Graphenes.

Binding also occurs in the model systems of Ca-adsorbed respectfully [8]. This clearly indicates that the GGA overestimation of exchange energy upon the bonding overestimation of exchange energy upon the bonding of wave function symmetry change: the highest occupied molecular orbital (HOMO) drastically changes from 4s to 3d_{xy} upon 4H_{2} adsorption [1]. Koch et al. discussed that similar DFT behaviors can be traced to the overestimation of exchange energy upon the s → d transfer [6].

The question arises whether the aforementioned s → d transfer takes place in more realistic systems. According to our calculations [7], when a Ca atom is placed onto aromatic planes, one of the Ca’s 4s electrons is transferred to the bonding πd orbital which is delocalized over the surface π network, while the other one remains in the singly occupied 4s orbital, yielding a triplet ground state. Upon adsorption of 4H_{2}, the separated two electrons tend to recombine in the Ca’s 3d_{xy} orbital, making a singlet ground state. For an explicit comparison, we calculated the energy of the singlet ground state of the 4H_{2}-adsorbed C_{25} coronene with respect to the triplet ground state of the Ca-coronene system and separated four H_{2} molecules. The MP2 and PBE results are found to be −0.19 and −0.66 eV, respectively [8]. This clearly indicates that the GGA overbinding also occurs in the model systems of Ca-adsorbed graphenes.

However, when a Ca atom adsorbs onto small aromatic molecules (e.g., benzene, anthracene, or naphthacene), the system develops a stable doubly occupied πd orbital even before 4H_{2} adsorption, yielding a singlet ground state [9]. As such, the chance of the adsorption-induced s → d transfer is effectively eliminated. For those systems, common DFT functionals can be better trusted, and the Sun et al.’s comparison of MP2 and PBE is noteworthy[9]. For the detailed understanding of the s → d transfer phenomenon and the related GGA overbinding problem, a more intensive study needs to be performed with various substrate conditions.

This work was supported by Dankook University project for funding RICT and by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (No. 2010-0001632).

Cha, Choi, and Park Reply: We suggested that flavors of density functional theory (DFT) lead to unrealistic stabilization of the bonded state of four hydrogen molecules onto the Ca cation center, in contrast to the results of correlated wave function theories [1]. Ohk et al. [2] commented pertinent that a larger basis set should have been used to obtain the converged results of correlated theories. Even with the elaborated calculations, the Ca^{1+}4H_{2} system constitutes an extraordinary example for which gradient-corrected density functionals (GGAs) lead to overbinding results. The same feature persists in charge neutral Ca4H_{2} system, as shown in Fig. 1. Here, BLYP and PBE denote the GGA functionals [3–5]. Such GGA overbinding should be due to the failure of these particular functionals in the description of wave function symmetry change: the highest occupied molecular orbital (HOMO) drastically changes from 4s to 3d_{xy} upon 4H_{2} adsorption [1]. Koch et al. discussed that similar DFT behaviors can be traced to the overestimation of exchange energy upon the s → d transfer [6].

FIG. 1. The potential energy curve for (a) Ca^{1+}4H_{2} and (b) Ca4H_{2}. The geometry and reaction coordinates are explained in Ref. [1]. Solid circles, open squares, and solid squares were calculated with MP2, BLYP, and PBE, respectively. The cc-pVQZ basis set was employed with the counterpoise correction. The insets indicate the molecular spin state.