DFT COMPUTATIONS OF EPR HYPERFINE COUPLING CONSTANTS OF SOME ISOTROPIC TRANSITION METAL COMPLEXES

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"together we can and we will make a difference"

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ABSTRACT

We had examined the performances of numerous DFT (Density Functional Theory) functional intended for the computation of EPR a special factor of hyperfine coupling constants for several 3d transition metal complexes namely [Cu(CO)3], [Ni(CO)3H] and [Mn(CO)5]. For this, BHPW91, B3LYP, B3PW91, and BPW91 functional were used and the outcome received was compared with their respective experimental values. The obtained values of Hyperfine coupling constant from different DFT were seen in the sequence of BPW91>B3LYP>B3PW91>EXP, for [Cu(CO)3], BHPW91>B3PW91>BPW91>B3LYP>EXP, for [Mn(CO)5], and BHPW91>B3PW91>B3LYP>BPW91>EXP for [Ni(CO) 3H] complex.

On the basis of our studies, we have concluded that even though the outcome received by some of the DFT functional shows similar values from various performed experiments. Still the performances of the dissimilar functional for dissimilar transition metal complexes were not found identical. The performances of the functional BHPW91 were found more superior for [Cu(CO)3], BPW91 for [Ni(CO)3H] and B3LYP for [Mn(CO)5] metal complexes.

Keywords: Density Functional Theory, Transition Metal Complexes, Hyperfine coupling, performances, Experimental values, etc.

INTRODUCTION

For exploration of molecular and electronic structure, Electron Paramagnetic Resonance phenomena are the most commonly used experimental techniques. These experiments generally in proper elucidation of records received from high resolution spectra shows novel confronts for pure and clean theoretical techniques. The new and advanced techniques is density functional theory which have an highly developed identity amongst the entire range of calculation techniques [14,15]. The estimation of the configuration of transition metal complexes has been a wide field of interest with apparent troubles not there in the parallel studies of complexes of period no. 1 and 2 [6]. Density functional theory is highly accepted by the Physics and Chemistry community due to its great achievement in study of fine exploration of molecular and electronic structures.

This proposal was introduced in the incredibly early years of quantum mechanics by means of the ground-breaking efforts of Thomas and Fermi in 1927 [12, 24] which was sustained with Slater in 1951 [28] the theorems of Hohenberg- Kohn in1964 [10]. These are considered as the actual foundation of DFT. The basics of these approaches were originated from the revolutionary efforts of Hartree and Fock in the 1920s [29]. Present DFT is based on theorems launched in 1964 by Hohenberg and Kohn [11]. The big issue of DFT is the use of correct functionals for substitute and correspondence which are not identified excluding for the free electron gas. On the other hand, many approximations also exist which allow the computation of properties of molecules at numerous stages of precision. Mainly the elementary and easiest estimation is the Local Density Approximation (LDA). In this, the force of energy is dependent only on the point of density where the functionalism is calculated (Kohn and Sham) LDA. It in real meaning says that the density at point keep up a correspondence to that of an harmonized electron gas, which verifies it to be an achievement over HF. Still, the LDA continues to be a chief workhorse in physics of solid state. Its achievement in chemistry is at peak of good reasons as it has high capacity for over binding. One of the foremost bonafide forward step was introduced with the electron of functionals originating from the alleged Generalized Gradient Approximation (GGA) which depends on both the characteristics of the electron, its density as well as its gradient. Hence, is

more capable to illustrate the inhomogeneusity of molecular densities. GGA functionals for instance BP86 [3] or PBE [24] can be executed more proficiently with better yields specially for structural parameters, and are frequently of not as much precise as for other molecular properties. The subsequently main step in the development of DFT was the beginning of hybrid functionals, that combines GGA with exact Hartree- Fock exchange [2]. Nowadays, hybrid DFT and B3LYP functional [3] is more overriding option in the study of molecules containing transition metals. This technique have beyond doubt revealed better presentation on studies of broad range of chemicals also its properties. Transition metal complexes have attained extensive importance in the area of Sciences with all its several core branches. These transition metal complexes show broad range of biological activities such as anti-tumoral [16-17,30 and 32] fungicidal [1,31] bactericidal, or antiviral [18]. These complexes are also utilized in metal investigation in various gadgets like tele-communications, optical computing, storage and information processings. Many researchers have worked hard on EPR parameters of transition metal complexes [5,19,21-23, 31-34] and have found good quality accordance with their practical results.

In this paper, we have focused on the earliest widespread valuation of DFT techniques for the calculation of constants of hyperfine coupling for $[Cu(CO)_3]$, $[Ni(CO)_3H]$ and $[Mn(CO)_5]$, 3d transition metal complexes. The outcomes of these complexes using four dissimilar density functionals BHPW91, B3LYP, B3PW91, and BPW91, EXP have been put side by side with trustworthy experimental data.

Experimental Data

Table-1 Hyperfine coupling constant: Hypothetically and experimentally calculated values for Isotropic metal complexes $[Cu(CO)_3]$, $[Ni(CO)_3H]$ and $[Mn(CO)_5]$

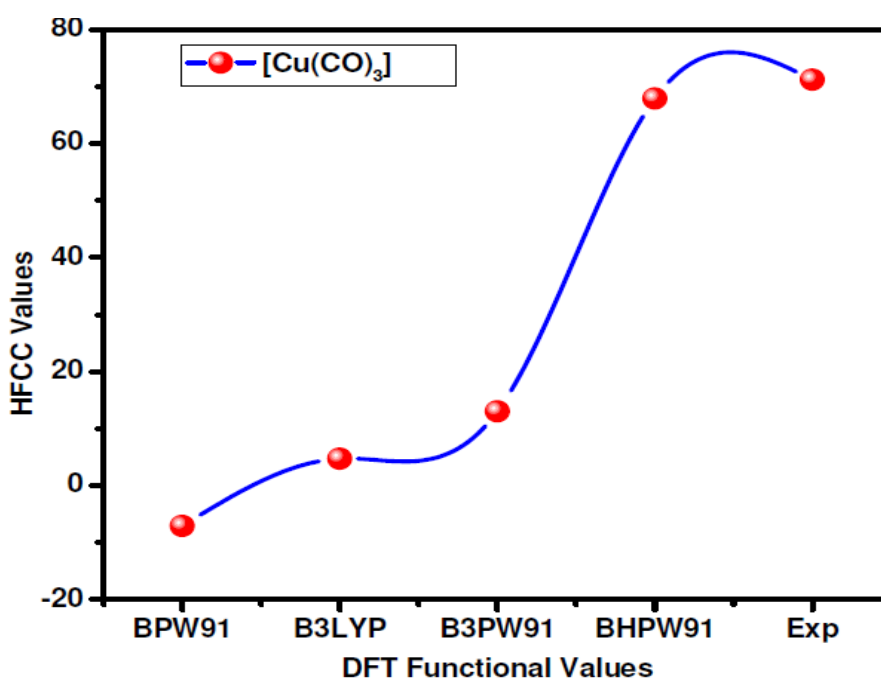| S.No.	DFT Functionals	HFCC Values of $[Mn(CO)_5]$	HFCC Values of $[Ni(CO)_3H]$	HFCC Values of $[Cu(CO)_3]$
1	BPW91	0.8	23.5	-7.1
2	B3LYP	-2.5	33.3	4.7
3	B3PW91	-12.1	33.9	13.0
4	BHPW91	-37.6	56.0	67.9
5	Exp	-2.8	9.0	71.2

Figure -1: Isotropic complex $[Cu(CO)_3]$: Values of hyperfine coupling constant A received by BPW91, B3LYP, B3PW91, and BHPW91 Density Functionals and Experiment.

Figure -2: Isotropic complex [Ni(CO)$_3$H]: Values of Hyperfine coupling constant A received by BPW91, B3LYP, B3PW91, and BHPW91 Density Functionals and Experiment.

Figure -3: sotropic metal [Mn(CO)$_5$]: Values of hyperfine coupling constant A received by BPW91, B3LYP, B3PW91, and BHPW91 Density Functionals and Experiment.

Results and discussion
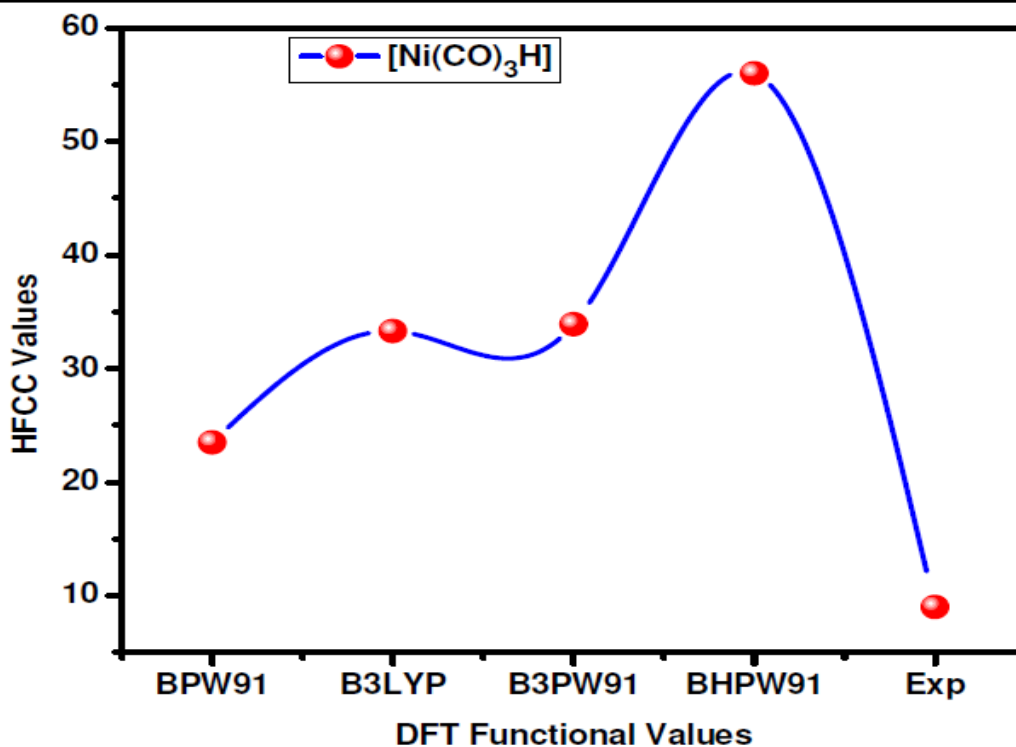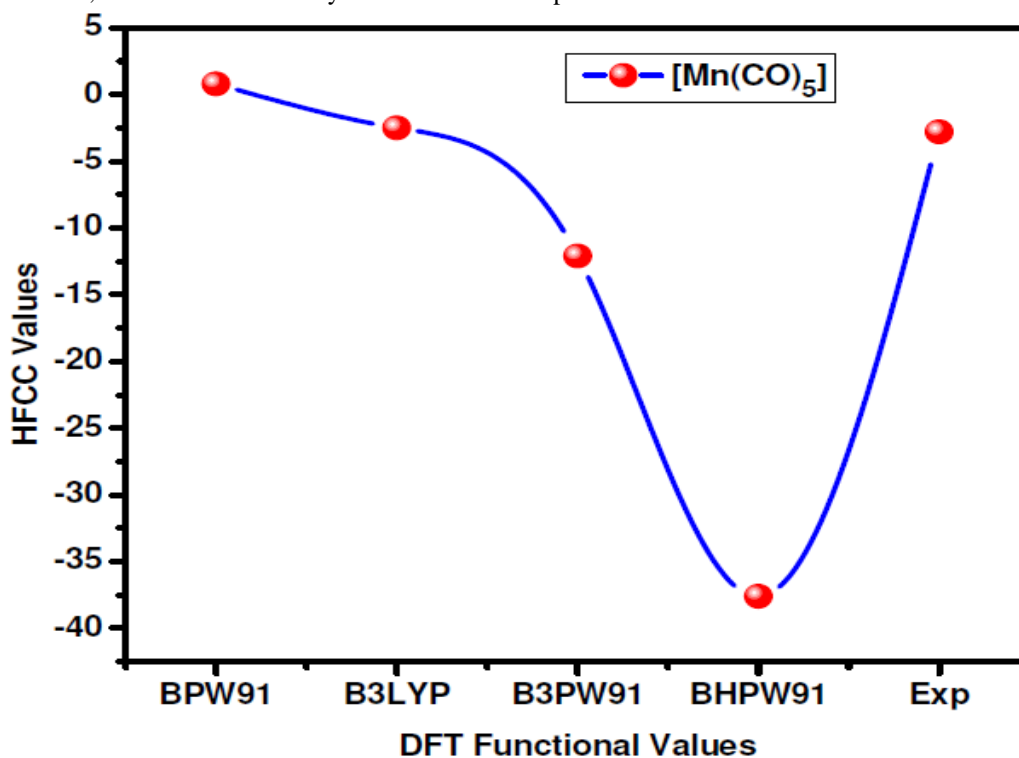
The outcome of the EPR parameter hyperfine coupling constant A of several transition metal complexes measured for the DFT computation attained from different density functionals **BPW91,** **B3LYP, B3PW91, BHPW91** and Experiments are the shown in Table-1. The values of Hyperfine coupling constant A received from dissimilar DFT functionals of several transitional metal compounds can also be visualized in Figures 1,2, and 3. The conclusion

obtained by the dissimilar density functional are compared with their performed practical or experimental values which can be seen in the Figures 1, 2, 3 and Table-1. After the comparison of hyperfine coupling constant of dissimilar Density Functional with obtained experimental values of the complexes determined in this research article, the performances of dissimilar Density Functionals are established as follows.

Isotropic Metal [Cu(CO)$_3$]
Results- BPW91>B3LYP>B3PW91>EXP
Isotropic Metal [Ni(CO)$_3$H]
BHPW91>B3PW91>B3LYP>BPW91>EXP
Isotropic Metal [Mn(CO)$_5$]
BHPW91>B3PW91>BPW91>B3LYP>EXP

RESULTS

The study of the Table-1 and Figure-1 illustrates that the outcomes of the hyperfine coupling constant of Isotropic Metal [Cu(CO)$_3$] complex, received by BHPW91 functional is in near accordance with the experimentally observed data. The presentation of this Density Functional is of high quality and hence can be used to calculate hyperfine coupling. Also, the performance of BPW91 functional was found deprived.

From the Table-1 and Figure -2, we have concluded that hyperfine coupling constant value of Isotropic Metal complex [Ni(CO)$_3$H] obtained by BPW91 Functional is found superior to the another functional but is in close accordance with its experimental outcomes. The performance of this functional is found fine and hence is advised to

calculate hyperfine coupling constant value of this complex but the performance of BHPW91, functional is not up to grade. so this functional cannot be used for hyperfine coupling constant calculations.

From the data obtained of Table-1 and Figure -3, it is proved that in case of Isotropic Metal complex [Mn(CO)$_5$], the outcomes of the hyperfine coupling constant by B3LYP functional is in close accordance with the experimental outcome and hence this functional can be used to analyze hyperfine coupling constant of Isotropic Metal complex [Mn(CO)$_5$]. The further study concludes, that the hyperfine coupling constant values received from the BHPW91 functional is large in assessment to experimental result and hence the performance of this functional is found very deprived for this complex and should not be used for the computation of its Hyperfine coupling constant.

CONCLUSION

The conclusion obtained from our studies is that the DFT values of hyperfine coupling constants acquired from dissimilar density functional are observed in near accordance with their experimentally observed data. The enhanced presentation of the dissimilar Functional have been found dissimilar in several studied metal complexes. We had not recognized any such in this study. The theoretical results obtained for hyperfine coupling constant values received in this study suggests with the purpose of more requirement of improvement in Density Functionals for better and precise structural parameters.

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