

**IJCRR**

Vol 04 issue 19

Section: General

Science

Category: Research

Received on: 16/07/12

Revised on: 02/08/12

Accepted on: 14/08/12

**CALCULATIONS OF EPR PARAMETER HYPERFINE  
COUPLING CONSTANTS OF SOME DIPOLAR METAL  
COMPLEXES USING DENSITY FUNCTIONAL METHODS**Vinita Prajapati<sup>1</sup>, P.L.Verma<sup>2</sup><sup>1</sup>Department of Chemistry, Govt. L. B. S. College Sironj Distt. Vidisha, M.P., India<sup>2</sup>Department of Physics, Govt. Vivekanand P.G. College Maihar Satna, M.P., India

E-mail of Corresponding Author: vinitap86@gmail.com

**ABSTRACT**

Calculations of the EPR spectral parameter hyperfine coupling constants of Dipolar Metal Complexes [Co (CO)<sub>4</sub>], [Mn(CN)<sub>5</sub>NO]<sup>2-</sup>, [Mn(CN)<sub>4</sub>N]<sup>-</sup>, [Ni(CO)<sub>3</sub>H] have been carried out using density functional theory (DFT) with BHPW91, B3LYP, B3PW91, BLYP, BHLYP, BPW91, BP86, BHP86 functionals and the results obtained have been compared with experimental values. The results obtained from the density functional methods have been found in close agreement with the result obtained from the experiments. The performances of the different functionals for different transition metal complexes have been found different. The performance of the functional BP86 have been found better for [Ni(CO)<sub>3</sub>H], [Mn(CN)<sub>5</sub>NO]<sup>2-</sup> BHLYP for [Co (CO)<sub>4</sub>] and B3LYP for [Mn(CN)<sub>4</sub>N]<sup>-</sup> Dipolar Metal Complexes. We have not identified any such functional, the performance of which is excellent for calculation of EPR parameter hyperfine coupling constant for all transition metal complexes considered in this study.

**Keywords** – Density Functional Theory (DFT). Transition Metal Complexes, Hyperfine Coupling Constants.

**INTRODUCTION**

In view of that, accurate quantum-chemical calculations of EPR parameters of transition metal complexes are of considerable importance in the prediction and analysis of EPR spectra [10]. Hyperfine coupling (HFC) and g-tensors provide a large part of the information of an EPR spectrum and are regarded as sensitive probes of the spin-density distribution in molecules [14], Spin density, in contrast to the electron density, is the density of unpaired electrons and can therefore possess negative or positive values. EPR spectroscopy has often been used to estimate the spin distribution from experimental data. In contrast, density functional calculations provide independent access to spin-density distributions. They therefore are particularly valuable tools for

investigating the electronic structure. Density functional theory (DFT) currently offers the only practical approach to reasonably accurate calculations of hyperfine tensors in transition metal systems. Recent systematic studies of both g-tensors and hyperfine tensors of transition metal complexes have shown that density functional theory (DFT) provides a useful basis for the calculation of both however, such computations still seem to be particularly difficult for transition metal complexes and usually do not achieve the precision which is found for organic main group radicals. For transition metal complexes a rather pronounced dependence of the results on the exchange-correlation functional is found. For example, gradient-corrected or local functionals

underestimate core-shell spin polarization at the metal, which is important in the calculation of isotropic metal hyperfine coupling constants (HFCC) [11, 12]. In particular, the isotropic hyperfine couplings are frequently difficult to calculate, due to the need to describe accurately the important core-shell spin polarization without introducing spin contamination due to exaggerated valence-shell spin polarization. The second problem to be dealt with are relativistic effects on the HFC tensors, including both scalar (spin free) relativistic (SR) and spin-orbit (SO) effects. These are known to influence the HFC results even for 3d and 4d transition metal complexes appreciably [16] and they have to be considered for quantitative evaluation. Density functional theory is an extremely successful approach for the description of ground state properties of metals, semiconductors, and insulators. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes. The basic idea behind DFT is to use the electron density rather than the quantum mechanical wave function to obtain information about atomic and molecular systems. While this idea came up in the very first years of quantum mechanics with the pioneering work of Thomas and Fermi in 1927 [11,] and was continued with Slater in 1951 [19] the Hohenberg-Kohn theorems from 1964 [4] are regarded as the real beginning of DFT. The most fundamental of these approaches originates from the pioneering work of Hartree and Fock in the 1920s [20]. Modern DFT rests on two theorems by Hohenberg and Kohn (1964) [16]. The major problem of DFT: the exact functional for exchange and correlation are not known except for the free electron gas. However, many approximations exist which permit the calculation of molecular properties at various levels of accuracy. The most fundamental and simplest approximation is the local-density

approximation (LDA), in which the energy depends only on the density at the point where the functional is evaluated (Kohn and Sham) [8]. LDA, which in essence assumes that the density corresponds to that of inhomogeneous electron gas, proved to be an improvement over HF. While LDA remains a major workhorse in solid state physics, its success in chemistry is at best moderate due to its strong tendency for over binding. The first real breakthrough came with the creation of functionals belonging to the so-called generalized gradient approximation (GGA) that incorporates dependence not only on the electron density but also on its gradient, thus being able to better describe the inhomogeneous nature of molecular densities. GGA functionals such as BP86 [1]) or PBE [17] can be implemented efficiently and yield good results, particularly for structural parameters, but are often less accurate for other properties. The next major step in the development of DFT was the introduction of hybrid functionals, which mix GGA with exact Hartree-Fock exchange. Now days, hybrid DFT with the use of the B3LYP functional is the dominant choice for the treatment of transition metal containing molecules. This method has shown good performance for a truly wide variety of chemical systems and properties.

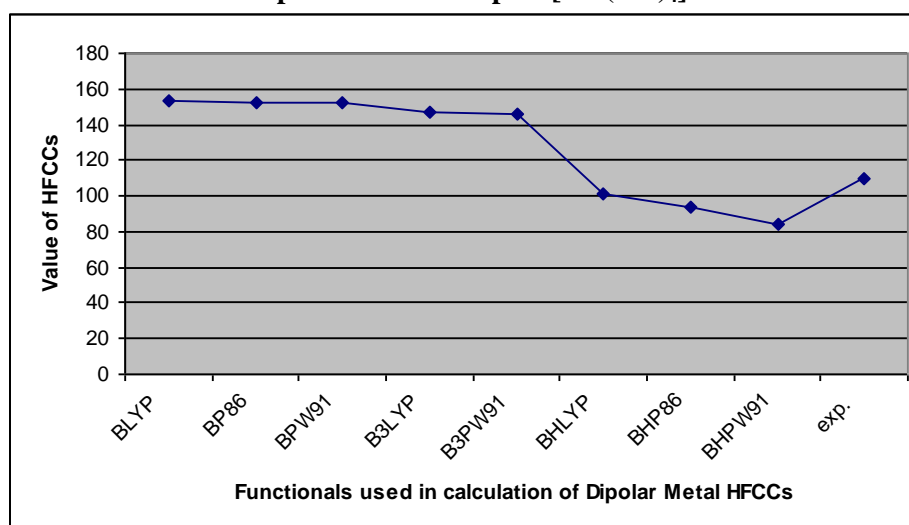
Several investigators have studied EPR parameters hyperfine coupling constant and g tensors using different density functional [2, 3, 6, 7, 13, 15, 18,21] and have been found close agreement with experimental results.

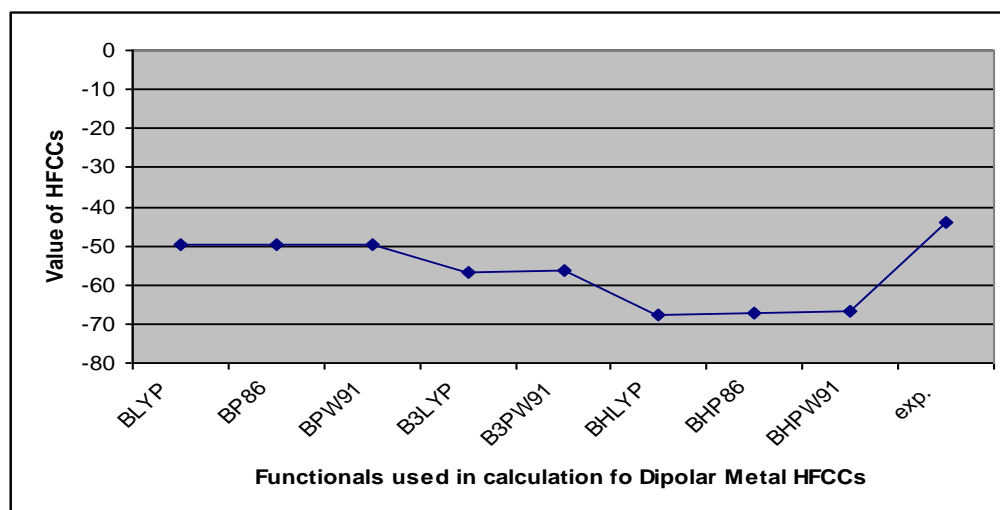
In this investigation we have applied several density functional to calculate EPR parameter hyperfine coupling constants for Dipolar Metal Complexes  $[\text{Co}(\text{CO})_4]$ ,  $[\text{Mn}(\text{CN})_5\text{NO}]^{2-}$ ,  $[\text{Mn}(\text{CN})_4\text{N}]$ ,  $[\text{Ni}(\text{CO})_3\text{H}]$  using Density Functional Theory. For these calculations, BHPW91, BHLYP, B3LYP, B3PW91, BLYP, BPW91, BP86, BHP86 functional have been used.

## DATA AND ANALYSIS

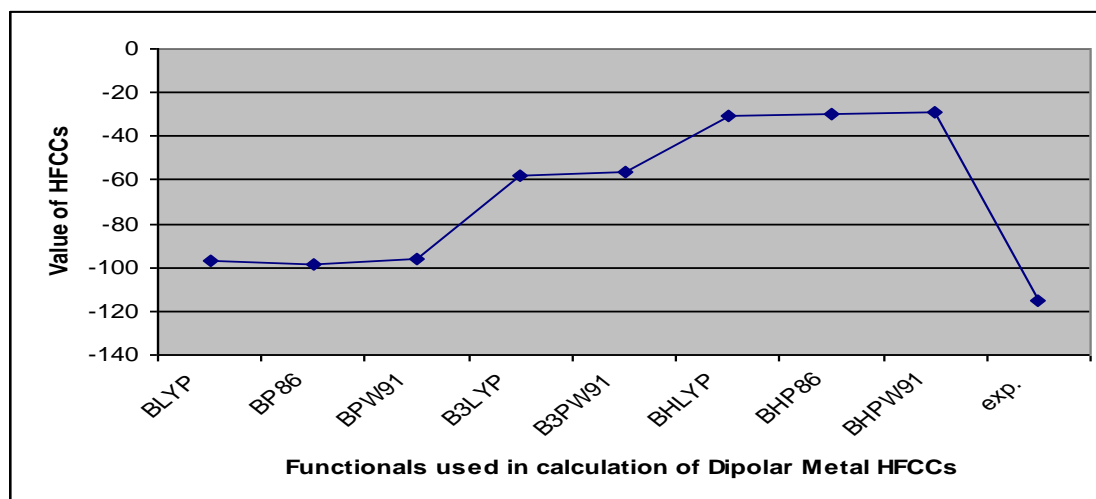
**TABLE 1.0-Theoretically Calculated and Experimentally observed Hyperfine Coupling Constant values for Dipolar metal complexes [Co(CO)<sub>4</sub>], [Ni(CO)<sub>3</sub>H], [Mn(CN)<sub>5</sub>NO]<sup>2-</sup> and [Mn(CN)<sub>4</sub>N]<sup>-</sup>**

Molecule	BLYP	BP86	BPW91	B3LYP	B3PW91	BHLYP	BHP86	BHPW91	exp.
[Co(CO) <sub>4</sub> ]	153.6	152.4	151.8	147.4	146.2	101.2	93.6	84.5	110.0
[Ni(CO) <sub>3</sub> H]	-49.8	-49.6	-49.6	-56.9	-56.5	-67.8	-67.2	-66.8	-44.0(2)
[Mn(CN) <sub>5</sub> NO] <sup>2-</sup>	-97.3	-98.2	-96.2	-58.1	-56.0	-30.3	-30.2	-29.0	-115.2
[Mn(CN) <sub>4</sub> N] <sup>-</sup>	-116.2	-115.2	-115.1	-117.2	-115.6	-88.5	-88.7	-89.2	-122.4

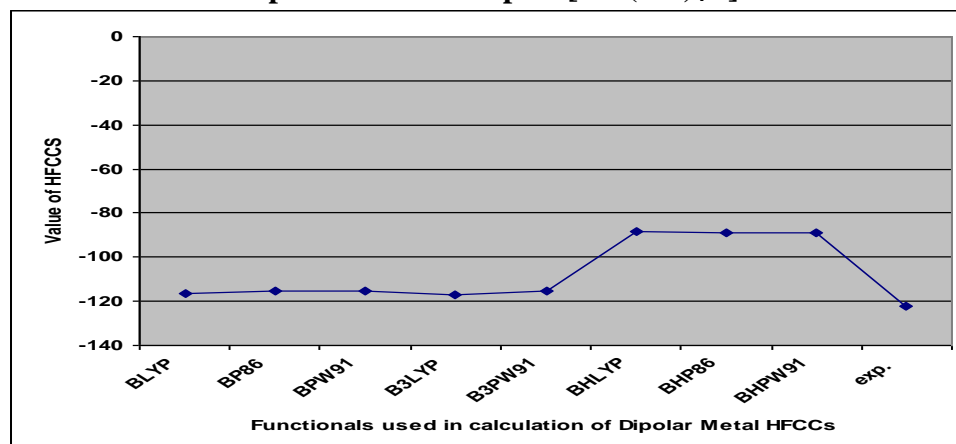
**Dipolar Metal Complex [Co (CO)<sub>4</sub>]****Figure 1.0-** Shows hyperfine coupling constant A values obtained from BLYP, BP86, BPW91, B3LYP, B3PW91, BHLYP, BHP86, BHPW91, density functionals and experiment for Dipolar Metal Complex [Co(CO)<sub>4</sub>]

**Dipolar Metal Complex [Ni(CO)<sub>3</sub>H]**

**Figure 2.0-** Shows hyperfine coupling constant A values obtained from BLYP, BP86, BPW91, B3LYP, B3PW91, BHLYP, BHP86, BHPW91, density functionals and experiment for Dipolar Metal Complex [Ni(CO)<sub>3</sub>H]

**Dipolar Metal Complex [Mn(CN)<sub>5</sub>NO]<sup>2-</sup>**

**Figure 3.0-** Shows hyperfine coupling constant A values obtained from BLYP, BP86, BPW91, B3LYP, B3PW91, BHLYP, BHP86, BHPW91, from density functionals and experiment for Dipolar Metal Complex [Mn(CN)<sub>5</sub>NO]<sup>2-</sup>

**Dipolar Metal Complex  $[\text{Mn}(\text{CN})_4\text{N}]^-$** 

**Figure 4.0-** Shows hyperfine coupling constant A values obtained from BLYP, BP86, BPW91, B3LYP, B3PW91, BHLYP, BHP86, BHPW91, from density functionals and experiment for Dipolar Metal Complex  $[\text{Mn}(\text{CN})_4\text{N}]^-$

**RESULTS**

The results of the EPR parameter hyperfine coupling constant of different transition metal complexes considered for the DFT calculation in this work, obtained by the application of different density functional BLYP, BP86, BPW91, B3LYP, B3PW91, BHLYP, BHP86, BHPW91, EXP are listed in table No-1. The hyperfine coupling constant values obtained from different DFT functional of different complexes are also shown in Figure 1, 2, 3 and 4 also. From the comparison of DFT value with experimentally observed values the performance of different functional for different complexes have been found as follows.

**1-Dipolar Metal Complex  $[\text{Co}(\text{CO})_4]$** 

**Results** - BLYP > BP86 > BPW91 > B3LYP > B3PW91 > BHPW91 > BHP86 > BHLYP > EXP.

**2-Dipolar Metal  $[\text{Ni}(\text{CO})_3\text{H}]$** 

**Results** - BHLYP > BHP86 > BHPW91 > B3LYP > B3PW91 > BLYP > BPW91 > BP86 > EXP.

**3-Dipolar Metal Complex  $[\text{Mn}(\text{CN})_5\text{NO}]^{2-}$** 

**Results**- BHPW91 > BHP86 > BHLYP > B3PW91 > B3LYP > BPW91 > BLYP > BP86 > EXP

**4-Dipolar Metal  $[\text{Mn}(\text{CN})_4\text{N}]^-$** 

**Results** - BHLYP > BHP86 > BHPW91 > B3PW91 > BP86 > BPW91 > BLYP > B3LYP > EXP.

The results obtained from Table 1 and Figure 1, we have inferred that BHLYP functional is better for Dipolar Metal Complex  $[\text{Co}(\text{CO})_4]$ . Further analysis shows that the performance of BLYP is poor for Dipolar Metal Complex  $[\text{Co}(\text{CO})_4]$ . These results suggesting that BHLYP functional may be used to calculate hyperfine coupling constant of Dipolar Metal Complex  $[\text{Co}(\text{CO})_4]$ . DFT results of Dipolar Metal Complex  $[\text{Ni}(\text{CO})_3\text{H}]$  obtained from the analysis of Table 1 and Figure 2, we have observed that the performance of BP86 functional is good for but the performance of BHLYP functional very poor. This result suggesting that BP86 functional may be used to calculate hyperfine coupling constant of Dipolar Metal Complex  $[\text{Ni}(\text{CO})_3\text{H}]$ . From the further analysis of Table and Figure 3, it is concluded that BP86 functional is best for the calculation of HFCC of Dipolar Metal Complex  $[\text{Mn}(\text{CN})_5\text{NO}]^{2-}$  but BHPW91 function is very poor. From the further analysis of table and figure 4, it is inferred that B3LYP functional is best for the calculation of HFCC of Dipolar Metal

Complex  $[\text{Mn}(\text{CN})_4\text{N}]^-$  but B3LYP function is very poor .

## CONCLUSION

From these results it is inferred that although the results of the density functional studies for hyperfine coupling constants A have been found in close agreement with the experimental results but the better performance of the functionals have been found different for different metal complexes. In our study we have obtained DFT functional B3LYP functional is better for Dipolar Metal Complex  $[\text{Co}(\text{CO})_4]$  , BP86 is better for Dipolar Metal  $[\text{Ni}(\text{CO})_3\text{H}]$  ,B3LYP and Dipolar Metal Complex  $[\text{Mn}(\text{CN})_5\text{NO}]^{2-}$  and B3LYP functional is better for the calculation of HFCC of Dipolar Metal Complex  $[\text{Mn}(\text{CN})_4\text{N}]^-$  .We have not identified any such functional, the results of which is excellent for all transition metal complexes considered for study in this work. From these results it is concluded that further studies is needed for development of density functional theory to search such functional which may be applicable for the majority of the complexes for calculation of EPR parameter, hyperfine coupling constant.

## ACKNOWLEDGMENT

The authors acknowledge the immense help received from the research scholars and scientists whose articles are cited and included in references of this manuscript. The authors are also grateful to authors/editors/publishers of all those articles, journals and books from where the literature for this article has been reviewed and discussed. The authors would like to thank Dr .R.N Patel, Prof.K.B.Ponday and Dr.H.Surya Prakash.Rao for valuable suggestions.

## REFERENCES

1. Becke AD Phys Rev A: 38, 3098, 1988.
2. Christian Remenyi, Markéta L. Munzarová, and Martin Kaupp J. Phys. Chem. B: 109 (9), 4227, 2005.
3. Dalmázio, Ilza; Anderon Duarte, Hélio J .Chem. Phys: 115, 1747, 2001.
4. Hohenberg, P. W. Kohn, Phys. Rev: 136, B864. 1964.
5. Hohenberg P, Kohn W Inhomogeneous electron gas. Phys Rev B :136,864, 1964.
6. Jorg Fritscher, Peter Hrobárik, and Martin Kaupp J. Phys. Chem. B: 111 (17), 4616, 2007.
7. Kaupp. Martin ; R. Roman ; M. Olga A. Alexei ; S. Bernd ; M .Vladimir G. ; Inc. J Comput Chem :23,794, 2002.
8. Kohn W, Sham LJ Phys Rev A :140,1133, 1965b.
9. Kaupp, M, Bühl, M. Malkin, V. G. Calculation of NMR and EPR Parameters: Theory and Applications, Wiley-VCH, Weinheim, 2004.
10. Kawamoto. T. B. S. Hammes. R. Ostrander. A. L. Rheingold and A. S. Borovik Inorg.Chem: 32, 3424, 1998.
11. Munzarova, M. Kaupp, M. J. Phys. Chem. A: 103, 9966, 1999.
12. Munzarova, M. L. Kubacek, P. Kaupp, M. J. Am. Chem. Soc: 122, 11900, 2000.
13. Markéta L. Munzarová and Martin Kaupp A J. Phys. Chem. B: 105 (50), 12644, 2001.
14. Mabbs, F. E. Collison, D. Electron Paramagnetic Resonance of d Transition Metal Compounds, Elsevier, Amsterdam, 1992.
15. Munzarova, M. L. Kubacek, P. Kaupp, M. J. Am. Chem. Soc: 122, 11900, 2000.
16. Neese, F. J. Chem. Phys: 118, 3939, 2003.
17. Perdew JP, Burke K, Ernzerhof M Phys Rev Lett: 77:3865, 1996.
18. Prajapati Vinita and Verma P.L. Acta Scientia India: 37, 3,295,295.
19. Slater, J. C. Phys. Rev: 81, 385. 1951.
20. Szabo A, Ostlund NS Modern quantum chemistry. McGraw-Hill, New 1989.
21. Verma P.L. and Prajapati Vinita, Acta Scientia India :37,3, 287,2011.