



Ab initio LC-DFT study of graphene, multilayer graphenes and graphite

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ARTICLE INFO

Article history:

Received 17 February 2011

In final form 4 April 2011

Available online 7 April 2011

ABSTRACT

Atomic structure of graphene, bi-, tri-, tetralayer graphenes and graphite as well was studied using *ab initio* HSE, LDA and PBE DFT approaches in periodic boundary conditions. Based on comparison of theoretical results with experimental data the performance of the methods was estimated. It was found that long-range corrected HSE potential is the most reliable DFT approximation to reproduce the atomic structure of weakly bound multilayer graphenes and graphite as well.

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Discovery of graphene [1] and multilayer graphenes [1–6] opens a new era in development of novel devices with exceptional charge and spin transport properties. It has been reported that the formation of multilayer graphene on the 4H-SiC substrate using epitaxial technique leads to numerous stacking faults of graphene layers caused by mutual lattice mismatching [2–6]. Weak van der Waals interactions determine the stacking order and interlayer distances of multilayer graphenes. Weak dispersion forces have been reported to play an important role in determination of enthalpies of even simple isothermic chemical reactions involving extended molecular systems like alkanes [7]. For extended structures like graphenes and graphite dispersion van der Waals forces determine the initial conditions and main features of potential energy surfaces (PES) of chemical reactions.

DFT theory is widely used to study atomic and electronic structure of molecules and condensed matters (see, for example, [8–11]). The accuracy of DFT methods to reproduce the main features of chemical reactions like potential energy surfaces and thermochemistry was tested mostly for cluster approximation. Local density approximation (LDA), the simplest and computationally the cheapest DFT potential coupled with periodic boundary conditions (PBC) and plane-wave basis sets is mostly used to study condensed matters and gives wholly satisfactory results in description of the electronic structure of metals. For covalently-bonded objects like carbon single-walled nanotubes, the LDA approach in combination with GAUSSIAN-type basis functions [12] underestimates the separation between the first van Hove singularities up to 25%. Also, the LDA-based description of atomization energies, reaction pathways and potential energy barriers of molecular

systems is rather poor [8–10]. In contrary, for weakly bound systems, LDA in both PBC and cluster approximations gives surprisingly satisfactory results in determination of structure of molecular solids [13] and enthalpies of chemical reactions [11] due to local nature of exchange–correlation hole.

In cluster approximation a widely used GGA PBE functional [14,15] gives reasonably good results in determination of atomic and electronic structure and reaction pathways of covalently bound molecules coupled with poor description of atomic structure of weakly bound complexes [8–10]. The electronic structure PBE PBC calculations [16] of covalently bound metallic single-walled carbon nanotubes display high accuracy in determination of the energy positions of the first van Hove singularities.

For extended systems and weakly bound complexes the long-corrected (LC) DFT schemes provide better description of atomic structure and stages of chemical reactions (including structure of transition complexes and potential energy surfaces) [8–11]. Long-corrected HSE potential [17,18], which is very suitable for PBC calculations coupled with GAUSSIAN-type basis sets provides very accurate results for structural and thermodynamic properties of covalently bound metallic carbon nanotubes, graphene nanoribbons and nanodots [19–22].

The accuracy of reproduction of interlayer distances in multilayer graphenes and graphite is very important for correct description of chemical reactions involving extended 2D and 3D species, like induced transformation of graphite to diamond and multilayer graphenes to diamonds [23,24], chemical interactions of graphene and fullerene-based materials with transition metals [25–27], etc. The goal of this Letter is to study the accuracy of HSE PBC method coupled with GAUSSIAN-based basis sets to reproduce structure and symmetry of 2D and 3D extended multilayer graphenes and graphite.

During decades the atomic structure of graphite has been extensively studied using several experimental techniques (see,

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for example, [28–32]) indicating quite controversial interatomic C–C and interlayer distances from 1.41 up to 1.42 Å and from 3.35 up to 3.438 Å, respectively. Probably the best and the most reliable experimental study [32] of the atomic structure of graphite, performed by neutron diffraction on high quality $2.0 \times 1.4 \times 0.2$ mm graphite crystal, reveals 1.422 ± 0.001 Å and 3.356 ± 0.002 Å C–C and interlayer bond lengths, respectively.

High-resolution high-angle annular dark field scanning transmission electron microscopy (STEM) observations have directly confirmed the hexagonal structure of free-standing 2D graphene [33]. However, the accuracy of determination of interatomic C–C distance in the STEM observations is not better than 1.4 Å which is insufficient for judging the agreement with calculations. Accordingly, the graphite C–C bond length (1.422 ± 0.001 Å, [32]) is used to compare with the results of our theoretical DFT PBC calculations.

To calculate the atomic structure of graphene, bi-, tri-, tetralayer graphenes and pristine graphite as well, long-corrected HSE DFT potential coupled with GAUSSIAN-type basis sets and PBC approximation was utilized. To run the electronic structure calculations GAUSSIAN 09 code [34] was used. The LDA and GGA PBE DFT potentials was used to eliminate the role of nature of exchange hole and LC scheme in determination of atomic structure of multilayer graphenes and graphite. STO-3G minimal basis set and a set of split-valence basis sets (3-21G*, 6-21G, 6-21G*, 4-31G, 4-31G*, 6-31G, 6-31G*, 6-311G and 6-311G*) were used to study the influence of basis set effect on the atomic structure of weakly bound systems.

To optimize the atomic structure of 2D multilayer graphenes and 3D graphite 128 points in k -space for the Brillouin zone integration were used. During SCF iterations we applied a 1×10^{-7} Hartree self-consistency threshold for the total energy, and geometry optimizations were performed until the gradient became

smaller than 10^{-4} Hartree/Bohr. All geometries were fully optimized in C_1 point group to avoid converging to higher energy solution wave functions imposed by preliminary determined symmetry restrictions.

The C–C distances obtained using different DFT potentials and basis sets are presented in Table 1. As it is expected, the LDA approach gives the worse results providing only qualitative reproduction of atomic structure of graphene sheets for 3-21G*, 6-31G* and 6-311G* basis sets with 0.018–0.010 Å errors in determination of C–C bond lengths. PBC PBE provides quantitative description of atomic structure of graphene sheets with 0.01–0.005 Å overestimation of C–C bond lengths. The LDA PW PBC calculations of graphite made by different authors (see, for example, [35]) demonstrate underestimation of the length of C–C interatomic distances by 0.009 Å.

Long-range correction scheme realized in HSE potential leads to the best description of graphene atomic structure (Table 1). Mostly PBC HSE slightly underestimates the length of C–C bonds (up to -0.004 Å in the case of 4-31G* calculations of graphite). In some cases the PBC HSE error in determination of the C–C bonds is equal to or even less the accuracy of experimental data (± 0.001 Å [32]). The 6-31G basis set with the error equal to 0.000 Å is the best for geometry optimization of graphite. For other systems (graphene and multilayer graphenes as well) the PBC HSE/6-31G also provides the best results for C–C bonds in respect with experimental data [32].

All DFT potentials (HSE, LDA and PBE) demonstrate strong basis set effects in determination of graphenes and graphite interlayer distances (Table 2, for tri- and tetragraphenes the averaged interlayer distances are presented. All data are compared with experimental data [32] for graphite). As it is expected, the PBC PBE calculations demonstrate unstable and unpredictable results for

Table 1

Interatomic C–C distances (Å) and (errors) (Å) for graphene, bi-, tri-, tetralayer graphenes and graphite as well, calculated using PBC HSE, PBC LDA and PBC PBE methods. The errors in determination of C–C bond lengths are presented in respect with 1.422 ± 0.001 Å experimental value for graphite [32].

Method	STO-3G	3-21G*	6-21G	6-21G*	4-31G	4-31G*	6-31G	6-31G*	6-311G	6-311G*
<i>Graphene</i>										
HSE	1.436 (0.014)	1.421 (–0.002)	1.421 (–0.001)	1.423 (0.001)	1.418 (–0.004)	1.417 (–0.004)	1.422 (0.000)	1.419 (–0.003)	1.4184 (–0.0036)	1.417 (–0.005)
LDA	1.448 (0.026)	1.436 (0.014)	–	–	–	–	–	1.436 (0.014)	–	1.433 (0.011)
PBE	1.447 (0.025)	1.430 (0.008)	–	–	–	–	–	1.429 (0.007)	–	1.427 (0.005)
<i>Bi-graphene</i>										
HSE	1.435 (0.013)	1.420 (0.002)	1.421 (–0.001)	1.423 (0.001)	1.418 (–0.004)	1.418 (–0.004)	1.421 (–0.001)	1.419 (–0.003)	1.418 (–0.004)	1.417 (–0.005)
LDA	1.448 (0.026)	1.435 (0.013)	–	–	–	–	–	1.435 (0.013)	–	1.433 (0.011)
PBE	1.447 (0.025)	1.430 (0.008)	–	–	–	–	–	1.429 (0.007)	–	1.427 (0.005)
<i>Trilayer graphene</i>										
HSE	1.436 (0.014)	1.420 (–0.002)	1.421 (–0.001)	1.423 (0.001)	1.418 (–0.004)	1.418 (–0.004)	1.421 (–0.001)	1.419 (–0.003)	1.418 (–0.004)	1.417 (–0.005)
LDA	1.448 (0.026)	1.435 (0.013)	–	–	–	–	–	1.436 (0.014)	–	1.433 (0.011)
PBE	1.447 (0.025)	1.430 (0.008)	–	–	–	–	–	1.429 (0.007)	–	1.427 (0.005)
<i>Tetralayer graphene</i>										
HSE	1.436 (0.014)	1.420 (–0.002)	1.421 (–0.001)	1.423 (0.001)	1.418 (–0.004)	1.418 (–0.004)	1.421 (–0.001)	1.419 (–0.003)	1.418 (–0.004)	1.417 (–0.005)
<i>Graphite</i>										
HSE	1.435 (0.013)	1.420 (–0.002)	1.421 (–0.001)	1.423 (0.001)	1.418 (–0.004)	1.418 (–0.004)	1.421 (0.000)	1.420 (–0.002)	1.420 (–0.003)	1.419 (–0.003)
LDA	1.448 (0.026)	1.435 (0.013)	1.435 (0.013)	1.440 (0.018)	1.436 (0.014)	1.434 (0.012)	1.440 (0.018)	1.436 (0.014)	1.4397 (0.018)	1.433 (0.011)
PBE	1.447 (0.025)	1.429 (0.007)	1.429 (0.007)	1.433 (0.011)	1.430 (0.008)	1.428 (0.006)	1.434 (0.012)	1.429 (0.007)	1.432 (0.010)	1.427 (0.005)

Table 2
Interlayer distances (Å) and (errors) (Å) for bi-, trilayer, tetralayer graphenes and graphite as well, calculated using PBC HSE, PBC LDA and PBC PBE methods. The errors in determination of interlayer distances are presented in respect with 3.356 ± 0.002 Å experimental value for graphite [32]. For tri- and tetralayer graphenes the averaged interlayer distances are presented.

Method	STO-3G	3-21G*	6-21G	6-21G*	4-31G	4-31G*	6-31G	6-31G*	6-311G	6-311G*
<i>Bi-graphene</i>										
HSE	4.090 (0.734)	3.121 (−0.235)	3.577 (0.221)	3.511 (0.155)	3.615 (0.259)	3.544 (0.188)	3.625 (0.269)	3.628 (0.272)	3.605 (0.248)	3.581 (0.225)
LDA	3.505 (0.149)	3.137 (−0.219)	–	–	–	–	–	3.471 (0.115)	–	3.535 (0.179)
PBE	4.105 (0.749)	4.053 (0.697)	–	–	–	–	–	4.030 (0.674)	–	3.621 (0.265)
<i>Trilayer graphene</i>										
HSE	4.125 (0.769)	3.144 (−0.212)	3.575 (0.219)	3.574 (0.218)	3.610 (0.254)	3.610 (0.254)	3.625 (0.269)	3.620 (0.267)	3.600 (0.244)	3.573 (0.220)
LDA	3.638 (0.282)	3.080 (−0.277)	–	–	–	–	–	3.606 (0.250)	–	3.515 (0.159)
PBE	4.012 (0.662)	4.069 (0.719)	–	–	–	–	–	4.080 (0.730)	–	4.097 (0.747)
<i>Tetralayer graphene</i>										
HSE	4.090 (0.734)	3.149 (−0.207)	3.575 (0.219)	3.577 (0.221)	3.608 (0.252)	3.608 (0.252)	3.620 (0.264)	3.620 (0.264)	3.602 (0.246)	3.584 (0.228)
<i>Graphite</i>										
HSE	4.090 (0.734)	3.146 (−0.210)	3.575 (0.219)	3.575 (0.219)	3.605 (0.249)	3.606 (0.250)	3.610 (0.254)	3.625 (0.269)	3.624 (0.268)	3.624 (0.268)
LDA	3.573 (0.217)	3.106 (−0.250)	3.158 (−0.199)	3.213 (−0.143)	3.507 (0.151)	3.528 (0.172)	3.536 (0.180)	3.546 (0.190)	3.534 (0.178)	3.537 (0.181)
PBE	3.988 (0.632)	3.150 (−0.206)	3.217 (−0.139)	4.052 (0.696)	3.616 (0.260)	3.633 (0.277)	3.642 (0.286)	3.458 (0.102)	3.604 (0.248)	3.612 (0.256)

interlayer distances ranging from 3.150 Å (−0.206 Å error) for graphite 3-21G* calculation and up to 4.097 Å (0.747 Å error) for trigraphene 6-311G*, respectively.

The PBC LDA results demonstrate the best performance in determination of interlayer distances for graphite and multilayered graphenes. The 6-21G* and 4-31G basis sets provide the best determination of the distances (3.213 Å (−0.143 Å error) and 3.507 Å (0.151 Å error), respectively). The small basis sets (3-21G*, 6-21G, 6-21G*) lead to underestimation of the distances, whereas medium and extended ones (4-31G, 4-31G*, 6-31G, 6-31G*, 6-311G and 6-311G*) leads to overestimation of the distances from 0.151 Å up to 0.190 Å for 4-31G and 6-31G*, respectively. The LDA PW PBC calculations of graphite made by different authors [35] demonstrate much better accuracy (0.016 Å error) in determination of graphene–graphene interlayer distances.

The HSE potential provides more stable, but less accurate results in determination of the interlayer distances (Table 2). In the wide range of basis sets (from 6-21G up to 6-311G*) the method overestimates the distance from 3.575 Å (6-21G, error 0.219 Å) up to 3.625 Å (6-31G*, error 0.269 Å), respectively. Extended basis

sets (6-311G and 6-311G*) provides slightly better result (3.624 Å or error 0.268 Å).

The quality of electronic structure calculations of the multilayer graphenes and graphite can be estimated by analyzing the displacements of the carbon hexagonal layers relative to each other (Table 3) in respect to perfect ABA stacking sequence. Overall, the PBC HSE method demonstrates stable satisfactory performance (displacements for graphite for medium and extended basis sets are in the range of 0.01–0.05 Å) with conservation of the hexagonal symmetry of multilayer graphenes and graphite. On the contrary in many cases PBC LDA approach fails to reproduce the correct stacking of the layers demonstrating the horizontal displacement of the graphene sheets up to 1.122 Å (trilayer graphene 6-311G*). Only in three cases (6-31G*, 6-311G and 6-311G* calculations of graphite) the LDA displacements are smaller than the PBC HSE ones (0.026/0.049, 0.022/0.047 and 0.021/0.047 Å, respectively).

It is necessary to note that the HSE potential provides the best results for interatomic C–C and interlayer graphene–graphene distances for medium basis sets (6-21G, 6-21G*, 4-31G, 4-31G*, 6-31G and 6-31G*), but not for the large ones (6-311 and 6-311G*, see

Table 3
Average graphene layer displacements (Å) from perfect ABA graphene layer stacking for bi-, tri- and tetralayer graphenes and graphite as well, calculated using PBC HSE and PBC LDA methods.

Method	STO-3G	3-21G*	6-21G	6-21G*	4-31G	4-31G*	6-31G	6-31G*	6-311G	6-311G*
<i>Bi-graphene</i>										
HSE	0.357	0.059	0.043	0.205	0.043	0.224	0.028	0.058	0.003	0.005
LDA	0.074	0.165	–	–	–	–	–	0.187	–	0.029
<i>Trilayer graphene</i>										
HSE	0.312	0.048	0.009	0.011	0.007	0.010	0.006	0.008	0.006	0.008
LDA	0.793	0.887	–	–	–	–	–	0.838	–	1.122
<i>Tetralayer graphene</i>										
HSE	0.178	0.060	0.016	0.038	0.003	0.009	0.004	0.004	0.003	0.003
<i>Graphite</i>										
HSE	0.356	0.014	0.020	0.014	0.008	0.008	0.016	0.049	0.047	0.047
LDA	0.246	0.015	0.020	0.018	0.047	0.033	0.037	0.026	0.022	0.021

Tables 1–3). In general, the smaller the basis set, the larger the errors in determination of the atomic structure of the species. The HSE PBC approach has its own error caused by both DFT and LC schemes. The combination of medium basis sets with HSE PBC approach leads to mutual cancelation of the basis set and LC-DFT errors and provides the best description of the atomic structure of weakly bound extended 2D carbon nanoclusters.

The LC scheme in combination with LDA and PBE DFT potentials also was used to calculate atomic structure of graphene and bi- and tri-layered graphenes as well. For minimal STO-3G basis set the LC scheme improves the agreement between theory and experiment by decreases of the C–C interatomic distances by 0.010 and 0.027 Å for LDA and PBE potentials, respectively. For interlayer graphene–graphene distances the LC scheme coupled with LDA significantly worsens the agreement for interlayer distances increasing them up to 0.950 Å for bi- and tri-layered graphenes in comparison with poor LDA due to double accounting of the local nature of the LDA exchange–correlation hole. The LC scheme slightly increases (by 0.011 Å) the accuracy of reproducing of the interlayer distances using PBE PBC approach. All attempts to use better basis sets (from 3-21G* and up to 6-311G*) coupled with LC-LDA PBC and LC-PBE PBC approaches were failed.

Based on our PBC HSE, PBC LDA and PBC PBE calculations of the atomic structure of graphene, bi-, tri-, tetragraphenes and graphite as well, the long-corrected HSE scheme demonstrates the best performance in determination of the C–C bond lengths of extended graphene-based materials. The PBC HSE approach satisfactorily reproduces the interlayer distances and conserves the symmetry of graphene–graphene stacking sequence. The *ab initio* PBC HSE approach can be used as reliable DFT-based approximation for theoretical study of chemical interactions and reactions involving layered graphene-based species.

Acknowledgements

This work was supported by JAEA Research fellowship (P.V.A.). P.V.A. also acknowledges JAEA ASRC and Molecular Spintronics Group for hospitality and fruitful collaboration.

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