Journal of Nuclear Materials 396 (2010) 307–308

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Letter to the Editor

On the use of the BLYP functional for the DFT calculation of graphite–hydrogen systems

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ARTICLE INFO

Article history:
Received 26 July 2009
Accepted 30 October 2009

ABSTRACT

This letter focuses on a possible pitfall that can occur in the DFT calculation of graphite–hydrogen interactions under tokamaks conditions. Calculations based on the BLYP functional, in fact, result in a stable $-C_2H_3$ group that other functionals (OLYP, XLYP, PBE and BP) do not confirm.

The use of *ab initio* methods and in particular of *ab initio* molecular dynamics in fusion related research (e.g. plasma–wall interaction) has assumed, in these years, a wider role due to the recent advances in both software and hardware that allow the simulation of systems of hundreds of atoms and tens of picoseconds. The BLYP functional is one of the most used in DFT calculations and has been employed in many circumstances including the case of *ab initio* simulations of graphite–hydrogen interaction under tokamaks conditions (e.g. [1]). In this letter, we show that, in the case of graphite–hydrogen systems, the BLYP functional shows an overbinding tendency towards certain C–H structures. Calculations of H adsorption over a graphitic surface, based on this functional, give stable $-C_2H_3$ groups that do not appear with any other functional and are probably artifacts due to the use of the BLYP functional in the case under study.

We calculated the electronic density of two layers of 18 carbon atoms each by means of density functional theory using the norm-conserving pseudopotential by Trouiller and Martins and the BLYP density functional. The wavefunction cutoff was set to 70 Rydberg. Meshes of $2 \times 2 \times 1$ k-points, chosen according to the Monkhorst–Pack scheme, were used. Additional calculations with various $k \times k \times 1$ meshes were carried out in order to ensure the adequacy of the $2 \times 2 \times 1$ mesh. The software CPMD [2], running in parallel on a 32 processor AMD-Opteron (2.2 GHz) cluster, was employed for all the simulations.

We looked for possible stable structures with three hydrogen atoms and configurations of the type $-C_2H_3$ (see Fig. 1) by means of geometry optimization (energy minimization at $T = 0$ K). Subsequently, the evolution of the system at 1 K, 500 K and 1000 K (Nosé–Hoover thermostat) is followed by means of Car-Parinello MD (time step = 0.1 fs). The case at 1 K is used to study the evolution of a system with negligible kinetic energy and, at the same time, to avoid certain unstable energetic equilibriums that are possible in the cases where a hydrogen atom is placed exactly in the middle of a C–C bond. The starting configurations are the cis-C_2H_2 (Fig. 1a, on the left, without the central H) and trans-C_2H_2 (Fig. 1b, on the left, without the central H) groups. Both of them, of course, are stable. Now, we suppose that a hydrogen atom arrives in the proximity of one of these two groups. We placed an H atom between the C1 and C2 atom (see Fig. 1a and b, on the left; the C1 and C2 atoms are the two carbons that belong to the initial $-C_2H_2$ group). In the case of trans-C_2H_2, MD simulations at 1 K show that hydrogen forms a short living $-CH_2$ group, which after approximately 0.8 ps decays to 3 –CH groups (Fig. 1b on the right). The hydrogen in Fig. 1b, on the right, that apparently is not connected to the graphite is actually bonded to an upper sheet due to the periodical boundary conditions. When the same procedure is used starting from the cis-C_2H_2 group however, the result is different. A $-C_2H_3$ stable group appears as shown in Fig. 1a on the right. In this case, a hydrogen bridge between two C atoms (–C–H–C–) appears. We ran three simulations at 1 K, 500 K and 1000 K. We used 1 K simulation because it is very close to a geometry optimization, 0 K, but the little additional kinetic energy ensures that the H atom does not get stuck in a saddle point when the hydrogen is placed between C1 and C2. The results show that the $-C_2H_3$ group is stable at 1 K and 500 K, but not at 1000 K. In this case, the group decays to 3 –CH bonds like in Fig. 1b. Subsequently, we calculated the potential energy surface (PES) in the vicinity of the stable $-C_2H_3$ group of Fig. 1b (right) by moving the position of the central H atom. In Fig. 2, the section of the PES calculated with respect to the z direction (perpendicular to the graphene plane), keeping fixed the other two coordinates to their initial values, is shown. The whole PES was calculated moving the H atom in all the three space directions, but in Fig. 2 only a section of the entire surface is reported. From the stable $-C_2H_3$ configuration, which corresponds to the minimum M_0 (x_0,

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doi:10.1016/j.jnucmat.2009.10.066

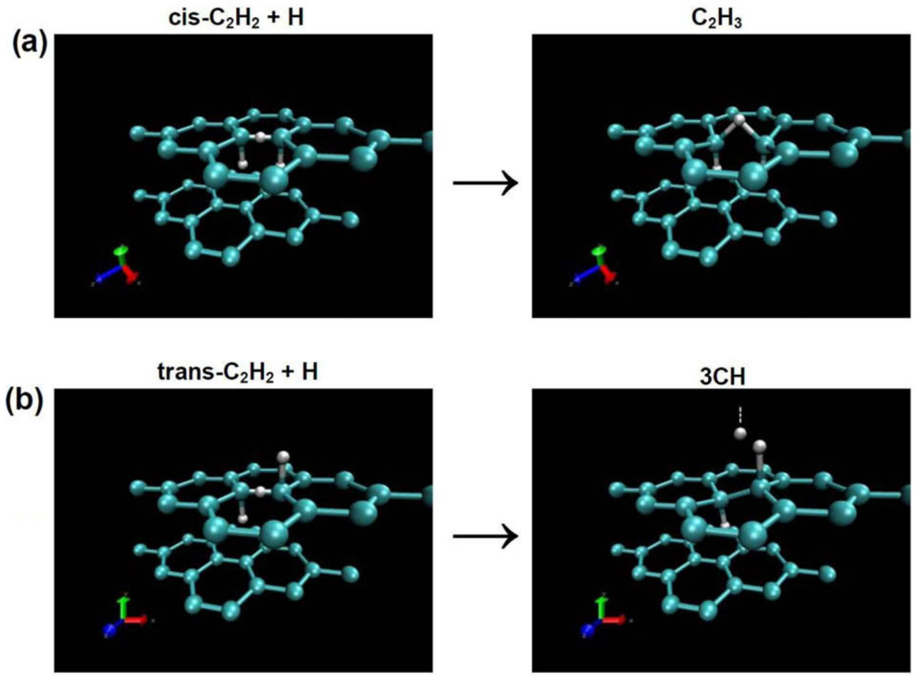

Fig. 1. Evolution of –C_2H_2 + H systems.

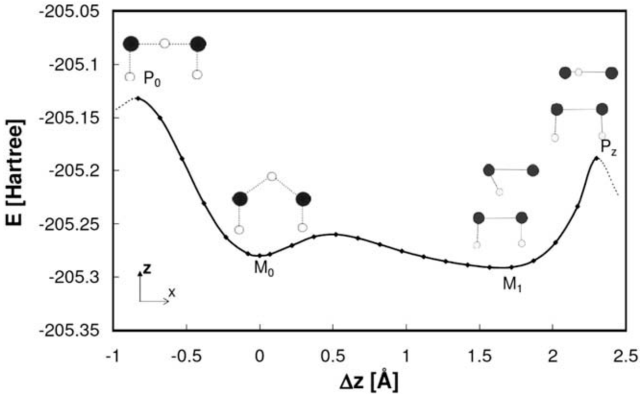

Fig. 2. Potential energy surface sections in *z* directions.

y_0, z_0) in Fig. 2, the central H atom is moved both downwards (towards point P_0) and upwards (towards point Pz). Point P_0 represents the state where the H atom is located in between the two C atoms (the cis-C_2H_2 + H of Fig. 1). Point Pz represents the situation where the H is between two C atoms of the upper graphene plane. The minimum at M_1 represents the situation when the C_2H_3 group is broken and the H atom forms a new CH group with the upper graphitic layer. Since Fig. 2 shows only the *z*-movements with x_0 and y_0 fixed to the initial H coordinates, M_1 in Fig. 2 is not the absolute minimum. The real absolute minimum corresponding to Pz is found when the H atoms form a CH group perpendicular to the graphitic layer. If we repeat our calculations with other functionals (i.e. OLYP, XLYP, PBE and BP), however, there are not stable structures and the minimum M_0 does not exist. Molecular dynamic simulations at 1 K (or geometry optimization calculations) starting from the BLYP-stable –C_2H_3 configuration (Fig. 1a, right) but carried out with the OLYP, XLYP, PBE or the BP functional show that the –C_2H_3 group decays to 3 CH single bonds as it happened for Fig. 1b (right).

We decided to compare the results of the BLYP functional with other GGA functionals in order to compare functionals belonging to the same category. Hybrid functionals, like the B3LYP, are probably more accurate and have been profitably used for similar systems [3]. They are, however, more complex and computationally demanding and, for this reason, we believe it would be out of the scope of this letter to go to the next step and address the comparison between GGA and Hybrid functionals.

In conclusion, the only considered functional that gives a stable –C_2H_3 group is the BLYP. For this reason, it is very likely that this group is simply an artifact and does not correspond to a real chemical structure. If this is the case, the BLYP functional should be used with care in calculation involving hydrogen and graphite since it can overestimate the interaction between the graphene and the hydrogen atoms and generate fictitious chemical structures.

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