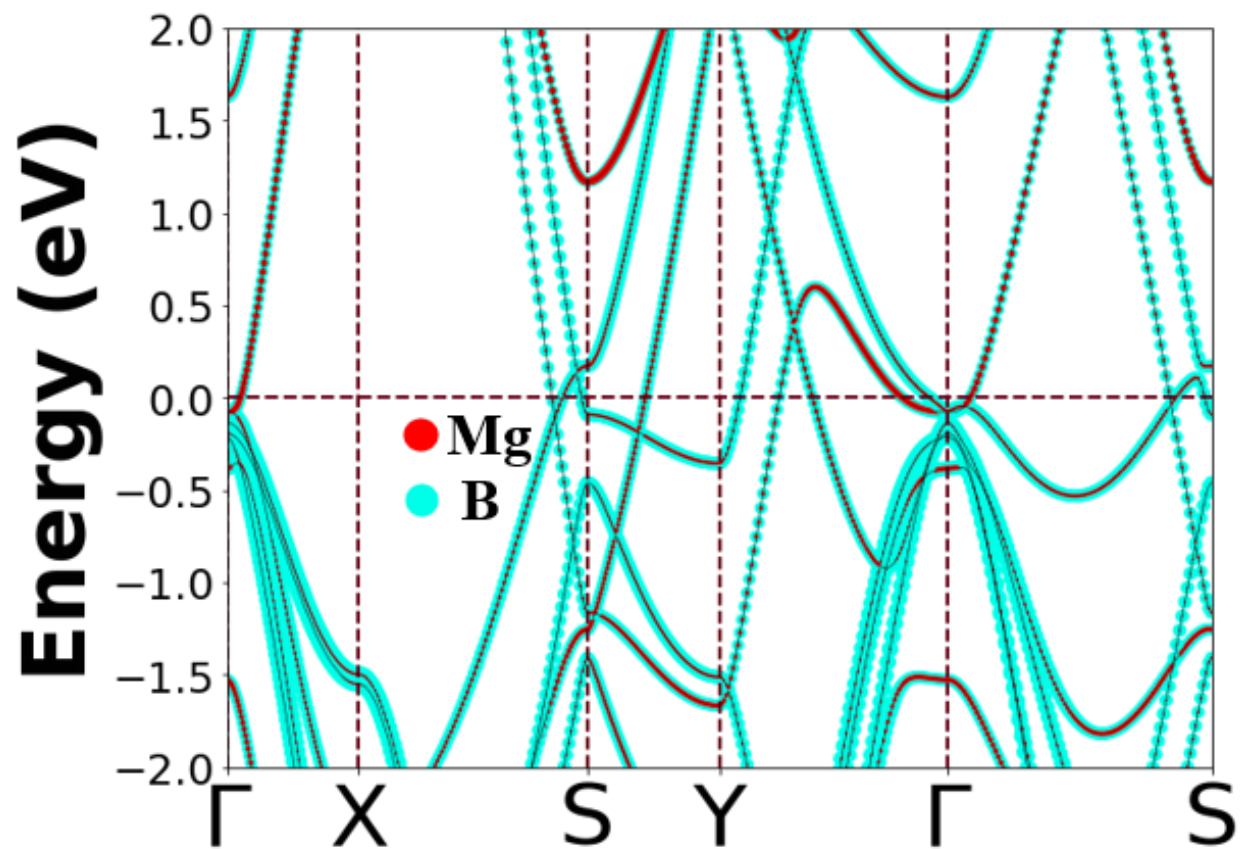


FIG. S13: Projected band structure of MgB₁₀ bilayer showing contributions from Mg (red), and B (aqua) separately.

S5. REFERENCES

- [1] G. Kresse and J. Hafner, Phys. Rev. B, 1993, **48**, 13115–13118.
- [2] G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, **54**, 11169–11186.
- [3] G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, **6**, 15–50.
- [4] G. Kresse and D. Joubert, Phys. Rev. B, 1999, **59**, 1758–1775.
- [5] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, **132**, 154104.
- [6] R. Dronskowski and P. E. Bloechl, J. Phys. Chem., 1993, **97**, 8617–8624.
- [7] A. Togo and I. Tanaka, Scr. Mater., 2015, **108**, 1–5.