§24. *Ab initio* Tight-Binding Molecular Dynamics Simulation of Hydrogen Adsorption on Graphite Surface

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

We applied this code to the adsorption process that occurs on a graphite surface, which is used as the material of the first wall in fusion devices [4]. It is also interesting in the filed of epitaxial growth by means of the chemical vapor deposition. In both the processes, the atomic hydrogen interacts with the graphite surface.

Our calculation is performed using the *ab initio* molecular dynamics method within the framework of the local density functional theory [1]. We employed the norm-conserving pseudopotential by Troullier and Martins in the separable form [5]. The energy cut-off is 200 Ryd. In the Brillouin zone sampling, we choose a Γ (gamma) 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 slab of graphite sheet (graphene) in a unit cell $(7.41 \times 8.56 \times 13.86 \text{Å}^3)$ for simplicity. The graphene in the unit cell contains 24 carbon atoms. All atoms in the cell are relaxed and optimized in the coordinate and energy spaces.

We have observed the methane forming process in the graphene: Fig. 1 shows the decomposition of the graphene sheet through interactions with hydrogen atoms. With these interactions, the bonds around the carbon consisted by *sp2* orbitals of the graphene change to the *sp3*-like orbitals, so that the hydrogen-bonded carbon atom sticks out of the graphene sheet. The interaction has no significant barrier except for the second hydrogen adsorption, which has a barrier of 0.67eV. As the result, a free CH_4 atom is formed.

$\Delta E = -3.65 eV$

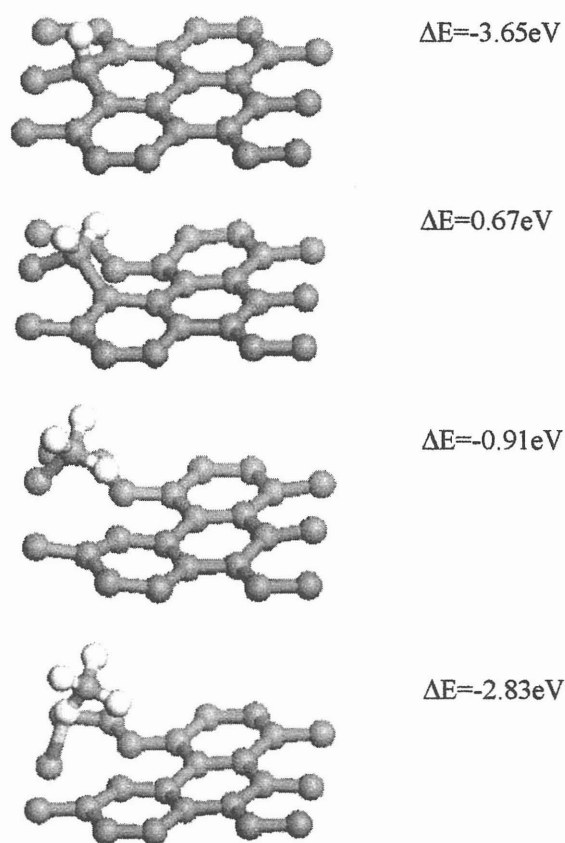$\Delta E = 0.67 eV$

$\Delta E = -0.91 eV$

$\Delta E = -2.83 eV$

Figure 1. Decomposition of the carbon network and formation of CH_4 through adsorption of hydrogen atoms on a graphene. White and black balls denote hydrogen and carbon atoms, respectively. ΔE is the energy difference.

References
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