

탄소 나노 튜브 구조의 특성에 대한 교환과 상관 효과: DFT 연구

K. Bakhshi*, F. Mollaamin[†], and M. Monajjemi[‡]

Ph.D Student, Science and Research Branch, Islamic Azad University, Tehran, Iran

[†]*Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran*

[‡]*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran*

(접수 2010. 2. 22; 수정 2010. 4. 27; 게재확정 2010. 7. 5)

The Effect of Exchange and Correlation on Properties of Carbon Nanotube Structure: A DFT study

K. Bakhshi*, F. Mollaamin[†], and M. Monajjemi[‡]

*Ph.D Student, Science and Research Branch, Islamic Azad University, Tehran, Iran. *E-mail: kamalbakhshi@hotmail.com*

[†]*Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran*

[‡]*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran*

(Received February 22, 2010; Revised April 27, 2010; Accepted July 5, 2010)

요 약. 전자구조의 계산에서 교환과 상관 효과에 대한 기술을 개선하기 위해서는 교환-상관범함수에 대한 개념을 명확히 하는 것이 바람직하다. 이 목적을 성취하기 위해서는 많은 그룹의 물질에 대하여 다른 이론 방법을 적용할 필요가 있다. 본 연구에서는 탄소나노튜브의 고리와 바구니 내원자들의 밀도 전하를 연구하기 위하여 혼성 밀도함수 이론(DFT) 계산을 수행하였다. 핵-핵 에너지, 전자-핵 에너지와 운동에너지에 대한 교환 및 상호작용을 관찰하였으며, B3P86, B3PW91, B1B96, BLYP와 B3LYP 수준에서 계산하였다.

주제어: 밀도함수 이론, 탄소나노튜브, 교환, 상관

ABSTRACT. As an aid towards improving the treatment of exchange and correlation effects in electronic structure calculations, it is desirable to have a clear picture of concepts of exchange-correlation functionals in computational calculations. For achieving this aim, it is necessary to perform different theoretical methods for many groups of materials. We have performed hybrid density functional theory (DFT) methods to investigate the density charges of atoms in rings and cages of carbon nanotube. DFT methods are engaged and compared their results. We have also been inclined to see the impression of exchange and correlation on nuclear-nuclear energy and electron-nuclear energy and kinetic energy. With due attention to existence methods, B3P86, B3PW91, B1B96, BLYP and B3LYP have used in this work.

Keywords: Density Functional Theory, Carbon nanotube, Exchange, Correlation

INTRODUCTION

Carbon nanotubes were discovered in 1991 by Iijima of NEC Corporation.¹ Then, efforts in synthesis, characterization and theoretical investigation on nanotubes has grown, rapidly. In 1993, the simplest kind of carbon nanotubes, single walled carbon nanotubes, SWNTs, were discovered independently by Iijima group² and Bethune IBM team.³ Thess and coworkers⁴ later produced carbon nanotubes with 100 to 500 SWNTs bundled into a 2-D triangular lattice. Classical molecular mechanics (MM), lattice dynamics (LD), molecular dynamics (MD), tight binding and ab initio level Quantum Mechanical (QM) methods⁵⁻²² are used for theoretical calculation. Also,

Density functional theory (DFT) is one of the methods is used in theoretical calculation successfully. In this paper, we present a detailed study of the energetic, structures, and mechanical properties for zigzag (4, 0) carbon nanotubes. We used an accurate force field, with using of exchange and correlation effect derived through quantum mechanical calculations, DFT, to calculate density charges between the carbon atoms and N-N energy (between nuclear and nuclear) and E-N energy (between nuclear and electrons) and KE (kinetic energy).

Computational details

Here, we have presented the results of a theoretical study by density functional theory (DFT), in this work we

have used Gaussian 98 code for our calculations and applied different DFT methods, B3P86, B3PW91, B1B96, BLYP and B3LYP. The basis set in our calculation is 6-31G*. We have shown the effect of exchange and correlation on density charges between the carbon atoms and N-N energy (between nuclear and nuclear) and E-N energy (between nuclear and electrons) and KE (kinetic energy). We selected zigzag (4, 0) carbon nanotubes. This nanotube has some rings and cages.

Gaussian 98 offers a wide variety of Density Functional Theory (DFT).²³⁻²⁶ Energies,²⁷ analytic gradients, and true analytic frequencies²⁸⁻³⁵ are available for all DFT models. In Hartree-Fock theory, the energy has the form:

$$E_{HF} = V + \langle h_p \rangle + \frac{1}{2} \langle P_j(\rho) \rangle - \frac{1}{2} \langle P_K(\rho) \rangle$$

Where: V is the nuclear repulsion energy, ρ is the density matrix, $\langle h_p \rangle$ is the one electron (kinetic plus potential) energy, $\frac{1}{2} \langle P_j(\rho) \rangle$ is the classical coulomb repulsion of the electrons, and $-\frac{1}{2} \langle P_K(\rho) \rangle$ is the exchange energy resulting from the quantum (fermion) nature of electrons.

In density functional theory, the exact exchange (HF) for a single determinant is replaced by a more general expression, the exchange-correlation functional, which can include terms accounting for both exchange energy and the electron correlation which is omitted from Hartree-Fock theory:

$$E_{KS} = V + \langle h_p \rangle + \frac{1}{2} \langle P_j(\rho) \rangle + E_X[\rho] + E_C[\rho]$$

Where $E_X[\rho]$ is the exchange functional, and $E_C[\rho]$ is the correlation functional.

Hartree-Fock theory is really a special case of density functional theory, with $E_X[\rho]$ given by the exchange integral $\frac{1}{2} \langle P_K(\rho) \rangle$ and $E_C = 0$. The functionals normally used in density functional are integrals of some function of the density and possibly the density gradient:

$$E_X[\rho] = \int f(\rho_\alpha(r), \rho_\beta(r), \nabla(\rho_\alpha(r)), \nabla(\rho_\beta(r))) dr$$

Where the methods differ in which function f is used for E_X and which (if any) f is used for E_C . In addition to pure DFT methods, Gaussian 98 supports hybrid methods in which the exchange functional is a linear combination of the Hartree-Fock exchange and a functional integral of the above form.

Proposed functionals lead to integrals which cannot be evaluated in closed form and are solved by numerical quadrature.

There are many correlation functional in DFT. VWN, Vosko, Wilk, and Nusair 1980 correlation functional fitting the RPA solution to the uniform electron gas, often referred to as Local Spin Density (LSD) correlation.³⁶ LYP the correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms.^{37,38} P86 the gradient corrections of Perdew, along with his 1981 local correlation functional³⁹ and other functionals. In DFT exchange functional combine with correlation functional and create hybrid Functionals, for example B3LYP, BLYP, B3P86, B3PW91, B1B96 and other hybrid functionals.

RESULTS AND DISCUSSION

In this work we have calculated some properties of zigzag carbon nanotube (4, 0) in Fig. 1. The results are summarized in Table 1. Where N-N is the nuclear repulsion energy, E-N is the attraction energy between electrons and nuclear and KE is the kinetic energy.

Some conclusions can be drawn from these results. First, the repulsion energy between nuclears in B3PW91,

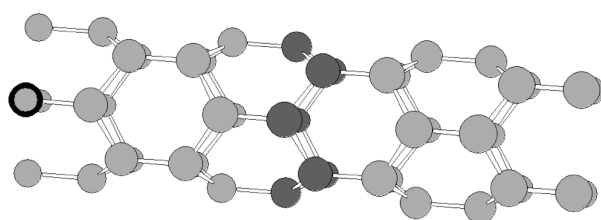


Fig. 1. Zigzag nanotube (4, 0).

Table 1. The properties of zigzag carbon nanotube (4, 0), calculated by DFT method with 6-31G*, N-N nuclear repulsion energy, E-N electron and nuclear attraction energy and KE kinetic energy

	SCF Energy (Hartrees)	Dipole moment (Debye)	N-N (Hartrees)	E-N (Hartrees)	KE (Hartrees)
B3P86	-1832.203	0.1671	5520.949	-15262.992	1812.701
B3PW91	-1826.328	0.1997	5521.016	-15262.701	1812.322
BVWN	-1841.101	0.6627	5521.016	-15271.485	1816.157
LSDA	-1816.590	0.8173	5521.016	-15252.221	1801.033
B1LYP	-1826.503	0.7215	5520.948	-15266.585	1813.464
B3LYP	-1826.995	0.1645	5520.949	-15264.509	1813.268

Table 2. The charge of atoms in zigzag(4, 0) nanotube with DFT methods by 6-31G* basis set

	B3P86	B3PW91	B3LYP	LSDA	BVWN
Number carbon					
1	0.016063	0.018547	0.025656	0.019735	0.039189
2	-0.063483	-0.066383	-0.078528	-0.053654	-0.058026
3	0.039247	0.037027	0.038319	0.037092	0.032140
4	0.010228	0.028391	0.022732	-0.014407	-0.005260
5	0.012273	0.009788	0.015977	0.020046	0.035448
6	-0.058829	-0.054575	-0.061983	-0.099559	-0.141234
7	0.035312	0.039722	0.038606	0.049633	0.042535
8	0.030673	0.013019	0.020334	0.053620	0.057022
9	0.016375	0.018313	0.025540	0.019578	0.037165
10	-0.063675	-0.066737	-0.079136	-0.041529	-0.051084
11	0.039108	0.036317	0.037847	0.034492	0.030944
12	0.010275	0.028123	0.022400	-0.010406	-0.004085
13	0.012536	0.009535	0.015731	0.019851	0.039941
14	-0.057114	-0.053758	-0.061887	-0.088691	-0.128558
15	0.035223	0.040164	0.038570	0.048191	0.043604
16	0.031174	0.013496	0.020657	0.051864	0.053684
17	0.005591	0.003406	0.004238	0.012820	0.019751
18	-0.018711	0.022277	-0.021705	-0.006056	0.005918
19	-0.023238	-0.012580	-0.016665	-0.045141	-0.040799
20	0.003293	0.008141	0.006609	-0.000785	-0.007321
21	0.007002	0.006650	0.009429	0.004146	-0.005636
22	-0.014636	0.012990	-0.009642	-0.026332	-0.039529
23	-0.011709	-0.020896	-0.018020	0.016057	0.011198
24	0.007529	-0.005066	0.005908	0.024348	0.021156
25	0.005848	0.003310	0.004235	0.012688	0.017860
26	-0.017980	-0.021972	-0.021290	0.006357	0.005295
27	-0.022935	-0.012572	-0.016796	-0.045072	-0.038238
28	0.003695	0.007962	0.006593	-0.003420	-0.003919
29	0.007283	0.006928	0.009277	0.000882	-0.007057
30	-0.014009	-0.012721	-0.009513	-0.027924	-0.042500
31	-0.011571	-0.020462	-0.017965	0.011964	0.014640
32	0.007565	0.005136	0.006041	0.021578	0.022945
33	0.015449	0.009973	0.010579	0.028125	0.054354
34	0.039286	0.039260	0.041112	0.043462	0.043164
35	-0.068741	-0.056510	-0.069702	-0.145960	-0.135345
36	0.018665	0.011840	0.019621	0.021451	0.038677
37	0.024570	0.028701	0.033443	0.004989	-0.000864
38	0.037621	0.035436	0.037075	0.040016	0.033660
39	-0.053411	-0.067205	-0.071302	-0.004827	-0.045873
40	0.008148	0.018393	0.020290	0.021921	0.037434
41	0.015763	0.009929	0.010812	0.031109	0.052796
42	0.038972	0.038741	0.040685	0.042157	0.041673
43	-0.068875	-0.056720	-0.070652	-0.136935	-0.140726
44	0.018202	0.011217	0.019058	0.020544	0.035546
45	0.024284	0.028772	0.032814	0.005069	-0.001682
46	0.037387	0.034962	0.036678	0.037424	0.033600
47	-0.053944	-0.066599	-0.072175	-0.016660	-0.042856
48	0.008224	0.018693	0.020095	0.018865	0.039254

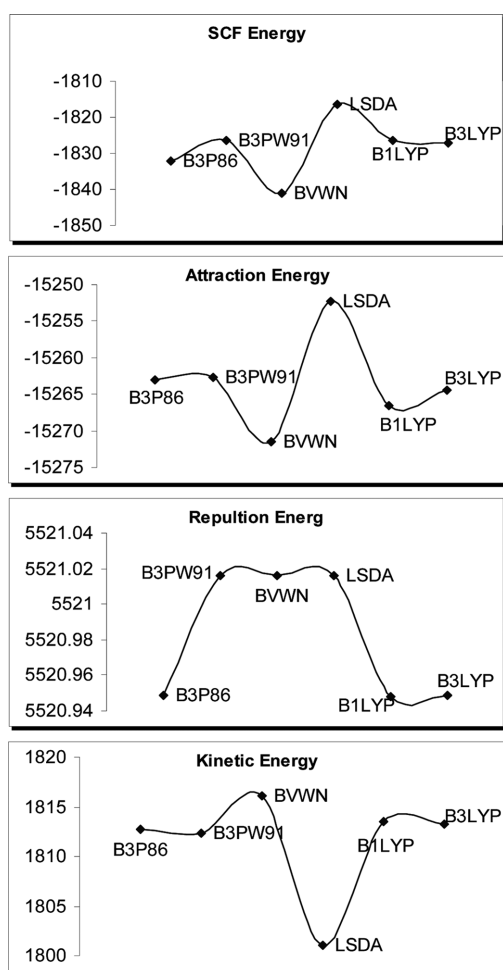


Fig. 2. SCF Energy, N-N (repulsion energy), E-N (attraction energy), KE (kinetic energy) with DFT method for zigzag (4, 0) nanotube.

BVWN and LSDA methods is maximum and equal. Second, we can also consider kinetic and attraction energy, the BVWN has a maximum values in repulsion and kinetic energy, 5521.016 and 1816.157 hartrees, respectively and has minimum SCF and attractive energy, -1841.101 and -15271.485 hartrees, because of the variety of attractive energy and SCF energy is same. We have shown it in *Fig. 2*. Finally, the LSDA (SVWN) has a maximum Dipole moment, 0.8173. Focusing on dipole moment result, will lead us this fact that any methods has B3 exchange functional, yields a small dipole moment. VWN as a correlation functional and S as an exchange functional yields a large dipole moment value. We have shown it in *Table 1*.

Difference energy among B3P86, B3PW91 and B3LYP demonstrates the correlation effect. They have same exchange functional, B3. This is Becke's 3 parameters functional,⁴⁰

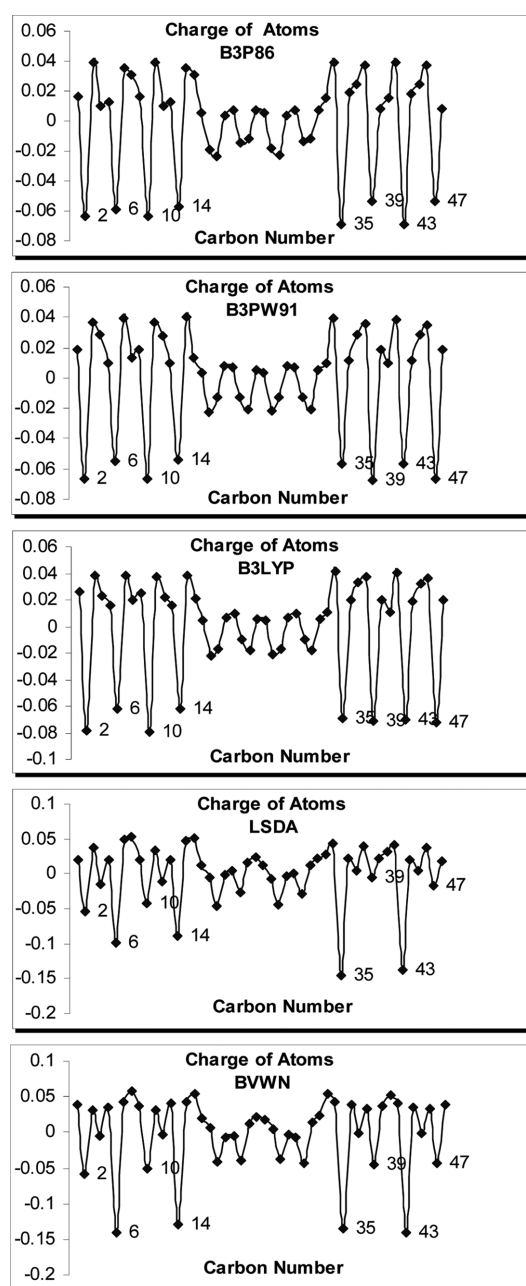


Fig. 3. The variety of charge of atoms with DFT method.

which has the form:

$$A.E_{X,Slater} + (1-A)E_{X,HF} + E_{X,Becke} + E_{C,VWN} + C.E_{C,non-local}$$

Difference energy between B3P86 and B3PW91 methods (5.875 hartrees) is related to correlation energy. It is 5.208 hartrees for B3P86 and B3LYP. If we repeat it for B3LYP and B3PW91, the result will be 0.667 hartrees. We can conclude the correlation functionals of the B3PW91 and B3LYP have a same effect on SCF energy of system

nearly, but it is not true about B3P86. We have also calculated the difference energy between B1 and B3 by comparison of energy B1LYP and B3LYP, 0.492 hartrees for obtaining the exchange effect. This result points out that the difference exchange energy between B1, B3 is not large. It was repeated for LSDA and BVWN. Difference energy between them demonstrates difference exchange energy between Becke and Slater functionals. In other word, it is 24.511 hartrees. This value is large. The charges of atoms of carbon nanotube have been collected in *Table 2*. We have shown and compared the variety charges of atoms among B3LYP, B3PW91 and B3P86 methods at 6-31G* basis set and it was also repeated for LSDA and BVWN in *Fig. 3*. From this Figure find that if the

exchange functional fixes, the charge of atoms will not change. For example in *Fig. 3* the carbon atoms with 2, 6, 10, 14, 35, 39, 43 and 47 numbers have the same variety in charge when B3P86, B3PW91 and B3LYP methods with B3 exchange functional were used. It has repeated for SVWN (LSDA) and BVWN with the same correlation functional.

The importance of electron exchange for the density of rings is demonstrated by a comparison of SVWN and BVWN results. We summarized the total density of rings for zigzag nanotube in *Table 3* and *Fig. 4*. The results calculated for rings of nanotube shows that the poetry in *Fig. 4* is less than of *Fig. 3*, because the rings are composed of some carbon atom. *Fig. 4* shows that the rings 13 and 15 numbers have the same variety in all methods. Then total

Table 3. The total density of rings in zigzag(4, 0) nanotube with DFT methods by 6-31G* basis set

	B3P86	B3PW91	B3LYP	LSDA	BVWN
Numberring					
1	0.03293	0.03150	0.03141	0.03250	0.03092
2	0.02871	0.02867	0.02801	0.02911	0.02753
3	0.03110	0.03270	0.03152	0.02902	0.02965
4	0.01267	0.01263	0.02841	0.03089	0.02735
5	0.02887	0.02898	0.01239	0.01253	0.01142
6	0.01269	0.01274	0.03155	0.03092	0.01162
7	0.03113	0.03272	0.03139	0.03246	0.02967
8	0.03292	0.03152	0.01230	0.02903	0.03090
9	0.02886	0.02899	0.02840	0.02912	0.02737
10	0.02873	0.02867	0.02802	0.02909	0.02755
11	0.02871	0.02823	0.02779	0.02890	0.02740
12	0.02827	0.02814	0.02748	0.01279	0.02734
13	0.01284	0.01283	0.01247	0.02859	0.01171
14	0.02806	0.02862	0.02782	0.01281	0.02700
15	0.01287	0.01284	0.01250	0.02875	0.01175
16	0.02851	0.02868	0.02815	0.02861	0.02701
17	0.02807	0.02865	0.02783	0.02908	0.02701
18	0.02867	0.02818	0.02774	0.02871	0.02737
19	0.02850	0.02867	0.02813	0.02892	0.02699
20	0.02825	0.02813	0.02747	0.02922	0.02733
21	0.02898	0.02872	0.02819	0.03205	0.02756
22	0.03174	0.03138	0.03053	0.01277	0.03083
23	0.01287	0.01282	0.01228	0.02894	0.01169
24	0.02860	0.02895	0.01248	0.03139	0.02733
25	0.03240	0.01267	0.02821	0.02896	0.02972
26	0.02861	0.03284	0.03234	0.02920	0.01145
27	0.02895	0.02896	0.02816	0.01254	0.02735
28	0.01272	0.02869	0.02823	0.01257	0.02753
29	0.01267	0.01275	0.01239	0.03146	0.01162
30	0.03241	0.03284	0.03235	0.03200	0.02972
31	0.03171	0.03134	0.03050	-	0.03079

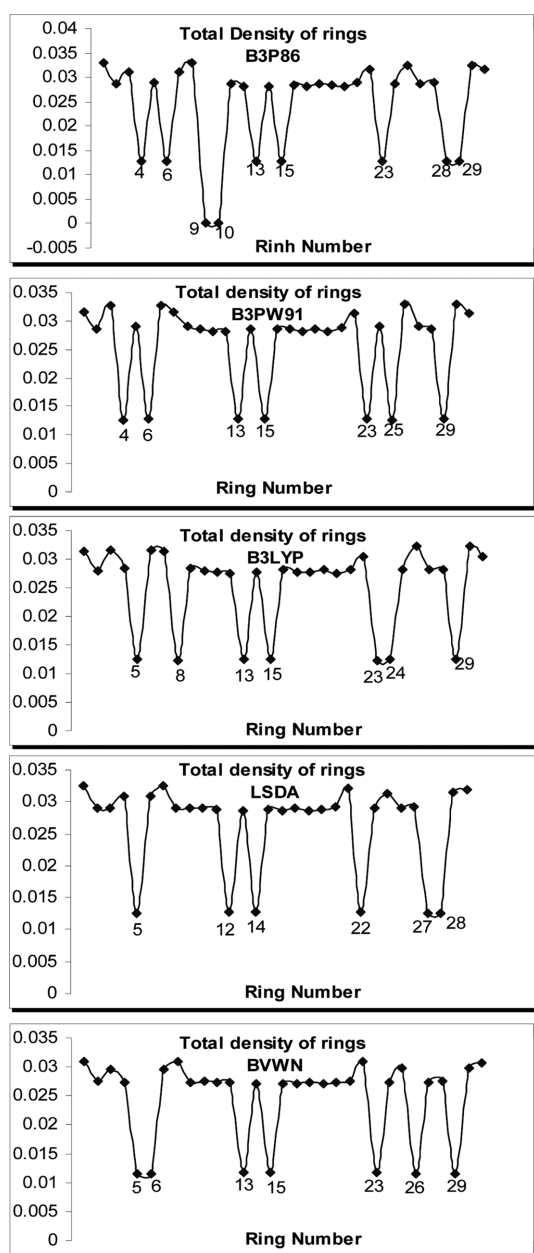


Fig. 4. The variety total density of rings for zigzag (4, 0) nanotube with DFT method.

Table 4. The total density of cages in zigzag(4, 0) nanotube with DFT methods by 6-31G* basis set

	B3P86	B3PW91	B3LYP	LSDA	BVWN
Number cage					
1	0.01173	0.01177	0.01133	0.01144	0.01038
2	0.01076	0.01071	0.01039	0.01060	0.09723
3	0.01030	0.01030	0.009933	0.01054	0.09424
4	0.01031	0.01026	0.009949	0.01096	0.09365
5	0.01075	0.01075	0.01038	0.1142	0.09773
6	0.01174	0.01175	0.01133	-	0.01035

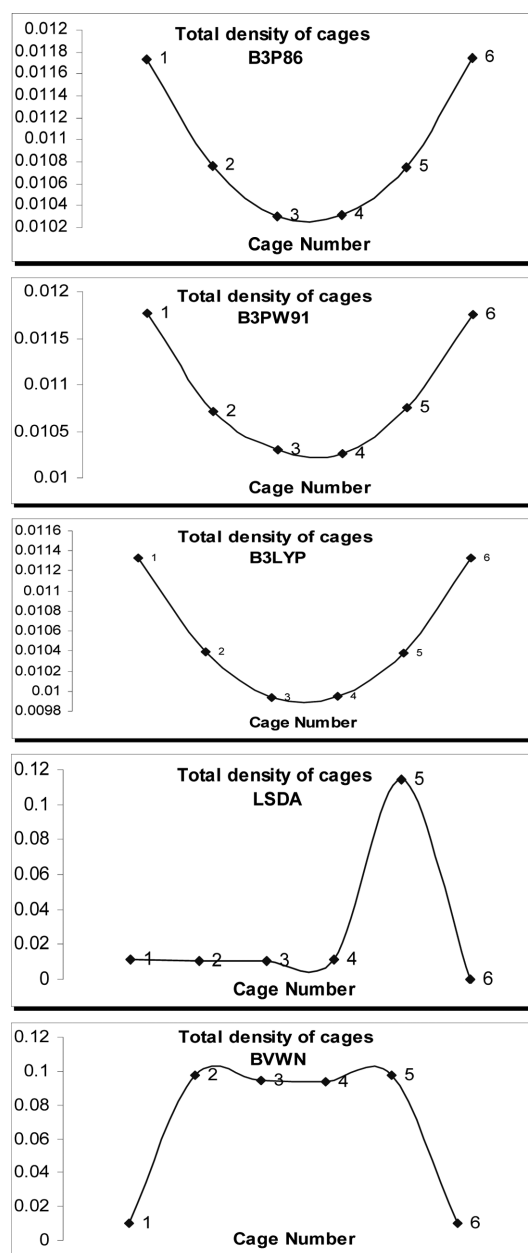


Fig. 5. The variety total density of cages for zigzag (4, 0) nanotube with DFT method.

density of cages depends on exchange functional. Fig. 5 shows that B3P86, B3LYP and B3PW91 because of having the same exchange functional (B3) point out the same variety. By changing the exchange functional for example SVWN and BVWN, we have proved it in Table 4 and Fig. 5.

CONCLUSION

While DFT in principle gives a good description of ground state properties, practical applications of DFT are

based on approximations for the so-called exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli principle and coulomb potential beyond a pure electrostatic interaction of the electrons. Possessing the exact exchange-correlation potential means that we solved the many-body problem exactly. The effect of the theoretical treatment of electron correlation and exchange for the description of the varying charges in cages and rings and atoms of carbon nanotube has been investigated by using DFT methods at 6-31G* basis set. In this work, it has been shown that the inclusion of electron exchange-correlation is essential for the description of these properties of carbon nanotube. In present case, we have shown the effect of correlation energy by fixing the exchange functional. For achieving pure correlation energy, it is necessary to combine the exact Hartree-Fock expression for the exchange with an approximate of electron correlation functional.

REFERENCES

- Iijima, S. *Nature* **1991**, 354, 56.
- Iijima, S.; Ichlhashi, T. *Nature* **1993**, 363, 603.
- Bethune, D. S.; Kiang, C. H.; Devries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, 363, 605.
- Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fisher, J. E.; Smalley, R. E. *Science* **1996**, 273, 483.
- Krotov, Y. A.; Lee D.-H.; Louie, S. G. *Phys. Rev. Lett.* **1997**, 78(22), 4245.
- Tuzun, R. E.; Noid, D. W.; Sumpter, B. G.; Merkle, R. C. *Nanotechnology* **1996**, 7(3), 241.
- Ihara, S.; Itoh, S. *Surf. Rev. Lett.* **1996**, 3(1), 827.
- Chopra, N. G.; Benedict, L. X.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Nature* **1996**, 377, 135.
- Menon, M.; Richter, E.; Subbaswamy, K. R. *J. Chem. Phys.* **1996**, 104(15), 5875.
- Hamada, N.; Sawada, S.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, 78(10), 1579.
- Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, 60, 2204.
- Blase, X.; Benedict, L. X.; Shirley, E. L.; Louie, S. G. *Phys. Rev. Lett.* **1994**, 72(12), 1878.
- Robertson, D. H.; Brenner, D. W.; Mintmire, J. W. *Phys. Rev. B.* **1992**, 45(21), 12592.
- Yakobson, B. I.; Campbell, M. P.; Brabec, C. J.; Bernholc, J. *Comp. Mater. Sci.* **1997**, 8(5), 341.
- Richter, E.; Subbaswamy, K. R. *Phys. Rev. Lett.* **1997**, 79(14), 2738.
- Iijima, S.; Brabec, C.; Maiti, A.; Bernholc, J. *J. Chem. Phys.* **1996**, 104(5), 2089.
- Tersoff, J.; Ruoff, R. S. *Phys. Rev. Lett.* **1994**, 73(5), 676.
- Ruoff, R. S.; Tersoff, J.; Lorents, D. C.; Subramoney, S.; Chan, B. *Nature* **1993**, 364, 514.
- Lee, V. S.; Nimmanpipug, P.; Mollaamin, F.; Kungwan, N.; Thanasanvorakun, S.; Monajjemi, M. *Russian Journal of Physical Chemistry A* **2009**, 83(13), 2288.
- Monajjemi, M.; Mahdavian, L.; Mollaamin, F.; Khaledghian, M. *Russian Journal of Inorganic Chemistry* **2009**, 54(9), 1465.
- Moradi, O.; Aghaie, M.; Zare, K.; Monajjemi, M.; Aghaie, H. *Journal of Hazardous Materials* **2009**, 170, 673.
- Mollaamin, F.; Baei, M. T.; Monajjemi, M.; Zhiani, R.; Honarparvar, B. *Russian Journal of Physical Chemistry A* **2008**, 82(13), 2354.
- Hohenberg, P.; Kohn, W. *Physical Review* **1964**, 136, B864.
- Kohn, W.; Sham, L. J. *Physical Review* **1965**, 140, A1133.
- The Challenge of d and f Electrons*; Salahub, D. R., Zerner, M. C., Eds.; ACS: Washington, D.C., 1989.
- Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford Univ. Press: Oxford, 1989.
- Pople, J. A.; Gill, P. M. W.; Johnson, B. G. *Chemical Physics Letters* **1992**, 199, 557.
- Johnson, B. G.; Frisch, M. J. *J. Chem. Phys.* **1994**, 100, 7429.
- Johnson, B. G.; Frisch, M. J. *J. Chem. Phys. Lett.* **1993**, 216, 133.
- Stratmann, R. E.; Burant, J. C.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1997**, 106, 10175.
- Monajjemi, M.; Baei, M. T.; Mollaamin, F. *Russian Journal of Inorganic Chemistry* **2008**, 53(9), 1430.
- Monajjemi, M.; Mahdavian, L.; Mollaamin, F. *Bull. Chem. Soc. Ethiop.* **2008**, 22(2), 1.
- Monajjemi, M.; Mollaamin, F.; Gholami. *Main Group Metal Chemistry* **2003**, 26(6), 349.
- Ariafard, A.; Fazaeli, R.; Aghabozorg, H. R.; Monajjemi, M. *Journal of Molecular Structure-theochem.* **2003**, 625, 305.
- Shabani, M.; Monajjemi, M.; Aghai, H. *Journal of Chemical Research-S* **2003**, 5, 249.
- Vosko, S. H.; Wilk, L.; Nusair, M. *Canadian J. Phys.* **1980**, 58, 1200.
- Lee, C.; Yang, W.; Parr, R. G. *Physical Review* **1988**, B 37, 785.
- Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, 157, 200.
- Perdew, J. P. *Phys. Rev.* **1986**, B33, 8822.
- Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.