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QUANTUM-CHEMICAL STUDY OF MIGRATION AND SORPTION OF CARBON ATOM ON GRAPHITE AND GRAPHENE SURFACE

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Different carbon structures cause interest of researchers, because they are very perspective materials for microelectronic, creation of new energy sourses and effective sorbents.

Ability to modify separate areas of graphene is essential to producing of devices based on graphene. One of methods that allows to make such modification is generation of different defects, as the example adatoms.

Theoretical methods allows to predict new properties of graphete, investigate different modification of it structure, and appearance of new superstructure. In calculation of carbon superstructure, it is essential to find calculation technique that allows to correctly describe the Van der Waals forces.

Purpose of our work is the theoretical study of adatom behavior in carbon structures.

At first we have chose the calculation technique. For selection of the calculation technique we have used NWChem program, density functional theory (DFT), SVWN5, B3LYP, LC-BOP, PBE, LC-PBE functionals, 6-311++G (3df,3pd); 6-311G**; 6-311G**++ basis sets, dispersion correction (DFT-D) and basis set superposition error correction (BSSE correction).

Comparison between different techniques was made by calculations of binding energy of benzene molecules in T-shaped dimer (figure 1).
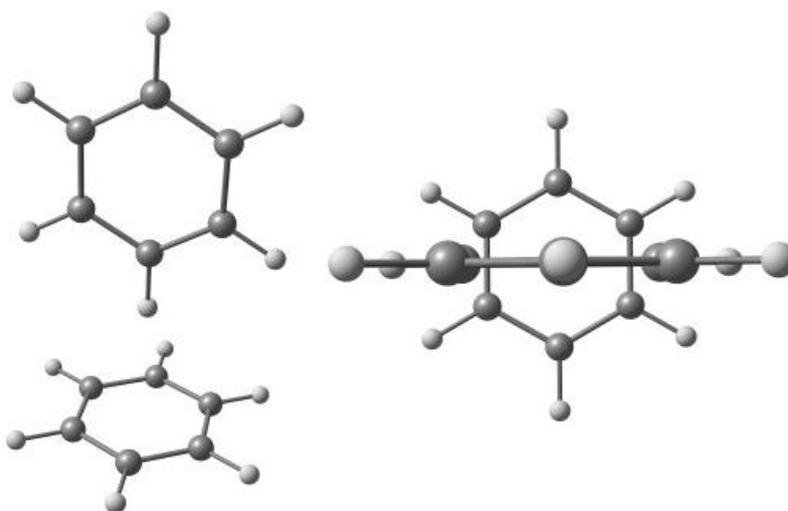

Figure 1 - T-shaped benzene dimmer

Was established that PBE-D+BSSE 6-311G**++ technique provides the best accuracy. According to the calculation in PBE-D+BSSE 6-311G**++ technique binding energy of benzene molecules in T-shaped dimmer is 12,2 kJ/mol, this value is comparable to experimental (10,0 ± 1,7 kJ/mol) and CCSD (11,4 kJ/mol) dates.

To confirm efficiency of the selected technique we have calculated binding energy of benzene molecules in PD-benzene dimmer (figure 2).
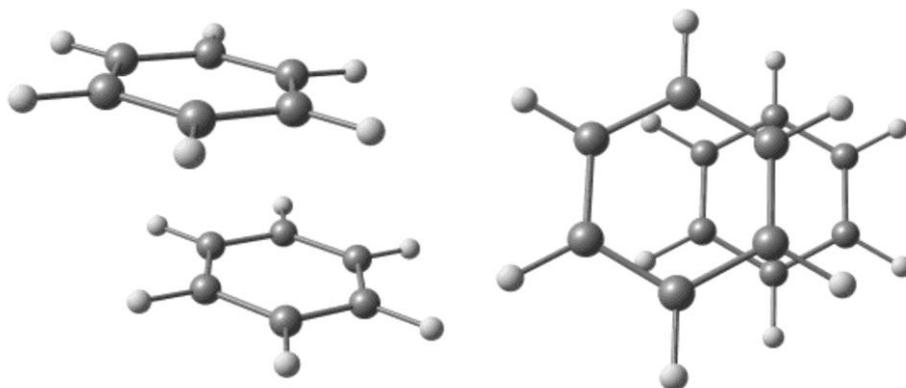
Figure 2 - PD-benzene dimmer

As the result efficiency of the chosen technique was confirmed. Binding energy of benzene molecules in PD-benzene dimmer, according to PBE-D+BSSE 6-311G**++ technique is 10,4 kJ/mol, while experimental and CCSD values of energy are $10,0 \pm 1,7$ kJ/mol and 11,5 kJ/mol, respectively.

Next we have calculated:
- binding energy between carbon adatom and the graphene;
- binding energy of graphite layers;
- binding energy between layers in double-layer AA-type graphene;
- binding energy between carbon adatom and the graphite.

Our researches were made in cluster approach and in periodic structures. Calculations in the cluster approach were made by using of NWChem program, density functional theory (DFT), PBE functional, 6-311G**++ basis set, dispersion correction (DFT-D) and basis set superposition error correction (BSSE correction). While calculations in periodic structures were made by using of VASP program, density functional theory (DFT), PBE functional, plane-wave functions, Vanderbilts ultra-soft pseudopotentials and dispersion correction (DFT-D). Moreover, all calculations were duplicated by density functional theory local density approximation (DFT LDA).

We have established that the most energetically favorable position of carbon atom on graphene surface is position over C-C bond (figure 3).
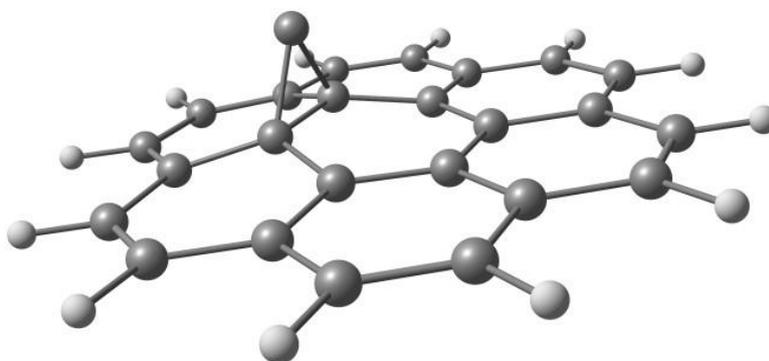

Figure 3 – Most energetically favorable position of carbon atom on graphene surface.

Binding energies in that position, according to the cluster approach PBE-D 6-311G**++, cluster approach DFT LDA, periodic PBE-D and periodic DFT LDA calculations are 136,2 kJ/mol, 201,8 kJ/mol, 153,1 kJ/mol and 208,3 kJ/mol, respectively.

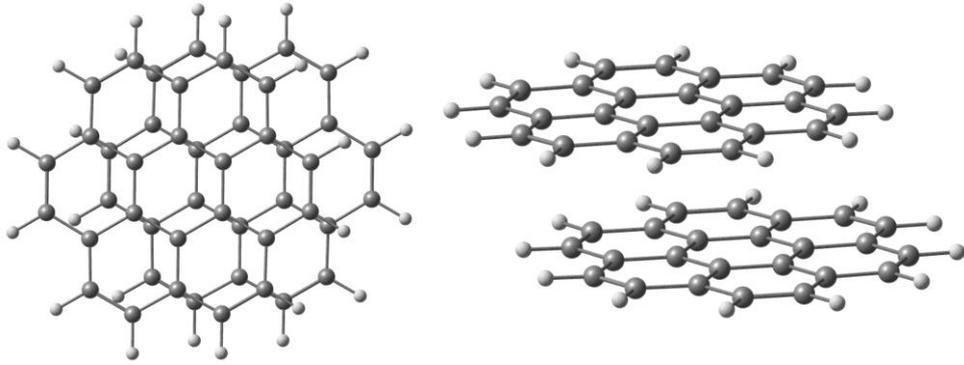Next we have calculated binding energy of graphite layers (figure 4).

Figure 4 - Model graphite area

We have established that binding energies of graphite layers, according to the cluster approach PBE-D+BSSE 6-311G**++, cluster approach DFT LDA, periodic PBE-D and periodic DFT LDA calculations are 18,1 kJ/mol, 13,5 kJ/mol, 30,6 kJ/mol and 31,2 kJ/mol, respectively.

Furthermore geometric optimization of double-layer AA-type graphene turns it into graphite (Figure 5). Therefore formation of double-layer AA-type graphene is energetically unfavorable.
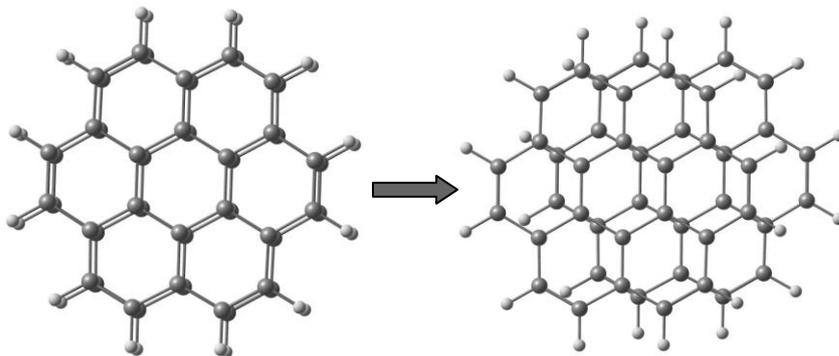

Figure 5 - Transition of double-layer AA-type graphene into double layer graphite

Next step was investigation of interaction between carbon adatom and the graphite.

We have established that the most energetically favorable position of carbon atom on graphite is position over C-C bond of the first layer and under the hexagon of the second layer (figure 6).
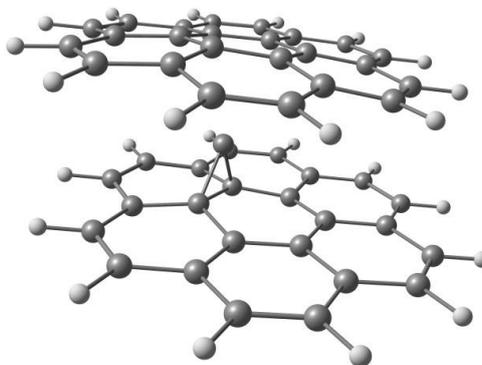

Figure 6 - Most energetically favorable position of carbon atom on graphite

Binding energies in that position, according to the cluster approach PBE-D+BSSE 6-311G**++, cluster approach DFT LDA, periodic PBE-D and periodic DFT LDA calculations are 47,5 kJ/mol, 127,9 kJ/mol, 68,1 kJ/mol and 141,7 kJ/mol, respectively.

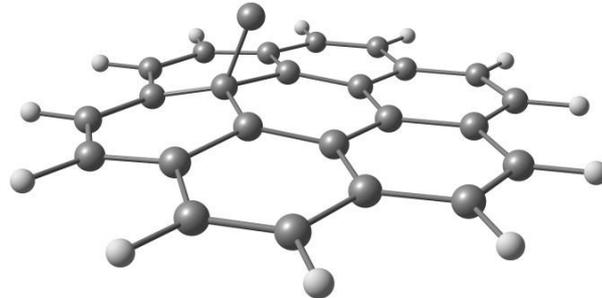Energies of the transition state in graphene (figure 7) and graphite (figure 8) were determined.

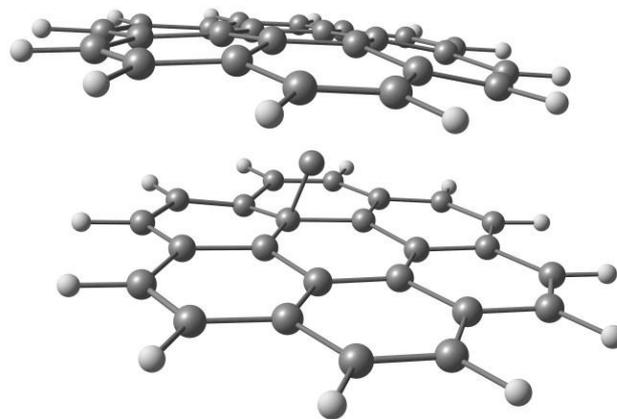Figure 7 - Transition state in graphene

Figure 8 - Transition state in graphite

As the result we have established that the values of the energy barrier in graphene, according to the cluster approach PBE-D+BSSE 6-311G**++, cluster approach DFT LDA, periodic PBE-D and periodic DFT LDA calculations are 52,9 kJ/mol, 50,5 kJ/mol, 43,7 kJ/mol and 35,0 kJ/mol, respectively. While the values of the energy barrier in graphite, according to the cluster approach PBE-D+BSSE 6-311G**++ and cluster approach DFT LDA calculations are 57,4 kJ/mol and 63,1 kJ/mol, respectively.

Conclusion

- The technique that allows to correctly describe the Van der Waals forces was presented.
- Binding energy between carbon adatom and the graphene was established.
- Binding energy between graphite layers was investigated.
- Was found that geometric optimization of double-layer AA-type graphene turns it into graphite. Therefore formation of double-layer AA-type graphene is energetically unfavorable.
- Binding energy between carbon adatom and the graphite was established.
- Values of the energy barrier in graphene and graphite were investigated
- Was found that intercalation of the carbon adatom on graphene and graphite causes partial distortion of their structures.