Ab initio Tight-Binding Molecular Dynamics Calculation of Hydrogen Adsorption on Graphite Surface

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To investigate the phenomena in an intermediate region between plasma and materials, *ab initio* molecular dynamics simulation provides fairly accurate results. It has been applied to various fields[1] since Car-Parrinello method[2] was invented. Recently, the fully self-consistent density functional method, based on a linear combination of atomic orbitals (LCAO) basis set, was being developed. The two-center integrals are dynamically determined by using norm-conserving pseudopotentials and pseudo-atomic wavefunctions. This technique is simple to describe complicated structures [3].

We applied this code to the adsorption on a graphite surface, which is known as the material for the first wall in fusion devices[4]. It is also interesting in the field of eptaxtial growth using the chemical vapor deposition. The etching process of atomic hydrogen on graphite is discussed in comparison of the hydrogen interaction with the diamond growth[5].

Our calculation is performed using the *ab initio* molecular dynamics method within the framework of the local density functional theory[6]. We employed the norm-conserving pseudopotential by Troullier and Martins in the separable form[7]. The energy cut-off is 200 Ryd. In the Brillouin zone sampling, we choose a Γ point to keep the degree of freedom in the atomic structure optimization in the simulating system. In the present calculation, graphite is replaced by a graphene sheet in a unit cell ($7.41\times8.56\times13.86\text{Å}^3$) for simplicity. The graphene in the unit cell contains 24 carbon atoms, as shown in Fig. 1. All atoms in the cell are relaxed in this work. A hydrogen atom is, as an initial configuration, placed 2.5 Å above the top of a carbon atom. The system is relaxed until the maximum atomic force is smaller than 0.04 eV/Å. The coordinate optimization is done by conjugate gradient molecular dynamics (MD) with no geometry constrain, and the maximum atomic displacement is limited in 0.1 Å for each MD step to realize the stability of calculation.

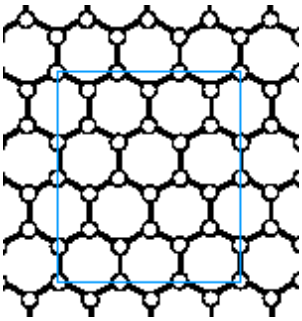

Fig. 1 Top view of graphene. Circles denote carbon atoms. Solid line shows the unit cell in the calculation.

As a result of our simulation, the atomic hydrogen adsorption to the graphene leads to monohydride formulation: This hydrogen adsorption proceeds without any barrier. The bonds around the carbon consist from *sp*2 to *sp*3-like orbitals, so that the hydrogen-bonded carbon atom sticks out 0.25 Å from the graphite plane. The bond length of C-H is 1.16 Å and the adsorbed hydrogen is 0.21 Å offset along to the C-C bond from the top site of the carbon atom, as is shown in Fig. 2. This means the possibility to make the easy break of the C-C bonds, which is formed between the hydrogen-adsorbed carbon atom and the others.

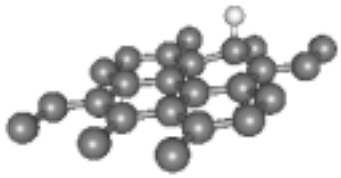

Fig. 2 Adsorption of hydrogen on a graphene. White and black balls denote hydrogen and carbon atoms, respectively.

In summary, we demonstrated the capability of the ab initio tight-binding molecular dynamics calculation through hydrogen adsorption on the graphene surface. The adsorption of hydrogen affects the local electronic states of graphene: the bonding structure changes sp^2 like to sp^3 like orbitals.

References

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