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ABSTRACT

Density Functional Theory (DFT) is one of the most widely used methods for “ab initio” calculations of the structure of atoms, molecules crystal, surfaces and their interactions. In this study we have composed experimental bond distances of a set of molecules C₂H₂, C₂H₄, C₂H₆, HCN, NH₃, O₃, Li₂, H₂, H₂O HF, BH, H₂CO, and N₂H₄ obtained from electron paramagnetic resonance (EPR) spectroscopy with the corresponding bond distances of the same molecule obtained from DFT functionals, local spin density approximation LSDA, and BLYP. The accuracy of DFT functionals LSDA and BLYP is investigated via statistical analysis of the error. We have found that the bond distances of the molecules obtained from the BLYP functionals are closer to the experimentally observed bond distances in comparison of the bond distances obtained from LSDA functionals are not recommended for calculation of the bond distances of the molecules.

Keywords: *Density functional theory, electron paramagnetic resonance, bond, functional etc.*

INTRODUCTION

Density Functional Theory is presently the most successful and most promising approach [1,2] to compute the electronic structure of matter. Its applicability ranges from atoms, molecules and solid to nuclei and quantum and classical fluids. DFT predicts a great variety of molecular properties; molecular structure, vibration frequencies, atomization energies, ionization energies, electron and magnetic properties, reaction path etc. The present implementations of density function theory (DFT) [1,3] are based upon the Kohn-Sham (KS) formalism whereas recent progress in the time dependent formulation DFT [4,6] furnishes new ways of calculating properties such as polarizability, hyper polarizability, excitation energies and bond distances of the molecules. Many techniques of density functional theory, especially in the local spin density approximation (LSDA), have recently become widely available as part of major quantum chemistry program. From their first appearance in molecular electronic structure calculations, LSDA methods have been hailed as superior to traditional quantum chemical methods in various ways. They have provided molecular geometries with an accuracy better than Hartree- Fock (HF) and they are computationally cheaper than even the simplest correlated methods such as low order many body perturbation theories. The more modern methods usually employ separate functionals for exchange and correlation and use functional forms that contain the electron density as

well its gradient for either one or both parts. The second class uses a gradient correlated exchange functional (Becke) either with no correlation functional or a non-gradient corrected correlation functional (BVWN, BPL). The third and most sophisticated class uses gradient corrected functionals for both exchange and correlation (BVWN5, BLYP, BP86). Finally, there are linear combinations of exchange and correlation functional with the Hartree- Fock exchange term. Examples of this fourth type of method are the “Becke-3” exchange functionals which can be combined with the non- colal perdew (B3P86) or LYP functionals (B3LYP) [7]. The performance of different density functional theory methods in the calculations of the bond length and binding energy of the molecules and some transition metal complexes have been investigated by some scientists R. Neumann et al [8] and some Susumu et al [9] non hybrid DFT methods such as BIP or PW91 are in good agreement with the experimental values. These parameters have been calculated by several investigators by the application of this theory in the past [10-13] and have obtained very good results.

In this investigation an attempt have been made we explore the accuracy of some recent DFT functionals for predicting bond distances of the molecules [14-19]. The functionals used in this work are the local spin density approximation [20-24], BLYP. We have compared experimentally observed bond distances of

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the C₂H₂, C₂H₄, C₂H₆, HCN, NH₃, O₃, Li₂, H₂, H₂O, HF, BH, H₂CO, and N₂H₄ with DFT functionals LSDA and BLYP. This will provide us necessary information about the quality of DFT functionals LSDA and BLYP and hopefully, will permit us to treat molecules for future studies.

EXPERIMENTAL METHODS

In this investigation we have taken experimental bond distances of a set of molecule C₂H₂, C₂H₄, C₂H₆, HCN, NH₃, O₃, Li₂, H₂, H₂O, HF, BH, H₂CO, and N₂H₄, obtained from electron paramagnetic resonance (EPR) spectroscopy by R. Neumann et al [8, 25] and the same bond distances are obtained from DFT functional LSDA and BLYP. The result obtained by these functionals are then compared with the experimental values. The experimental bond distances and bond distances obtained from the DFT functionals are listed in table no.1.

RESULTS AND DISCUSSION

From the analysis of the bond distances obtained from the experimental and DFT methods listed in table-1. We have found that the percentage derivation in bond

distances obtained from Becke, 3-parameter, Lee–Yang–Parr (BLYP) functional with corresponding experimental values of the molecules are less than bond distances obtained from LSDA functionals. These are 21 bond distances of the 14 molecules listed in table out of these 21 percentage deviation in 17 bond distances are less than corresponding deviation in LSDA values. In focus cases C₂H₂ r(CC), O₃ r(OO), H₂O r(OH), and H₂CO r(CO) the deviation in the bond distances are greater than deviation in LSDA values. To get our result more clear we have plotted frequency polygon between experimental values of bond distances of the molecules and percentage deviation in bond distances obtained from the DFT functionals LSDA and BLYP. The resulting polygon are shown in Figure 1, 2 and 3. From the all figure it is very clear that LSDA bond distances have larger deviation from experimental values in comparison to BLYP bond distances. So LSDA functionals are not better to calculate bond distances of the molecules. Hence it is concluded that BLYP functionals are much better to calculate bond distances of the molecules.

Table-1 Comparison of LSDA and BLYP bond distances of molecules with experimental values

Name of the Molecule Bond and Bond S.No.	Bond S.No. and Name of bond	LSDA	BLYP	Experimental	rEx-rLSDA	rEx-rLSDA%	rEx-rBLYP	rEx-rBLYP%
1 C ₂ H ₂	1 r(CC)	1.201	1.205	1.205	0.002	0.16	-0.003	0.24
	2 r(CH)	1.024	1.067	1.067	0.049	4.6	-0.004	0.37
2 C ₂ H ₄	3 r(CC)	1.323	1.335	1.331	0.008	0.6	-0.004	0.3
	4 r(CH)	1.093	1.088	1.081	-0.012	1.1	-0.007	0.64
3 C ₂ H ₆	5 r(CC)	1.51	1.54	1.526	0.016	1.04	-0.014	0.91
4 CH ₄	6 r(CH)	1.097	1.094	1.086	-0.011	1.01	-0.008	0.73
	7 r(CH)	1.1	1.096	1.088	-0.012	1.1	-0.008	0.73
5 HCN	8 r(CN)	1.151	1.158	1.153	0.002	0.17	-0.005	0.43
	9 r(CH)	1.079	1.072	1.065	-0.014	1.31	-0.007	0.65
6 NH ₃	10 r(NH)	1.021	1.021	1.012	-0.009	0.88	-0.009	0.88
7 O ₃	11 r(OO)	1.257	1.293	1.272	0.015	1.1	-0.021	1.7
8 Li ₂	12 r(LiLi)	2.724	2.724	2.673	-0.051	1.9	-0.051	1.9

9 H ₂	13 r(HH)	0.763	0.744	0.741	-0.022	2.9	-0.003	0.4
10 H ₂ O	14 r(OH)	0.97	0.971	0.957	-0.013	1.3	-0.014	1.4
11 HF	15 r(HF)	0.932	0.933	0.917	-0.015	1.6	-0.016	1.7
12 BH	16 r(BH)	1.256	1.24	1.232	0.024	1.94	-0.008	0.64
13 H ₂ CO	17 r(CO)	1.199	1.212	1.203	0.004	0.33	-0.009	0.74
	18 r(CH)	1.121	1.114	1.102	-0.019	1.7	-0.012	1.08
14 N ₂ H ₄	19 r(NN)	1.408	1.462	1.447	0.039	2.6	-0.015	1.03
	20 r(NHb)	1.024	1.023	1	-0.016	1.58	-0.015	1.48
	21 r(NHa)	1.02	1.02	1.008	-0.012	1.2	-0.012	1.19

Deviation in LSDA Bond distances of molecules from corresponding experimental values

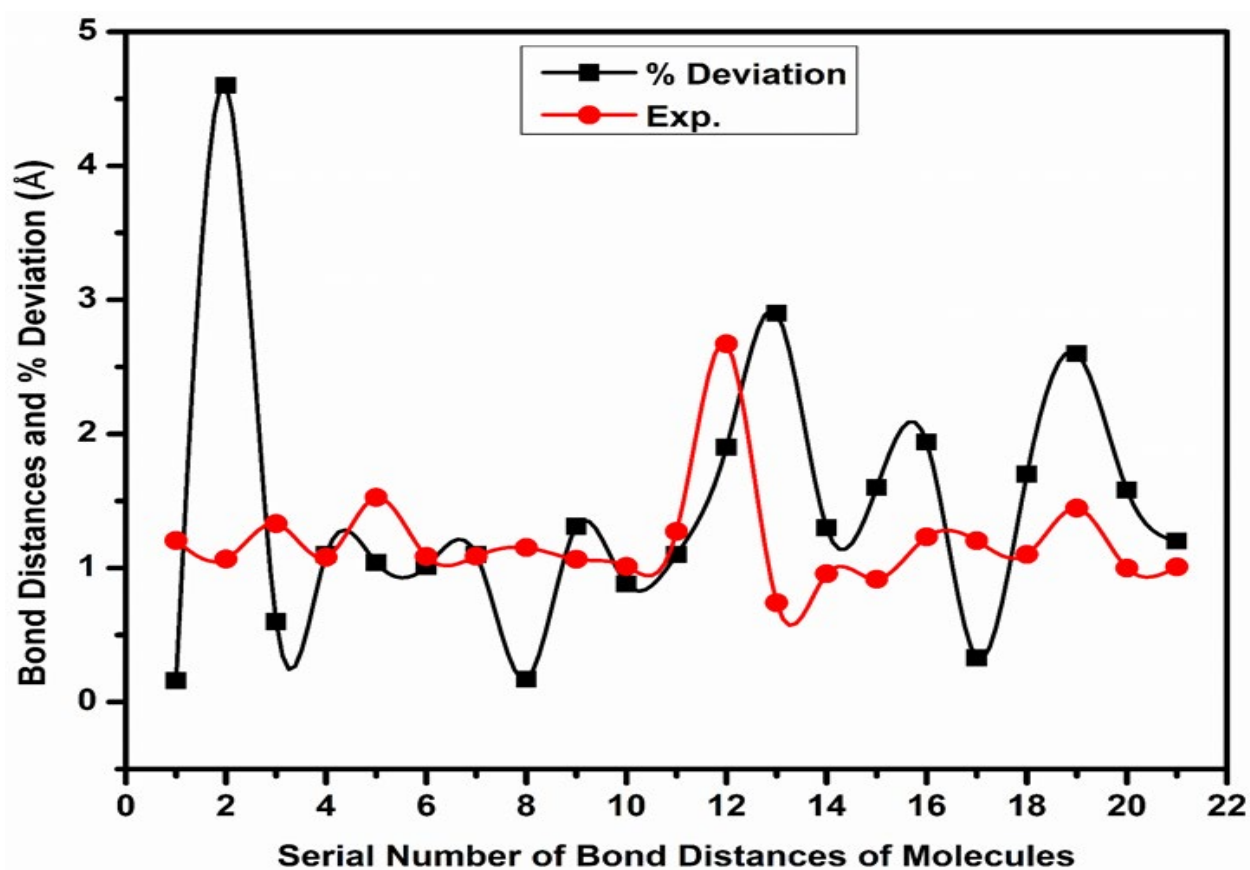


Fig. 1: Shows percentage deviation in LSDA bond distances of the molecules from corresponding experimental values.

Deviation in BLYP Bond Distances from Experimental values

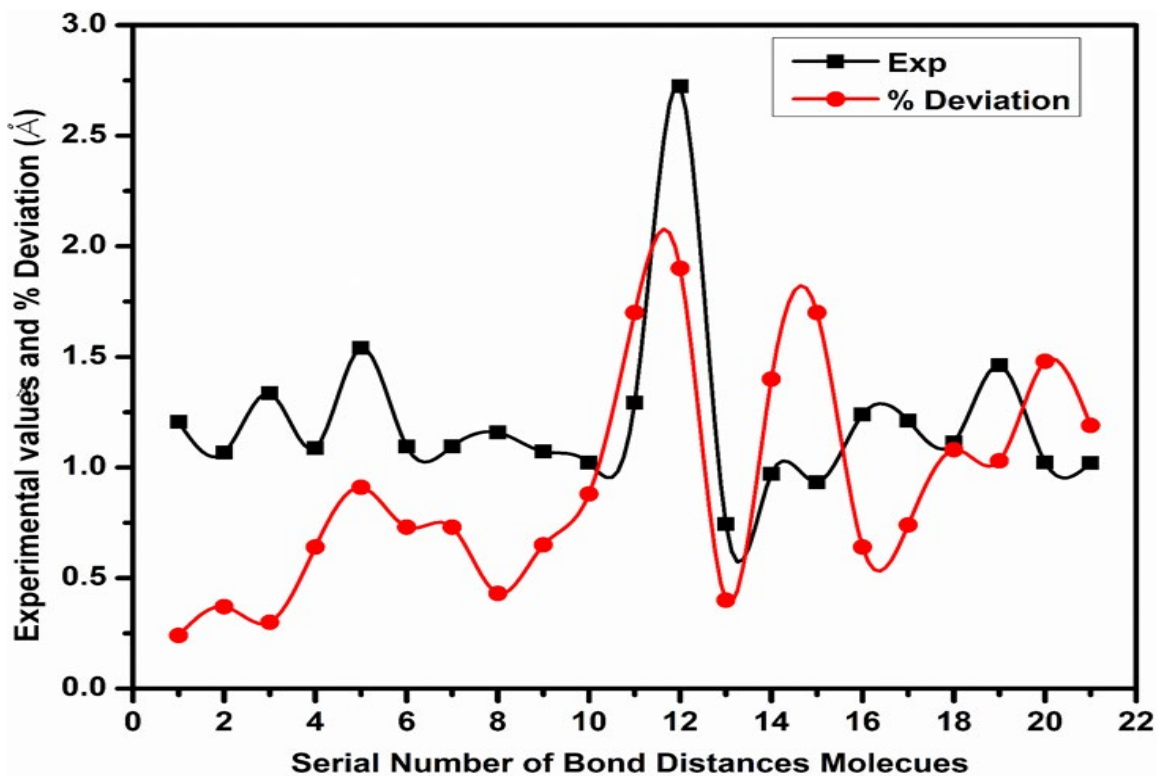


Fig. 2: Shows percentage deviation in BLYP bond distances of the molecules from corresponding experimental values.

Comparison of deviation in LSDA and BLYP bond distances from experimental values

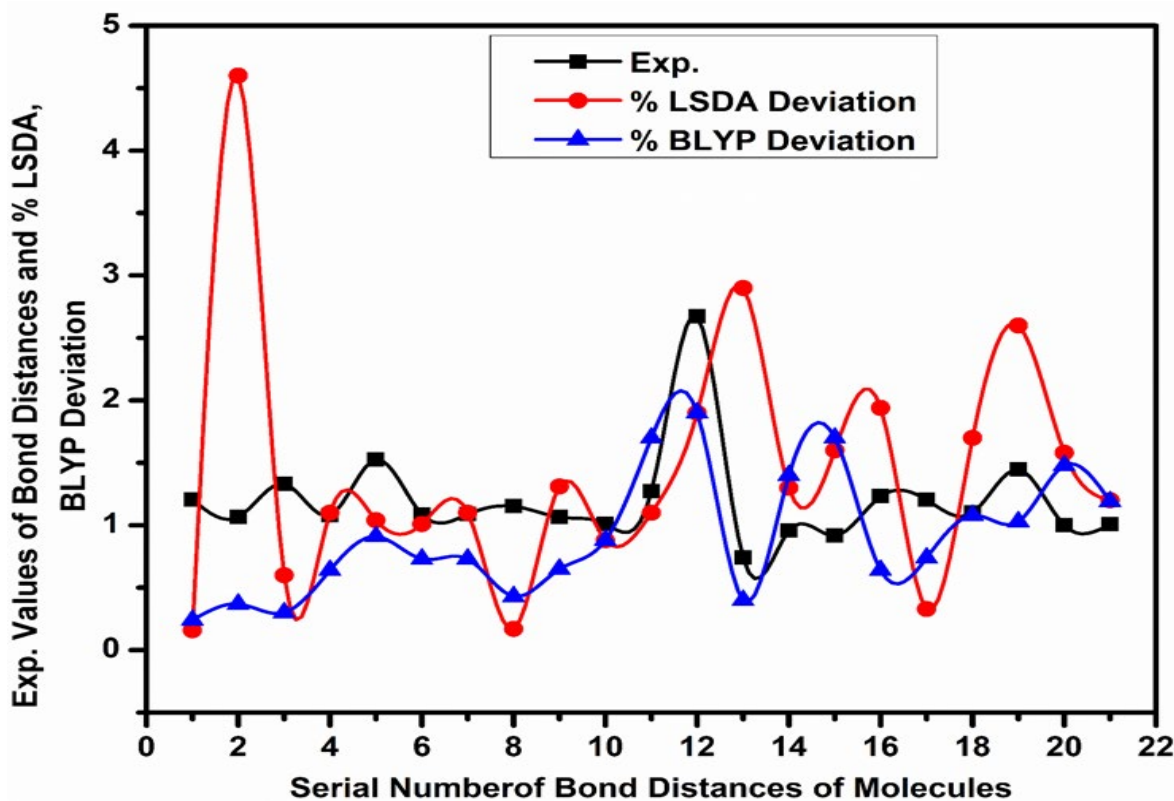


Figure 3: Shows the comparison of percentage deviation in LSDA and BLYP bond distances of the molecules from corresponding experimental values.

CONCLUSION

This work presents analysis of the bond distances

obtained from the experimental and Density Functional Theory (DFT) methods calculations of the structure of atoms, molecules crystal, surfaces and their interactions. In the present approach the experimental bond distances of a set of molecules with the corresponding bond distances of the same molecule obtained from various DFT functionals. The resulting experimental bond distance of molecules and percentage deviation in LSDA and BLYP bond

distances of the molecules were shown by different graphs for various bond distances. Density functional theory focused on experimental values of bond distances and percentage dilation bond distances of set of a set of molecules. Consequently, BLYP functionals are much better to calculate bond distances of the molecules.

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