# Rapid communication:
# Permeability of hydrogen in two-dimensional graphene and hexagonal boron nitride sheets

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**Abstract.** We study the permeability of atomic hydrogen in monolayer hexagonal boron nitride (h-BN) and graphene using first-principles density functional theory-based simulations. For the specific cases of physisorption and chemisorption, barrier heights are calculated using the nudged elastic band approach. We find that the barrier potential for physisorption through the ring is lower for graphene than for h-BN. In the case of chemisorption, we have studied three specific cases where the H atom passes through by making bonds with the atoms at different sites in the ring. The chemisorption barrier height for graphene is found to be, in general, higher than that of h-BN. We conclude that the dominant mechanism of tunnelling through the graphene sheet and h-BN sheets would be physisorption and chemisorption, respectively.

## 1. Introduction

Transport of matter through two-dimensional (2D) materials has attracted much interest [1,2]. As ultimate membranes, a single monolayer may allow highly selective sieving of gases, liquids, dissolved ions and other species of interest. While electronic charge transport in graphene attracted much of the initial attention due to graphene's unique band structure [3,4], molecular, ionic and gas transport have since been investigated [5–7]. Graphene is considered to be impermeable to most atoms and molecules under ambient conditions due to its dense electron cloud. However, accelerated atoms may be able to penetrate through the sheet [8,9], and this property is being explored for developing novel separation technologies [10]. Although graphene was the first isolated 2D material, other layered materials have since been isolated into 2D sheets; the simplest example being hexagonal boron nitride (h-BN). Monolayer h-BN contains one boron atom and one nitrogen atom in its unit cell and shares the same hexagonal lattice structure with graphene but with a lattice constant 1.7% larger than graphene. It is a wide band gap semiconductor with an energy gap of 5.97 eV [11], resulting from

the fact that $p_z$ orbitals in boron atoms are vacant while in nitrogen atoms they are occupied by paired electrons. As electrons are localised in boron nitride, a lower electron density is expected within the hexagonal rings.

Recent experimental transport and mass spectroscopy measurements have established that monolayers of graphene and h-BN are highly permeable to thermal protons under ambient conditions [12], whereas no proton transport is detected for thicker crystals such as monolayer molybdenum disulphide, bilayer graphene or multilayer h-BN. Highest room-temperature proton conductivity has been reported for monolayer h-BN, with a resistivity to proton flow of about 10 $\Omega$ cm$^2$ and a low activation energy of about 0.3 eV. At temperatures above 450 K, h-BN is outperformed by graphene, with a resistivity of $10^3$ $\Omega$ cm$^2$. As protons can be considered as an intermediate case between electrons and atoms, for the sake of simplicity, we consider the diffusion of hydrogen atoms through graphene and BN membranes to understand the fundamental details of the transport process. Interestingly, the interaction of hydrogen with graphene/graphite is of considerable interest in hydrogen storage applications [13] and for thermalisation and cooling in nuclear fusion devices [14,15].

While the adsorption and diffusion of H on graphene have been studied experimentally and theoretically by numerous researchers [16–18], the difference in conduction mechanisms of transport through h-BN and graphene has not been explored, to the best of our knowledge.

In this rapid communication, we present a first-principles comparative study of hydrogen permeation through h-BN and graphene sheets, using a nudged elastic band (NEB) approach. We consider separately the cases of physisorption and chemisorption through the sheets. We find that the barrier potential for physisorption through the ring is lower for graphene than for h-BN. In the case of chemisorption, we study three specific cases where the H atom passes through by making bonds with the atoms at different sites in the ring. The chemisorption barrier height for graphene is found to be higher than that of h-BN for most of the cases. The barrier heights for proton conduction are, in general, expected to be lower. Our results further suggest that the dominant diffusion mechanism through a graphene ring is through physisorption or tunnelling without any chemical bond formation. On the other hand, it is energetically favourable to tunnel through the bond formation, or chemisorption, for h-BN.
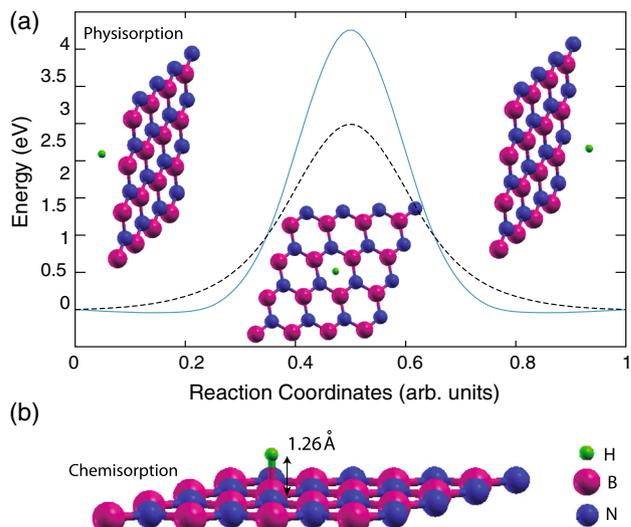


**Figure 1.** (**a**) Barrier height as a function of reaction coordinate for the physisorption of a hydrogen atom through graphene (black dashed line) and h-BN (blue solid line) monolayers. A schematic of the physisorption process is shown highlighting the tunnelling of the H atom through the centre of the ring without bond formation to any of the ring members. (**b**) Schematic illustrating the chemisorption process where the H atom first forms a bond with a member of the ring.

## 2. Computational method

Computational calculations have been performed with the Quantum-Espresso code [19] under periodic boundary conditions. We have used ultrasoft pseudopotentials within the generalised gradient approximation [20]. An energy cut-off of 40 Ry on the plane-wave basis was used in the representation of Kohn–Sham wave functions. Brillouin zone integrations were sampled with a $12 \times 12 \times 2$ Monkhorst–Pack mesh [21]. Structural optimisation was carried out with Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm to minimise energy using Hellman–Feynman forces.

The optimised lattice parameters of graphene and h-BN are found to be $a = b = 2.462$ and $2.5097$ Å, respectively, which are in good agreement with the experimentally observed values (2.456 and 2.4982 Å). We calculated the potential energy barrier for the conduction of a hydrogen atom through the hollow site (centre of the ring) of the monolayer of graphene and h-BN to test the effect of the size of the supercell. We found that the potential barriers for a $4 \times 4$ supercell (32 atoms) and $5 \times 5$ supercell (50 atoms) differ by a small value of energy (order of 0.01 eV). The small difference between these values indicates that a $4 \times 4$ supercell is sufficient to obtain the required accuracy in the energetics of these systems. For these calculations,

we sample the Brillouin zone for the $3 \times 3 \times 1$ $k$-point mesh. The reaction pathways for H diffusion were calculated using the climbing-image nudged elastic band (CI-NEB) method [22] with seven images for our reaction pathway. We set the initial position of the hydrogen atom at a height of 3 Å above the centre of the hexagonal ring to dismiss any major interactions. The final image is a lateral inversion of the initial one.

## 3. Results and discussion

### 3.1 *Physisorption*

We first consider the tunnelling of a hydrogen atom through graphene and h-BN sheets. In the case of graphene, we find an energy barrier of 2.53 eV, whereas, for h-BN, the barrier was 3.73 eV, as shown in figure 1. Our barrier heights for graphene are slightly lower than the previously reported value in the literature (2.86 eV [18]). The slight disagreement is perhaps not surprising, given the complex nature of the possible transport pathways and the sensitivity of the calculations to the pseudopotentials, exchange correlation functional and supercell sizes. This barrier is thought to be due to the Coulomb interactions only as the hydrogen atom directly passes through the hexagonal ring without

making any bond (as shown in the schematics of figure 1a). The NEB calculation estimates the minimum energy pathway as the system moves through a reaction from an initial to a final state. This produces a reaction coordinate, which is a collective coordinate that can be transformed into system atomic configurations along the reaction pathway. The reaction coordinate (expressed in arbitrary units) has been normalised to unity. The midpoint represents the configuration where the H atom is the plane of the ring. From the results of the simulation, it is observed that the hexagonal rings expand as the hydrogen atom approaches the centre and relaxes back as the atom moves away. The diameter of the h-BN ring changes from 2.89 to 2.95 Å whereas the graphene ring expands from 2.84 to 2.90 Å. In the transition state of graphene (reaction coordinate = 0.5), the hydrogen atom is equidistant from all carbon atoms as it passes through the centre of the ring ($d = 1.45$ Å). However, in the transition state of h-BN, the hydrogen atom is farther away from the boron atoms at 1.51 Å, and closer to the nitrogen atoms, 1.43 Å. This difference in distance for h-BN is presumably caused by the higher electronegativity of nitrogen compared to boron. This can explain the large energy difference of 1.20 eV in the barrier heights between graphene and h-BN.

## 3.2 *Chemisorption*

Chemisorption involves the migration of H atom through bond formation with an atom in the lattice, as shown in figure 1b and the rotation of C–H, N–H or B–H bonds from one side to the other. The H atom in its initial state ($i$) bonds with an atom in the ring and after passing through can have the final bond with the same or any other member of the ring. As shown in figure 2a, the relative substituents in the hexagonal ring are indicated by the names sublattice ($s$), ortho ($o$) and meta ($m$), similar to the benzene ring nomenclature. The downward and upward arrows in figure 2a are on the opposite side of the BN ring. We study specific cases of diffusion from an initial state ($i$) to a final state of H bonding with sites $s$, $o$ and $m$.

We find that the hydrogen atom is adsorbed on the monolayer BN at a height of 1.267 Å above the boron atom and 1.12 Å above the nitrogen atom. In graphene, the hydrogen atom is adsorbed at a height of 1.17 Å above the carbon atoms. The barrier energies for penetration through the graphene monolayer through the migration pathways $i \to s$, $i \to o$ and $i \to m$ are 3.24, 4.02 and 3.24 eV, as shown in figures 2b–2d, respectively. Reaction pathways for $i \to s$ and $i \to m$ involve the expansion of the hexagonal ring and the rotation of the bond from one side to the other, resulting in
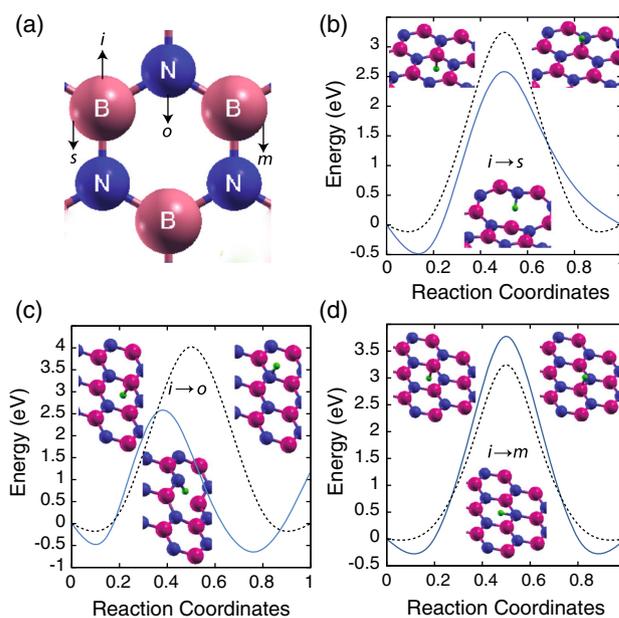


**Figure 2.** (**a**) The model represents the different chemisorption sites of the H atom on a BN sheet. The sites $s$, $o$ and $m$ are on the opposite side of BN compared to site $i$. Migration pathways and energy barriers for a hydrogen atom from one side to the opposite side of the BN sheet in chemisorption for (**b**) $i \to s$, (**c**) $i \to o$ and (**d**) $i \to m$.

similarly sized energy barriers. As a bond is formed with a C atom, the penetrations do not occur through the centre of the ring. The reaction pathway from $i \to o$ is higher than other cases due to a seven-membered ring formation in the intermediate state. We note that the energy barriers for chemisorption in graphene are higher than those observed for physisorption.

For hydrogen diffusion through the h-BN sheet, we consider the hydrogen atom initially bonded to a boron atom. The energy barriers for $i \to s$, $i \to o$ and $i \to m$ are found to be 2.88, 3.19 and 3.79 eV, as shown in figures 2b–2d, respectively. The $i \to m$ case has the highest barrier as the hydrogen atom initially attached to a boron atom makes an intermediate passing bond with a nitrogen atom. The asymmetry of the curves for BN possibly arises from the two different basis atoms, as opposed to graphene where the basis consists of two carbon atoms. The asymmetry is most pronounced for the $i \to o$ transition where the H atom forms an initial bond with a B atom, and the final state involves a bond formation with the N atom. The energy of the initial and final states is also different for this case. For the other chemisorption cases, the intermediate positions of the H atom decide the degree of asymmetry of the curves, but the energy of the initial and final states remains the same. If the initial bonding is done to a nitrogen atom as opposed to a boron atom, a variation
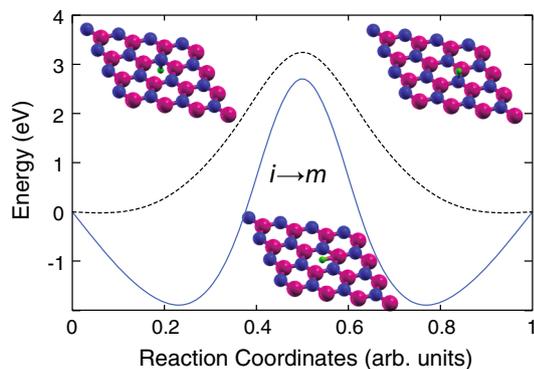
**Figure 3.** Reaction pathway and barrier height for chemisorption from $i \rightarrow m$, where the initial site is given by the hydrogen atom attached to a nitrogen atom instead of a boron atom.

in the barrier height is observed. We consider only the $i \rightarrow m$ route with nitrogen as the initial atomic site ($i$) in the ring. While the energy landscape also appears to be modified, the barrier height from the minimum energy configuration changes from 3.79 to 4.42 eV, as shown in figure 3.

We now discuss the three distinct chemisorption possibilities in detail: $i \rightarrow s$, $i \rightarrow o$ and $i \rightarrow m$. The $i \rightarrow s$ configuration merely involves a rotation of the bond, as the initial and final configurations are on the opposite side of the same atom. This is more favourable for BN compared to graphene. The $i \rightarrow o$ and $i \rightarrow m$ configurations involve bonding to an atom different from the initial atom. The $i \rightarrow o$ process for BN is different from graphene as it involves breaking of a B–H (or N–H) bond and the formation of a N–H (or B–H) bond, i.e. the initial and final atoms are of different types. This difference can be understood in terms of activation energy required by hydrogen to break a strong C–C bond ($\sim$6.4 eV) compared to the relatively weaker B–N bond ($\sim$4 eV).

The $i \rightarrow m$ process for graphene and BN is comparable, as the initial and final configurations result in bonding to the same type of atom (B–H to B–H or N–H to N–H). Furthermore, the minimum energy reaction pathway involves a bond rotation and for the H atom to pass through the plane of the ring, similar to but not exactly what is seen in the physisorption process. It is easier for H atoms to pass through the centre of a graphene ring compared to the centre of a BN ring (by simply looking at physisorption barriers as an estimate), and this could explain why the $i \rightarrow m$ transition could be more favourable for graphene. We would have expected a larger difference in the barrier heights, but this would be offset by the bond formation with atoms in the ring resulting in a lower energy cost for tunnelling.

**Table 1.** Calculated energy barriers for the physisorption case and the different chemisorption pathways for the considered monolayers.

| Reaction pathway | Graphene (eV) | h-BN (eV) |
|---|---|---|
| Physisorption | 2.53 | 3.73 |
| Chemisorption | | |
| $i \rightarrow s$ | 3.24 | 2.88 |
| $i \rightarrow o$ | 4.02 | 3.19 |
| $i \rightarrow m$ | 3.24 | 3.79 |

## 4. Conclusion

In conclusion, we studied hydrogen tunnelling through a monolayer graphene and h-BN sheet to explore and compare their permeabilities. The obtained energy values are consolidated in table 1. We find that the hexagonal ring expands when a hydrogen atom passes through it, highlighting the effects of atomic size. The smaller-sized proton would, therefore, be able to penetrate the sheets more easily than a hydrogen atom. Interestingly, even with a larger ring size, the barrier potential for physisorption is 1.20 eV higher (table 1) for h-BN than for graphene. This is understood in terms of the structural changes of the ring as the hydrogen atom passes through the ring. The hydrogen atom passes through the centre of the graphene ring and is equidistant from all C atoms in the ring. However, due to different electronegativities of boron and nitrogen, the B–H and B–N distances are unequal.

In the case of chemisorption, the barrier heights for graphene are much higher than those observed for physisorption (table 1), highlighting the difficulty for a hydrogen atom to tunnel through the graphene sheet once a C–H bond is formed. However, a lower barrier potential is observed for chemisorption through a h-BN sheet, consistent with lower bond energies of the B–N bond compared with the C–C bond. The lowest energy pathways are $i \rightarrow s$, involving a simple rotation of the B–H bond, and $i \rightarrow o$, involving breaking of the B–H bond and formation of the B–N bond. Our results further suggest that the dominant diffusion mechanism through a graphene ring is through physisorption or tunnelling without any chemical bond formation. On the other hand, it is energetically favourable to tunnel through the bond formation or chemisorption, for h-BN. The lowest energy pathway for chemisorption involves a simple rotation of the B–H or B–N bond. This insight into the conduction mechanism can help fuel the search for more 2D materials for a membrane-like application, and possibly provide a new purpose for graphene and h-BN in potentially revolutionary applications.

## Acknowledgements

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