

# Influence of Orbital Hybridization on the Atomic and Electronic Structures in Hydrogenated Monolayer Graphene

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The relation of orbital hybridization between graphene and an adsorbate to the atomic and electronic structures of monolayer graphene was studied using first-principles calculations, where hydrogenated graphene was used as a prototype. The atomic and electronic structures of hydrogenated graphene were calculated as functions of the distance between graphene and hydrogen. The hybridization gap between the  $s$  orbital of hydrogen and the  $\pi$  orbital of graphene was tuned by changing the distance. The effect of the hybridization gap on the energy gap at the Dirac energy and the atomic structure deformation of graphene was schematically investigated, particularly when hydrogen breaks the in-plane symmetry.

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## I. INTRODUCTION

Graphene with a hexagonally closed packed structure is considered as a promising material in electronic devices [1–3]. In the applications of graphene to semiconductor devices, graphene, which is intrinsically an undoped zero gap semiconductor, requires band engineering to open an energy gap at the Dirac energy  $E_g^D$  [3, 4].  $E_g^D$  is opened when the out-of-plane symmetry is broken in bilayer graphene [5,6]. An external electric field was applied along the direction perpendicular to bilayer graphene in a field effect transistor, and electrons or holes were doped asymmetrically on bilayer graphene by using molecules or metals to break the out-of-plane symmetry [7, 8]. In monolayer graphene, the in-plane symmetry needs to be broken to produce  $E_g^D$  [9]. In particular, a potential energy difference between the two identical carbon atoms in the unit cell needs to be induced, and various approaches such as the interaction between monolayer graphene and a substrate and the adsorption of a metal (or molecule) on graphene have been reported to open  $E_g^D$  [4,10]. In the in-plane symmetry breaking, one of the important parameters is orbital hybridization between a metal (or molecule) and monolayer graphene. However, there has been no systematic

theoretical study on the relations between the orbital hybridization and  $E_g^D$ . Orbital hybridization depends on molecules (or metals), but it is not efficient to use various metals or molecules for systematic theoretical studies. In this study, the most simplistic system, hydrogen on monolayer graphene, was chosen as the prototype. The orbital hybridization gap of hydrogenated graphene was varied by controlling the distance between hydrogen and monolayer graphene. A closer distance between the hydrogen and the monolayer graphene produced stronger orbital hybridization between them.  $E_g^D$  was first calculated as a function of the orbital hybridization gap by using first-principles calculations. This leads to the conclusion that  $E_g^D$  can be opened up to approximately 1 eV while maintaining the  $sp^2$  configuration of graphene. This is important because a local  $sp^3$  configuration of graphene acts as an impurity and sequentially reduces the mobility [11].

## II. COMPUTATIONAL METHODS

The VASP package was used for the first-principles calculations based on density functional theory [12]. The potentials of the electron-ion interactions and the exchange and correlation parts of the electron-electron interactions were described by using the projected aug-

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mented wave and the generalized gradient approximations, respectively [13, 14]. Plane waves were used to describe the electron wave functions, where the kinetic energies of the electrons were below 500 eV. A  $10 \times 10$  Monkhorst-Pack  $\vec{k}$ -point mesh on the surface Brillouin zone was used to calculate the total energy [15]. The energy gap by orbital hybridization between the  $s$  orbital of hydrogen and the  $\pi$  orbital of graphene is denoted by  $E_g^H$ .  $E_g^D$  and  $E_g^H$  are the local energy gaps rather than the energy gaps of the whole electronic band structures. The surface unit cell was fixed in the calculations.

### III. RESULTS AND DISCUSSION

Figure 1 shows the change in the electronic structure of monolayer graphene as a function of the distance between the hydrogen and the monolayer graphene when hydrogen is located on the on-top site of one of the two carbon atoms in the  $1 \times 1$  unit cell, as shown in Fig. 1(a). The distance between hydrogen and carbon without bonding to hydrogen was fixed to maintain the distance between the hydrogen and the monolayer graphene under relaxation. Here, only the carbon atom bonding to hydrogen is relaxed, and the distance between hydrogen and carbon is denoted by  $R_1$ , as shown in Fig. 1(b). When hydrogen is located far away from the graphene, the electronic structure, as shown in Fig. 1(c), is similar to the overlapped energy bands of the graphene and the hydrogen. In this case,  $E_g^D$  is close to zero, maintaining a energy band similar to that of the pristine monolayer graphene. As hydrogen was placed closer to the graphene, the hybridization between the  $s$  orbital of hydrogen and the  $\pi$  orbital of graphene became stronger and visible, resulting in a finite  $E_g^H$ , as shown in Fig. 1(d).  $E_g^H$  was inversely proportional to  $R_1$ . This suggests that the strength of the orbital hybridization depends explicitly on  $R_1$ .  $E_g^H$  led to energy gap opening at the Dirac energy at the K point.  $E_g^D$  became larger with increasing  $E_g^H$  [see Figs. 1(c) – (f)].

Figure 2 shows the  $E_g^H$  and  $E_g^D$  as functions of  $R_1$ . The hybridization between the  $s$  orbital of hydrogen and the  $\pi$  orbital of graphene also induced a structural deformation of graphene. The hybridization results in the transformation of the  $sp^2$  configuration of graphene to the  $sp^3$  configuration. The in-plane angle between carbon atoms in the unit cell, which is defined by  $\theta$ , was also calculated to estimate the structural transformation from the  $sp^2$  to the  $sp^3$  configuration. When  $R_1$  was longer than 2.0 Å,  $E_g^H$  and  $E_g^D$  increased gradually. In this region,  $\delta\theta = 120^\circ - \theta$  was almost zero. This suggests that the  $sp^2$  configuration of graphene is sustained in the region denoted by the ‘ $sp^2$  region’.  $E_g^D$  at  $R_1 = 2.0$  Å was approximately 1.0 eV. This suggests that graphene with  $E_g^D$  below 1.0 eV can be produced with minimal structural distortion of pristine graphene. When  $R_1$  was below 2.0 Å,  $\delta\theta$  increased drastically; the region is de-

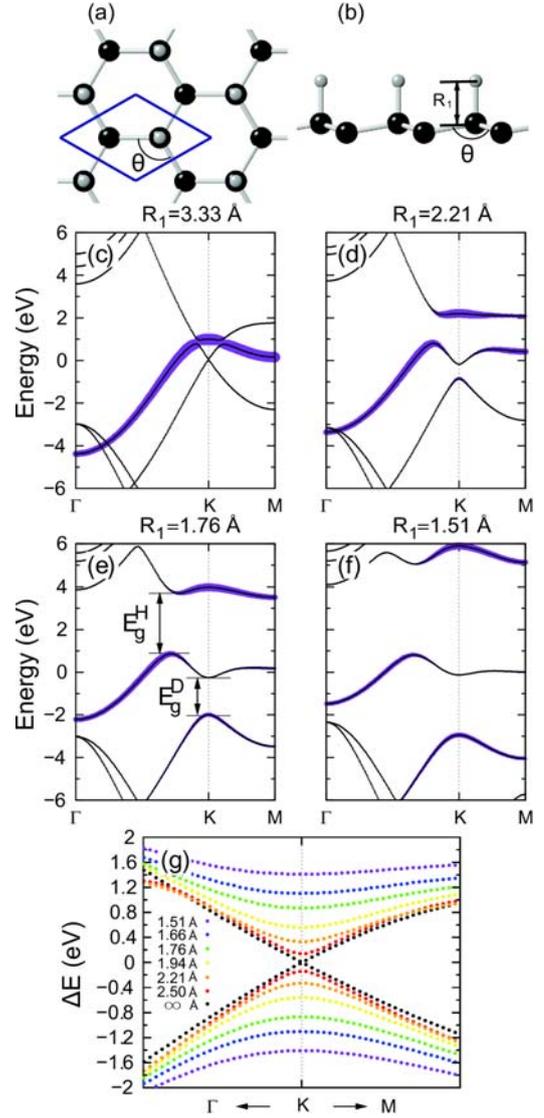


Fig. 1. (Color online) (a) Top and (b) side views of the atomic structure of hydrogenated graphene, where hydrogen is located at the on-top site of one of the two carbon atoms in the  $1 \times 1$  unit cell. The distance between hydrogen and carbon is denoted by  $R_1$ , and the angle between carbon atoms is denoted by  $\theta$ . (c) – (f) The electronic structure of hydrogenated graphene as a function of  $R_1$ , where the thick and the thin energy bands originate mainly from the hydrogen and the carbon orbitals, respectively. (g) The change of the electronic structure at the K-point as a function of  $R_1$ , where  $\Delta E$  is the energy relative to the Dirac energy.

noted by the ‘ $sp^3$  region’. This was accompanied by steep variation of  $E_g^H$ , resulting in a large  $E_g^D$ . Usually, the reactions of molecules such as hydrogen and oxygen with graphene induce a large  $E_g^D$ , resulting in the  $sp^3$  configuration of graphene, which can correspond to the  $sp^3$  region [16,17]. In contrast, the interactions between metals and graphene result in a small  $E_g^D$  and maintain the  $sp^2$  configuration of graphene, which can be understood

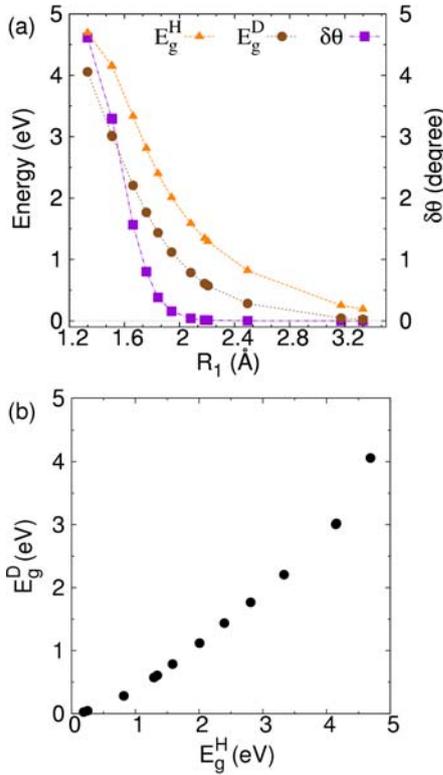


Fig. 2. (Color online) (a)  $E_g^H$ ,  $E_g^D$ , and  $\delta\theta$  as functions of  $R_1$ , where  $\delta\theta = 120^\circ - \theta$ . (b)  $E_g^D$  as functions of  $E_g^H$ .

within the  $sp^2$  region [18].

Figure 2(b) shows the correlation between  $E_g^D$  and  $E_g^H$  to understand the effect of orbital hybridization on the gap opening.  $E_g^D$  increases almost linearly with increasing  $E_g^H$ . This suggests that the strength of orbital hybridization is strongly related to the gap opening at the Dirac energy and is one of dominant parameters in the gap opening. The correlation can support quantitatively the photoemission experiments of graphene [19–25]. The  $E_g^D$  of graphene located on transition metals such as Ni, Co, and Ru was relatively larger than that on noble metals such as Cu, Ag, and Au, as reported in previous photoemission experiments [19–25]. The interaction strength between the  $s$  orbital of the noble metal and the  $\pi$  orbital of graphene is weaker than that between the  $d$  orbital of the transition metal and the  $\pi$  orbital of graphene. Therefore, the relatively larger  $E_g^D$  of graphene located on the transition metal can be understood based on the correlation between  $E_g^D$  and  $E_g^H$ . In these first-principles calculations, incommensurability between graphene and metal, which is induced by a lattice mismatch and/or a corrugation, cannot be considered. Incommensurability can act as an external periodic potential [26]. When there is an external periodic potential, the group velocity is renormalized, but  $E_g^D$  is not opened [27]. Furthermore, C 1s photoemission experiments reported that the interaction strength between

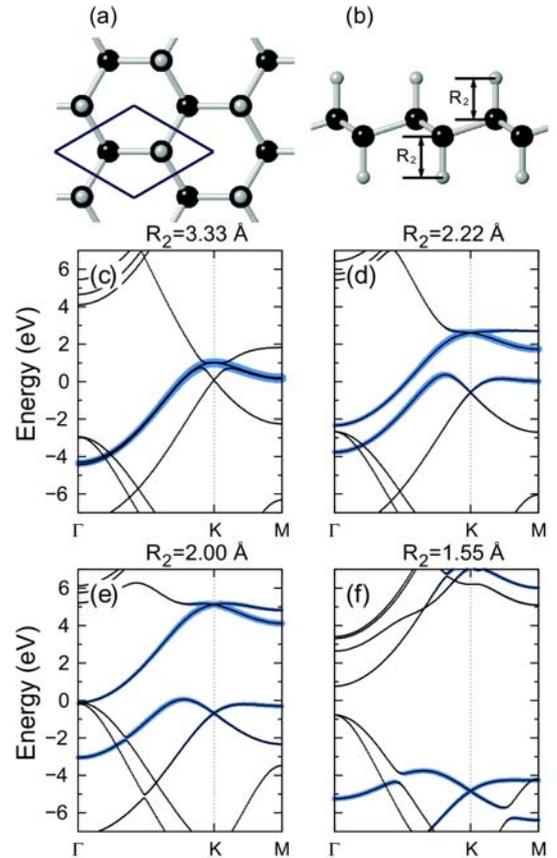


Fig. 3. (Color online) (a) Top and (b) side views of the atomic structure of hydrogenated graphene, where hydrogen is located at the on-top site of both carbon atoms in the  $1 \times 1$  unit cell on alternating sides of the graphene sheet. The distance between hydrogen and carbon is denoted by  $R_2$ . (c) – (f) The electronic structure of hydrogenated graphene as a function of  $R_2$ , where the thick and the thin energy bands originate mainly from the hydrogen and the carbon orbitals, respectively.

graphene and metal increases in the series Pt-Ir-Rh-Ru [28]. Angle-resolved photoemission experiments reported that  $E_g^D$  became larger in the series Pt-Ir-Rh-Ru, even though the lattice mismatches between graphene and metals are different [24, 29, 30]. This suggests that the interaction strength could be a more important parameter than the incommensurability in the gap opening.

Figure 3 shows the change in the electronic structure of monlayer graphene when hydrogen is attached to both carbon atoms in the  $1 \times 1$  unit cell. In the calculations, the upper and the lower hydrogen atoms were kept at the same distance from the two carbon atoms, and the distance between the upper and lower hydrogen atoms was maintained under relaxation. The electronic structure of hydrogenated graphene was calculated as a function of the distance between hydrogen and carbon  $R_2$ . When  $R_2$  was sufficiently large, the electronic structure was close to the overlapped energy bands of hydrogen and graphene, as observed in the asymmetric case in Fig. 1.

When hydrogen was closer to graphene, energy bands were split by hybridization between the  $s$  orbital of hydrogen and the  $\pi$  orbital of graphene. In contrast to the asymmetric case, the energy gap at the Dirac energy was not opened, even by a stronger orbital hybridization, at a closer distance because the two carbon atoms are still symmetric even though the  $sp^2$  configuration changes to the  $sp^3$  configuration after the interaction between hydrogen and carbon. When hydrogen is located at the same  $R_2$  as graphane, its electronic structure becomes identical to that of graphane [16].

#### IV. CONCLUSION

In conclusions, the changes in the electronic structure of monolayer graphene as a function of the distance between hydrogen and graphene were studied schematically by using first-principles calculations to understand the effect of the strength of the interaction between graphene and a metal (or molecule) on the electronic structure of monolayer graphene. As the distance decreased, the  $s$  orbital of hydrogen is hybridized with the  $\pi$  orbital of graphene, resulting in a hybridization gap. When hydrogen is attached to one of the two carbon atoms in the  $1 \times 1$  unit cell, breaking the in-plane symmetry, the energy gap at the Dirac energy at the K point was almost linearly proportional to the hybridization gap. In addition, the energy gap could be opened up to approximately 1 eV while maintaining the  $sp^2$  configuration of graphene. In contrast to the asymmetric case, the energy gap was not opened when hydrogen was attached to both carbon atoms in the  $1 \times 1$  unit cell, even though the distance was changed. These results can help experimental approaches to band engineering of monolayer graphene by using metal (or molecule) adsorption or a substrate.

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