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# Does a Hydrogen Atom/Proton Diffuse Through Graphene ?

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## 1. Introduction

With the rapid development of manufacturing technology, microelectronics is gradually approaching the nanometer scale, and in the nanoscale range, due to the existence of quantum effects and other considerations, many of the macroscopical concepts and law may not apply. Graphene can be considered as an ideal membrane; taking into account the fact that the size of atomic hydrogen (with a Bohr radius of 0.5 Å) is considerably smaller than the distance between meta carbons of six-membered ring of graphite (2.46 Å), whether a hydrogen atom can pass through a graphene sheet is a problem we are curious about. This work focuses on the diffusion mechanism of hydrogen atoms through a graphene sheet, investigating the energy barrier and the change of the electron structure for this process.

## 2. Methods

Periodic DFT calculations have been carried out using the Quantum Espresso code package, within the generalized gradient approximation (GGA) of the Perdew–Wang 91 (PW91) functional. An energy cut-off of 35 Ry and 350 Ry were used for the wave function and the charge density, respectively. A 4×4×1 k-point mesh was used to obtain convergence criteria of $1\times10^{-6}$ eV for energies and 0.01 eV/Å for forces, respectively. The values of optimized graphite lattice parameters are $a = b = 2.466$ Å, $c = 6.802$ Å, and the optimized C–C bond length is 1.424 Å, which are close to the experimental values (2.456 Å, 6.696 Å and 1.418 Å, respectively)[1]. A 5×5 periodic supercell of graphene with a 15 Å vacuum along the direction perpendicular to the surface was modeled. The reaction paths were described by the minimum energy paths (MEPs) using the climbing-image nudged elastic band method with 7 images [2].

## 3. Results and Discussion

The energy profile and selected intermediates along the reaction path involving initial, transition and final states of a hydrogen atom penetrating the graphene are displayed in Figure 1(a). The hydrogen atom directly penetrates the hexagonal carbon structure of graphene without bonding with the graphene. The calculated energy barrier for the diffusion of a hydrogen atom through the six-membered ring of graphene is 2.86 eV, which is smaller than 4 eV through total energy calculation based on DFT in the work of Miura et al. [3]. We suspect that a proton diffusing through the graphene should

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be easier, because the radius is smaller due to the loss of the electron. Figure 1(b) shows the process of a proton passing through the center of a hexagonal ring in the graphene. Unlike the hydrogen atom directly diffusing through the graphene plane, the proton experiences a process of bond forming and breaking between the proton and the carbon atoms in graphene. Thus there is a trend of decline and rise in the calculated energy barrier profile corresponding to the bond forming and breaking. The calculated energy barrier is only 0.47 eV, which is much smaller than 1.17 eV estimated by Wang and Kaxiras [4] using spin-resolved molecular dynamics simulations. These values are much smaller than 2.86 eV, the energy barrier estimated for a hydrogen atom diffusing through the graphene. For the geometry of the transition state, the relative position of the proton to graphene is the same as the hydrogen atom that is in the graphene plane, but the difference is that the distances between the proton and the six nearest carbon atoms are not equal (in the range of 1.23 Å to 1.68 Å), that is to say the proton is not in the center of the hexagonal ring.

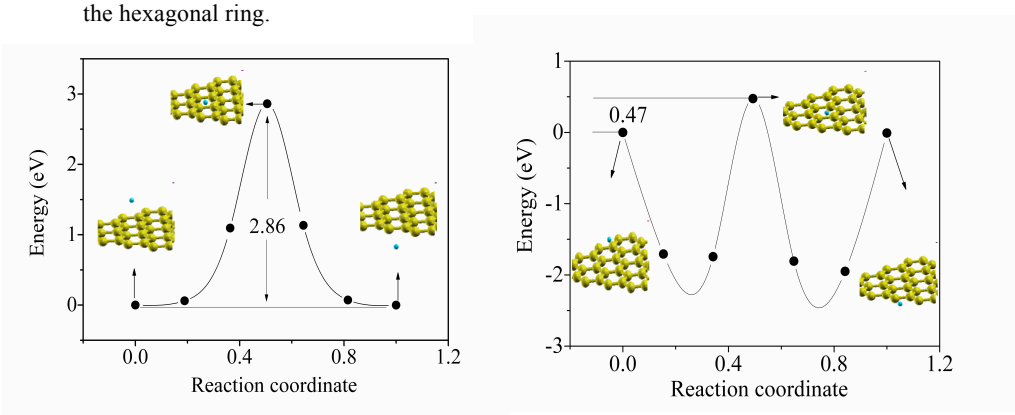


Fig. 1. Calculated reaction energy profile of a hydrogen atom (a) and a proton (b) diffusing to the other side of the graphene sheet and the structures of initial, transition and final states.

## 4. Conclusion

Although there is only a charge difference, the diffusion mechanism is different. The energy barrier for a hydrogen atom penetrating the graphene sheet is 2.86 eV, much larger than 0.47 eV for the proton case. The hydrogen atom directly penetrates a hexagonal carbon ring of the graphene, while the proton experiences a trend of bond forming and breaking with the carbon atoms in the graphene.

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