
Chapter 5

Performance of the Widely Used Minnesota Density Functionals for the Prediction of Heat of Formations, Ionization Potentials of Some Benchmarked First Row Transition Metal Complexes

We have computed and investigated the performance of Minnesota density functionals especially the M05, M06 and M08 suite of complementary density functionals for the prediction of the heat of formations (HOFs) and the ionisation potentials (IPs) of various benchmark complexes containing nine different first row transition metals. The eight functionals of M0X family, viz. the M05, M05-2X, M06-L, M06, M06-2X, M06-HF, M08-SO and M08-HX are taken for the computation of the above mentioned physical properties of such metal complexes along with popular Los Alamos National Laboratory 2 double- ζ (LANL2DZ) basis set. Total 54 benchmark systems are taken for HOF calculation, whereas the 47 systems among these benchmark complexes are chosen for the calculation of IPs due to lack of experimental results on rest of the 7 systems. The computed values of HOFs and IPs are compared with the experimental results obtained from the literature. The deviation of these computed values from the actual experimental results is calculated for each eight different M0X functionals to judge their performances in evaluating these properties. Finally, a clear relationship between the exchange correlation energy of eight M0X functionals and their efficiency are made to predict the different physical properties.

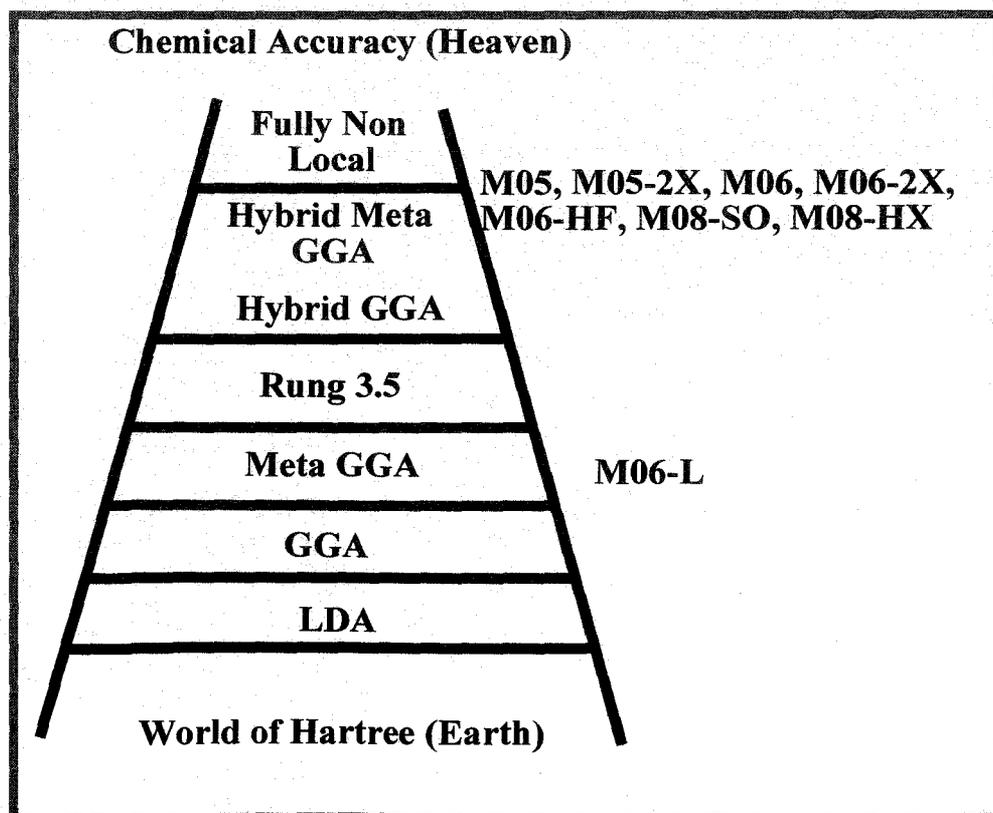
5.1 Introduction

The performance to cost ratio advantage makes Kohn-Sham density functional theory (KS-DFT), one of the most accepted tools to the researchers of theoretical and computational chemistry. Lots have been said and published about DFT in the last two decades.¹ A simple Google search about DFT fetches 16,600,000 wave pages just in 0.15 second where much of the content is about theory, methodical developments, applications and so on. The DFT is a powerful methodology for chemical simulation where the energy of the systems can be defined in terms of its electron probability density (ρ), that is, in DFT formalism the electronic energy E is treated as the functional of the electron density $E(\rho)$. Further, the simplicity of the DFT based methods over *ab initio* methods can be best understood by considering a system having n electrons. In such systems the wavefunctions have 3 coordinates for each electron and there must be one extra coordinate if spin is taken into consideration. However, the electron density actually depends on the 3 coordinates and is independent of the number of total electrons of the system. As a matter of fact, if complexity in the wavefunction is increased for the large systems the electron density keeps up the same number of variables, irrespective of the size of the system.²

Today, one can find different functionals which are developed by manipulating the different values of exchange and correlation contributions. However, Perdew and Schmidt³ have successfully represented their vision on the progress of DFT functionals in the form of Jacob's ladder, the famous allusion from the book of *Genesis* (28, 10-12), in a DFT symposium in Menton, France. The ladder has five different rungs depicting the five different generations of DFT functionals (Scheme 5.1). One gets local density approximation (LDA) in the first rung, generalized gradient approximation (GGA) stands in the second rung, meta generalized gradient approximation (M-GGA) remains in the third rung, whereas the hybrid generalized gradient approximation (H-GGA) and hybrid meta generalized gradient approximation (HM-GGA) stand in the fourth rung and the fully nonlocal approximation remains in the last rung when moving from the lower to the higher steps in the Jacob's ladder. One should note that, the HM-GGA functional is the

combination of GGA, M-GGA and H-GGA functionals. If one climbs up with the ladder one needs to assume more and more sophisticated and complicated approximation and eventually reach the heaven of chemical accuracy. A point to be mentioned here is that, each rung has its own drawbacks and advantages. Although the better rung gives better results than its lower one, however, the choice of functionals somehow depends on the nature of the problems. All the above mentioned discussions are nicely portrayed in an elaborate review of Ramos et al.⁴ Another point to be mentioned here is that a new class of rung on the Jacob's ladder called "rung 3.5" which is an intermediate between the local and hybrid functionals is implemented by Janesko.⁵ The rung 3.5 has the potential to produce more accurate results than the local and semilocal functionals.

Scheme 5.1 The vision of Perdew for Jacob's ladder of five generation DFT functionals from the world of Hartree to the heaven of chemical accuracy, with the indication of most popular eight different M0X density functionals.



After, early 1990s with the appearance of Becke 3 parameter exchange and Lee, Yang, Parr correlation functional (B3LYP),⁶ the computational treatment has multiplied the wide possibilities of this field of research. The most admired and robust exchange correlation functional B3LYP having 20% exact exchange assorted with exact GGA functional gives excellent results in myriad studies. However, in predicting the energy barriers, weak intramolecular interactions, and bonding in transition metals (TMs), B3LYP has faced some serious drawbacks. The hybrid B3LYP functional has failed to predict properties of different extended systems than other hybrid functionals. Even in the prediction of atomization energies the semiempirical B3PW98 functional has shown improved performance compared to the hybrid B3LYP functional.⁷ As a result, past decade has witnessed the development and validation of different exchange correlation functionals by various research groups in order to surmount these pitfalls. A notable point is that, the choice of functionals depends on the problem in hand, that is, on the nature of the systems, property of the systems, and obviously on the computational cost and accessibility of these functionals. Zhao and Truhlar⁸ have presented and parameterized new suite of functionals with flourishing performances. To carry out both for TMs and main group chemistries they have proposed Minnesota 2005 hybrid meta GGA exchange correlation functional, the M05 functional,⁹ with 28% exact exchange (χ) which reduces the self interaction error (SIE) and the self correlation error (SCE) from the calculations. In the next year, M05-2X¹⁰ functional has been developed in which they have doubled the exact exchange ($\chi=56\%$) contribution while trimming down the SIE. In 2006, with the next attempt they have developed two other functionals, the non-hybrid meta GGA, the M06-L¹¹ functional with $\chi=0\%$ and the hybrid meta GGA M06-HF functional¹² having $\chi=100\%$. Being a local functional M06-L can be applied for large systems with low costs. The M06-L functional is also very suitable for TM systems. The M06-HF functional is constructed as a variant of M06-L having full Hartree Fock exchange which completely takes out SIE from the functional, although due to the multireference character it is generally recommended for main group elements. After designing M06-L and M06-HF they have redesigned and reoptimized M05 to get M06¹³ with $\chi=27\%$ instead of $\chi=28\%$ in M05. After that, they have developed the M06-2X functional¹¹ in doubling the amount of exact exchange correlation ($\chi=54\%$), as in M06. In

2008 they have further developed two improved versions of M06-2X namely Minnesota 2008 high X represented as M08-HX and Minnesota 2008 second order designated as M08-SO, both having fractional HF exchange viz. $\chi=52.23\%$ and 56.79% respectively. In M08-HX functional the 'X' is the usual HF exchange, and in M08-SO the 'SO' denotes second order gradient expansion. These two functionals are mainly parameterized for the main group thermo chemistry, kinetics and non-covalent interactions. Nonetheless, the execution of M08-HX functional in the calculation of main group thermochemistry, non-covalent interactions and kinetics is slightly better than the other two functionals viz. M08-SO and M06-2X functionals and considerably better than M05-2X functional as advocated by the developers.¹⁴ One can consider that, the M05 and the M05-2X functionals are the earlier version of M06 and M06-2X functionals, whereas, the M08-HX and M08-SO are regarded as two improved future versions of the M06-2X functionals. The readership may note that, in paper after paper, the poor performances of the M05-2X,^{8,10} M06-2X,^{8,10} M06-HF,^{8,12} M08-SO¹⁴ and M08-HX¹⁴ functionals in predicting the thermochemical parameters in TM systems are advocated by Zhao and Truhlar. The eight different M0X functionals, their year of invention, their type according to Perdew ladder and the percentage of HF exchange are depicted in Table 5.1. It is to be noted here that, except non hybrid meta GGA functional M06-L which resides in the third rung of Jacob's ladder, all other above mentioned functionals are HM-GGA functionals and correspond to the fourth rung of Jacob's ladder (Scheme 5.1) as proposed by Perdew et al.³

In different literatures Merz and co-workers¹⁵ have studied lots of TM- complexes with different DFT functionals from GGA to HMGGA (excluding LSDA) as DFT is not a single method rather a family of methods.³ The accuracy in predicting exchange coupling constants through M0X suite of functionals has been studied by Ruiz.¹⁶ The application and validation of Minnesota density functionals highlighting nanochemistry, organic, inorganic, biological and medicinal chemistry, catalysis etc. have been illustratively reviewed by Zhao and Truhlar.⁸

Table 5.1 The eight M0X suite of functionals, their year of invention, type and percentage of Hartree-Fock (HF) exchange which are used in this work are depicted below.

| Functionals | Year of invention | Type | Percent of HF exchange (χ) |
|-------------|-------------------|-------|-----------------------------------|
| M05 | 2005 | HMGGA | 28 |
| M05-2X | 2006 | HMGGA | 56 |
| M06-L | 2006 | MGGA | 0 |
| M06 | 2008 | HMGGA | 27 |
| M06-2X | 2008 | HMGGA | 54 |
| M06-HF | 2006 | HMGGA | 100 |
| M08-SO | 2008 | HMGGA | 56.79 |
| M08-HX | 2008 | HMGGA | 52.23 |

Ionisation potential (IP) is a significant property of a molecule or atom from which one can assess the firmness by which an electron is bound with the system and therefore it is a descriptor of stability and reactivity of that substance. On the other hand, the heat of formation (HOF) is the enthalpy change due to the formation of one mole of a substance in its most stable state from its constituent elements. This property is used to evaluate the stability as well as other different thermodynamic parameters. However, these two physical parameters have momentous impact on photoelectron spectroscopy, thermo chemistry and so on.

Recent past has witnessed the performance of DFT methodology to describe the several properties for systems containing TMs.¹⁷ Merz and co-workers have carried out two different works on first row TM complexes applying four different rungs of DFT functionals with varying basis sets to analyze their different physical properties.¹⁵ Quadruple ζ -quality basis set has been used to evaluate bond energies, molecular structures, dipole moments etc. of TM complexes by Furche and coworkers.¹⁸ The B3LYP exchange correlation functional along with LANL2DZ and CEP-31G* basis set have been used by Cundari et al. to evaluate the accuracy in predicting HOF for metal based systems.¹⁹ Several iron containing systems have been studied by Glukhovtsev et

al.²⁰ to assess their bond dissociation energies, ionization potentials, enthalpies of formations etc. with B3LYP functional and pseudo-potential based basis set. Truhlar and coworkers have theoretically studied different coordination compounds of zinc to focus on the metal-ligand bond distance, dipole moments and so on with two different basis sets along with 39 DFT methodologies.²¹ Logically, as a matter of fact, the diverse work with TM complexes have inspired our urge to analyse thoroughly the different physical properties of first row TM complexes by applying eight different M0X functionals with most popular LANL2DZ basis set and to compare these results with the recent experimental data which are found in literature. The main goal of this work is to analyze the accuracy and consistency of eight different M0X suite of functionals on different first row TM complexes in predicting the ionization potentials (IPs) and the heat of formations (HOFs). Further one may note that, all these M0X functionals are being tested in predicting different physical parameters outside our recommended usage domain in the recent past.^{8,14}

5.2 Methodology

We are in an era of change. Although B3LYP is the most widely used functional in the quantum chemistry panacea; however, the different M0X group of functionals have the ability to compete with the B3LYP results in defining several chemical properties.⁴ Here, on one hand, we have taken one non-hybrid meta GGA functional and on the otherhand seven hybrid meta GGA functionals to form the M0X family of functionals for our study. The calculations in this study have been done using Gaussian 09W quantum chemical software.²² As Gaussian 09W does not consider M08 set of functionals; hence, we have chosen Gamess²³ code to evaluate the HOF and IP values in M08-SO¹⁴ and M08-HX¹⁴ functionals. Gauss view 5.0²⁴ is used for the structural analysis, frequencies, and forces of these different transition metal complexes. Riley et al. have advocated over the fact that in calculating the IP values, the hybrid meta GGA functionals give best results, whereas the meta GGA functionals along with the earlier hybrid meta GGA functionals is found suitable to evaluate the HOF results.²⁵ Along with this M0X suite of functionals we have used pseudo-potential based Los Alamos National Laboratory 2

double- ζ (LANL2DZ) basis set. In this economic and widely applied basis set, the core electrons correspond to the effective core potential and the outer electrons are represented by double- ζ atomic orbitals. In general, the metals are well described by this LANL2DZ basis set.²⁶ We have calculated the IPs in the adiabatic framework. The HOFs values are calculated from the method described in the white paper “*Thermochemistry in Gaussian*” as always available in web. The experimental results are taken from *NIST Chemistry WebBook* for both IPs and HOFs as suggested by Merz and co-workers.¹⁵ We have optimized the molecular geometries of these TM complexes at first and then with the optimized structures having lowest electronic energy we have computed HOFs and IPs at the same level of theory. The gas phase optimizations have been carried out with four different spin multiplicities of each system in accordance with the total number of electrons in such system as advocated by Merz et al,¹⁵ and then the single point calculations for the evaluation of zero point energy and enthalpy correction have also been carried out with the geometry of the particular multiplicity where the energy is lowest. The readers may note that, we have used the multiplicities from 1 to 7 for the systems where the multiplicity is odd, whereas for the even multiplicity systems we have considered the multiplicities from 2 to 8 as different DFT methods predict different ground spin states. The tight key word is used for calculating single point calculations of atoms. The spin state with lowest Hartree-Fock energy is taken as ground state of that particular TM complex. The ground state spin multiplicity of the each complex is given categorically in the tabular form in the appendix. This ground state of each complex is further used for the frequency calculations required for IP and HOF estimations. One point to be noted here is that, error means the difference between experimental and theoretical values of the respective parameters. The experimental HOF and IP results in tabular form (Table 1 and Table 2, Appendix) and the required corresponding references from where these experimental values are taken are given in the appendix.

5.3 Results and discussion

The accuracy which is expected from the keen readership of M0X functionals in predicting the HOF and IP values is the main goal of this work as already mentioned. We

have chosen first row TM based benchmark molecules to evaluate their HOF, IP values. All the computed results have been compared with recent experimental (the references 1-12, available in appendix) and the theoretical¹⁵ results. Here, we have taken 54 different TM complexes (six complexes from each nine metals) for calculating HOFs and among them only 47 systems have been taken for the calculation of IP values due to lack of experimental results on the rest 7 systems. IP is a significant character of a molecule or atom by which one can estimate the firmness of an electron to bind with the particular species. As a matter of fact, the IP is a descriptor of stability and reactivity of a substance. On the other hand, HOF basically is the enthalpy change due to the formation of one mole of a substance from its constituent elements. This is another physical parameter which is used to measure the stability as well as to estimate different thermodynamic parameters. These two physical parameters have momentous impact on the photoelectron spectroscopy, thermochemistry and so on.

5.3.1 Heat of Formation (HOF)

In this study, the HOF values of each of the 54 benchmark transition metal based complexes are calculated with eight Minnesota density functionals in combination with LANL2DZ basis set as already mentioned in the methodology section. These computed and experimental HOF values along with the respective deviations are shown in the group of tables represented as Table 4 in Appendix. Figure 5.1 depicts the average unsigned HOF errors for the complete set of TM complexes highlighting the performances of the different M0X suite of functionals. At a first glance of Figure 5.1, one can see that the local functional M06-L is the best performer among all eight M0X functionals which are used in this study. The HOF results obtained from the M05 and M06 functionals show little bit more deviation than the M06-L results. On the other hand, much more deviated results are obtained from M05-2X, M06-2X, M08-SO and M08-HX functionals compared to the other three brethren functionals as mentioned previously. Nonetheless, the M06-HF functional gives the highest deviation in unsigned HOF results. From the above discussion it seems that the

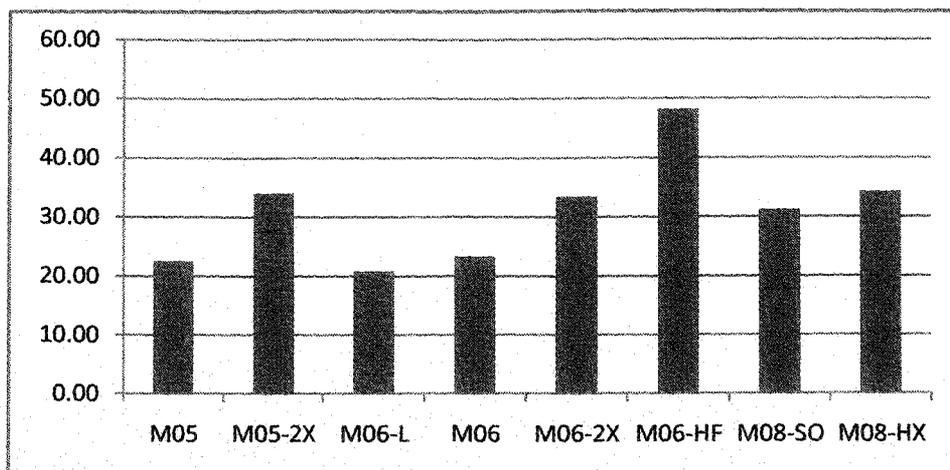


Figure 5.1 The average unsigned heat of formation errors (Kcal/mole) for the complete set of complexes, highlighting the performance of different M0X suite of functionals with LANL2DZ basis set, containing transition metals taken in this study.

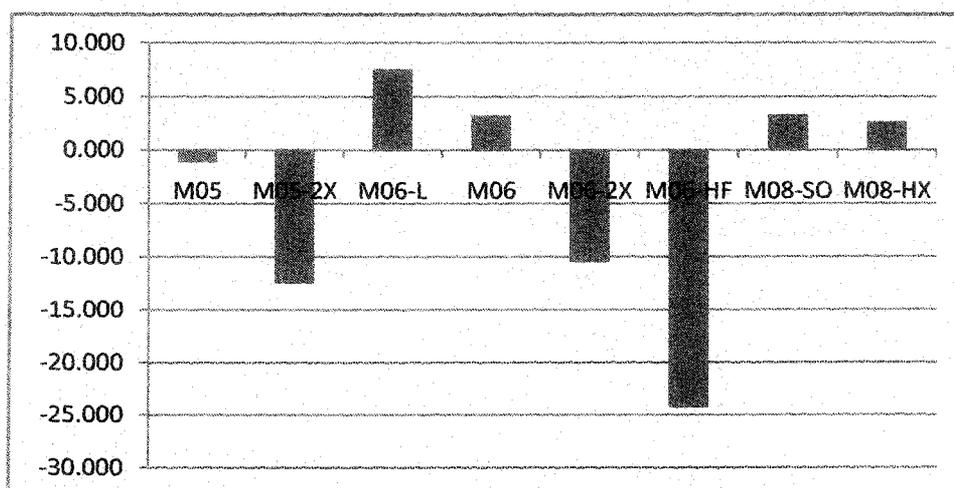


Figure 5.2 The average signed heat of formation errors (Kcal/mole) for the complete set of complexes, highlighting the performance of different M0X suite of functionals with LANL2DZ basis set, containing transition metals taken in this study.

quality of the computed averaged unsigned HOF errors for different TM complexes is increased with the decreased HF exchange. Figure 5.2 describes the average signed HOF errors for the entire 54 TM complexes, where the performances of eight different M0X functionals are decorated. Here, we find that the M06-L, M06, M08-SO and M08-HX

functionals have underestimated the signed HOF errors, whereas another four functionals which are considered in this study have overestimated the same. It is to be noted here is that, among the four best performer functionals mentioned above the performance of the M05 functional is markedly the best. Although the efficiencies of the functionals M06-2X, M08-SO and M08-HX are almost remain in the same range in calculating different thermochemical parameters are claimed by the developers,¹⁴ however, the better performances from the last two functionals (M08-SO and M08-HX) compared to the first one (M06-2X) in predicting HOF errors are found from our study. Nonetheless, the M08-HX functional is found to be the second best performer among the M0X functionals series in predicting the signed HOF errors. The M05-2X and M06-2X have performed almost in a similar fashion whereas the M06-HF is the worst performer among all functionals in predicting the signed HOF errors for these complexes. Here, the M06-L functional gives the average performance in predicting the signed HOF errors, although for the determination of unsigned HOF error its performance is excellent compared to other functionals.

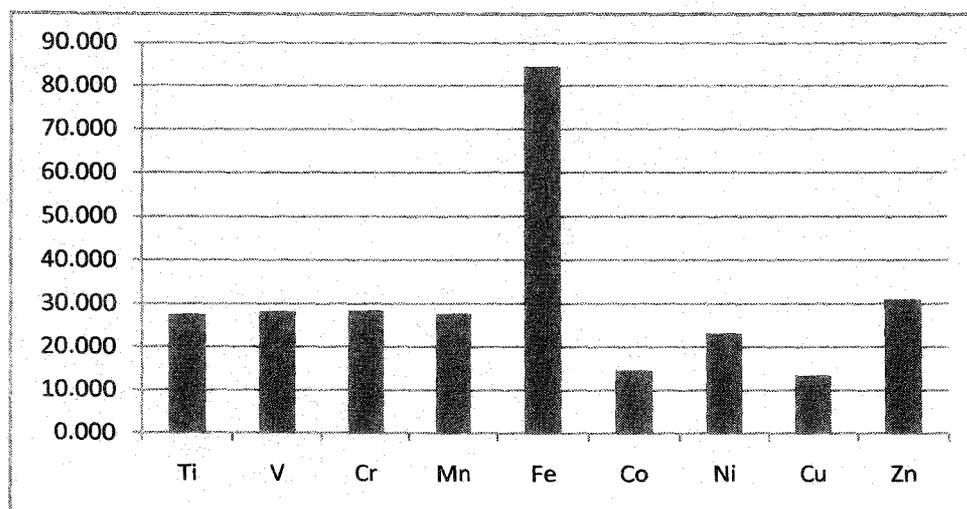


Figure 5.3 The average unsigned heat of formation errors (Kcal/mole) for nine different transition metal complexes considered in this study.

The average unsigned HOF errors for the different TM complex systems are shown in Figure 5.3. If we focus on the Figure 5.3, it is clear that the Co and Cu containing

complexes give the best performances, compared to the complexes containing Ti, V, Cr, Mn, Ni and Zn. These TMs (stated afterwards) containing complexes show average performances in predicting signed HOF errors. However, the Fe containing complexes give very poor results among the whole TMs series. Riley and Merz have found that the Cr, Ni and Cu are the most problematic transition elements with 6-31G(d,p) basis set; however, this problem is overcome by using mixed basis set approach.^{15a} On the other hand, Yang et al.^{15b} have found that the Cu complexes give the best average performance

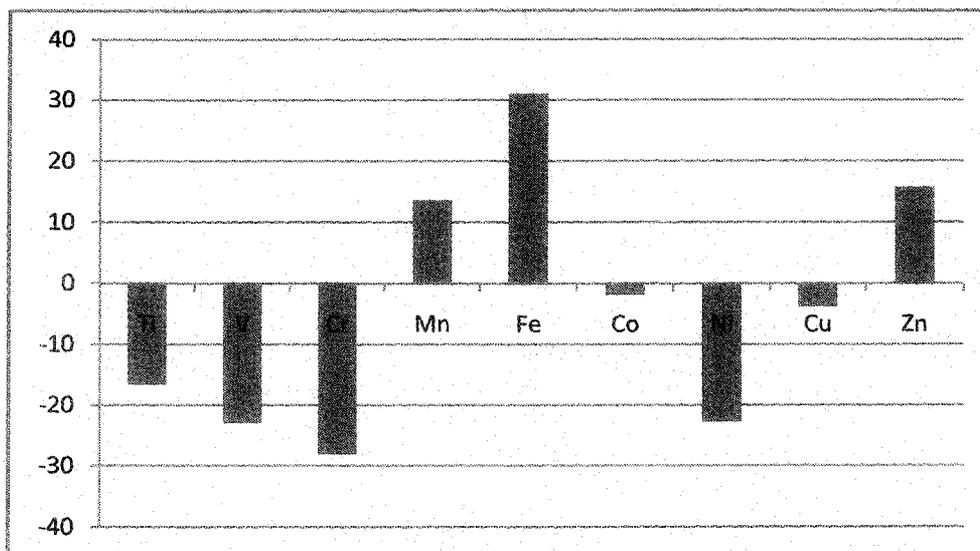


Figure 5.4 The average signed heat of formation errors (Kcal/mole) for nine different transition metal complexes considered in this study.

and Zn complexes give impressive result for its closed shell structure. The Figure 5.4 depicts the average signed HOF errors for the different TM complex systems which are considered in this work. From this Figure, we find that the average signed HOF errors for the Mn, Fe and Zn containing complexes are positive, whereas for other TM complexes these values are negative. Here, in predicting the average signed HOF errors, we also have found that the Co and Cu containing complexes are the best performers, although the Co complexes are the best in accordance with their performances. The Mn and Zn complexes show the almost the same average value of signed HOF errors. This fact is attributed due to the half filled and full filled *d*-orbitals of such metals. Other TMs like Ti, V, Cr, Fe, Ni produce almost similar errors in predicting the average signed HOF

results. One may note that, like unsigned HOF errors the Fe complexes also produce larger deviation of results in predicting the signed HOF.

The Figure 5.5 exhibits the average unsigned HOF errors for various TM-coordinating groups which are considered in this study. It is clear from Figure 5.5 that the carbonyl and methyl ligands containing complexes show most poor results, while the hydride and hydroxide ligands appear to be the most worthy in nature. From Figure 5.6, which gives the average signed HOF errors for various TM ligands used in this study, it

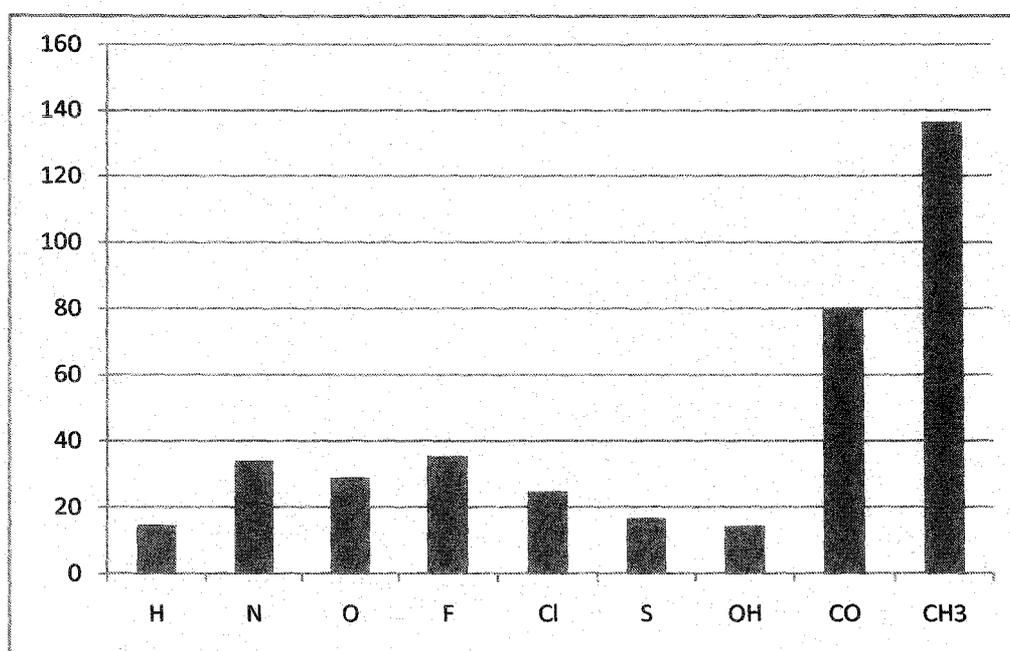


Figure 5.5 The average unsigned heat of formation errors (Kcal/mole) for different transition metal bonding partners treated in this study.

is observed that the hydride, chloride and methyl ligands (3 ligands out of 9) containing TM complexes have overestimated the results, while the other coordinating groups have underestimated the same. Like Figure 5.5, from Figure 5.6 we also have found that the methyl and carbonyl groups containing TM complexes show poor results. However, these latter stated two ligands show errors in opposite direction (Figure 5.6). The admirable signed HOF results are observed from the $-H$ and $-F$ ligands containing complexes.

Nonetheless, it is also observed both from the Figure 5.5 and Figure 5.6 that the $-\text{CH}_3$ ligands containing TM complexes show the most disappointment in HOF results.

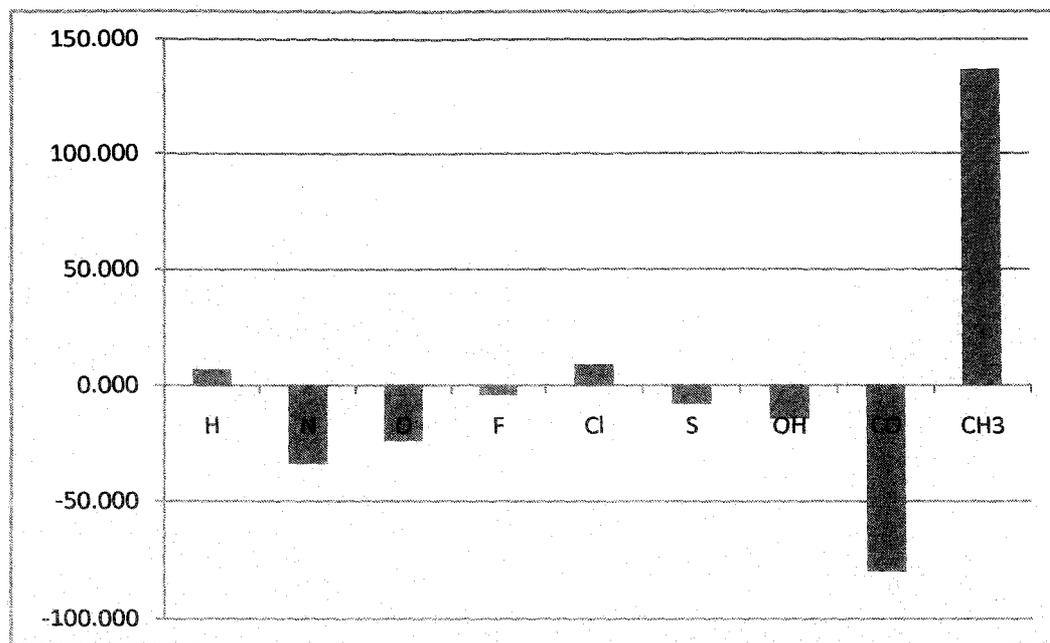


Figure 5.6 The average signed heat of formation errors (Kcal/mole) for different transition metal bonding partners treated in this study.

The Table 5.2 shows the average unsigned HOF errors for the entire set of systems containing various first row TMs against eight different DFT functionals taken in this study. At a first glance on Table 5.2, one can see from the average value that the M06-L functional gives the best performance among all the eight functionals. We also find that the complexes of the Mn, Fe and Zn are the most problematic in predicting their unsigned HOF values with the M06-L functional. The M05 functional shows the best performance for Co complexes only, whereas for Fe and Zn complexes the same functional show the worst results. If we consider the performances of the M05-2X and M06-2X functionals, the Ti, V, Cr, Mn, Fe, Ni and Zn complexes furnish poor results (7 out of 9 cases), whereas the Cu complexes bring better results compared to the other TM complexes. The Fe complexes are shown most erroneous when calculating with the M05-2X, M06-2X, M08-SO, M08-HX and M06-HF functionals. Please be noted that, from the average values (Table 5.2), one can easily surmise that these four M0X functionals,

Table 5.2 The average unsigned heat of formation errors (Kcal/mol) for different TM complexes in different M0X family of functional with LANL2DZ basis set.

| Functional | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Average |
|------------|--------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| M05 | 15.805 | 10.903 | 18.515 | 16.377 | 68.105 | 8.923 | 19.362 | 13.348 | 31.322 | 22.518 |
| M05-2X | 34.570 | 32.438 | 39.532 | 22.632 | 83.042 | 21.163 | 29.272 | 12.595 | 31.347 | 34.066 |
| M06-L | 18.763 | 10.242 | 8.653 | 30.670 | 66.847 | 8.330 | 9.563 | 5.955 | 27.773 | 20.755 |
| M06 | 18.783 | 11.802 | 19.868 | 23.910 | 66.708 | 4.785 | 19.180 | 12.847 | 31.397 | 23.253 |
| M06-2X | 28.570 | 35.187 | 41.040 | 25.977 | 84.855 | 18.392 | 20.752 | 17.157 | 29.058 | 33.443 |
| M06-HF | 52.782 | 60.802 | 41.502 | 48.135 | 99.090 | 23.867 | 54.297 | 23.502 | 29.293 | 48.141 |
| M08-SO | 28.271 | 13.839 | 29.692 | 18.069 | 106.262 | 13.999 | 20.277 | 14.882 | 35.561 | 31.206 |
| M08-HX | 22.515 | 51.080 | 28.465 | 36.163 | 100.563 | 17.266 | 12.486 | 7.020 | 32.287 | 34.205 |

Table 5.3 The average signed heat of formation errors (Kcal/mol) for different TM complexes in different M0X family of functionals with LANL2DZ basis set.

| Functional | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Average |
|------------|---------|---------|---------|---------|--------|---------|---------|---------|--------|---------|
| M05 | -7.775 | -10.903 | -18.515 | 16.377 | 29.005 | 4.123 | -19.362 | -13.348 | 10.108 | -1.143 |
| M05-2X | -34.570 | -32.438 | -39.532 | 22.632 | 16.738 | -12.960 | -29.272 | -11.368 | 8.317 | -12.495 |
| M06-L | -6.233 | 3.872 | -7.990 | 30.670 | 40.193 | 2.917 | -7.670 | 0.382 | 12.120 | 7.585 |
| M06 | -9.577 | -6.095 | -19.868 | 23.910 | 37.185 | 2.722 | -19.180 | 11.353 | 8.727 | 3.242 |
| M06-2X | -27.107 | -35.187 | -41.040 | 25.977 | 19.998 | -11.675 | -20.752 | -17.157 | 12.378 | -10.507 |
| M06-HF | -51.368 | -60.803 | -40.125 | -47.562 | 5.643 | -12.810 | -54.297 | 21.555 | 20.903 | -24.318 |
| M08-SO | -3.951 | 8.535 | -29.692 | 6.796 | 45.600 | 13.197 | -20.277 | -14.882 | 24.138 | 3.274 |
| M08-HX | 8.016 | -51.080 | -28.184 | 30.047 | 54.322 | -0.502 | -11.535 | -6.734 | 29.286 | 2.626 |

namely, M05-2X, M06-2X, M08-SO and M08-HX having higher but almost closer HF exchange perform almost in a similar fashion in predicting the unsigned HOF errors. The M06-HF functional is the worst performer among all the M0X series of functionals in predicting the unsigned HOF values for all the TM complexes as evident from the average value. The Table 5.3 lists the average signed HOF errors of the entire set of TM

complexes against different M0X group of functionals considered in this work. From the Table 5.3 it is clear that among the 5 out of 8 functionals the Fe complexes are found to be most problematic. However, the Fe complexes show best result with M06-HF functional (5.643 Kcal/mol) and worst results are furnished by the M08-SO (45.600 Kcal/mol) and M08-HX (54.322 Kcal/mol) functionals. Here, we find from Table 5.3 that the M06-L functional shows the least amount of signed HOF errors for the five out of total nine cases. Nonetheless, these results are found to be lower or nearly equal to the B3LYP results.¹⁵

Table 5.4 The average unsigned heat of formation errors (Kcal/mol) for the various transition metal bonding partners against different M0X set of functional with LANL2DZ basis set.

| Atoms | M05 | M05-2X | M06-L | M06 | M06-2X | M06-HF | M08-SO | M08-HX | Average |
|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| H | 7.950 | 11.808 | 14.188 | 10.464 | 10.830 | 15.564 | 19.551 | 26.264 | 14.577 |
| N | 18.080 | 50.990 | 0.250 | 20.720 | 46.450 | 77.030 | 0.041 | 58.192 | 33.969 |
| O | 14.886 | 33.417 | 9.252 | 15.116 | 34.129 | 58.817 | 28.850 | 36.409 | 28.859 |
| F | 29.837 | 37.906 | 27.722 | 33.265 | 40.286 | 54.958 | 32.024 | 27.377 | 35.422 |
| Cl | 21.376 | 30.059 | 20.631 | 21.502 | 28.397 | 28.299 | 25.517 | 22.694 | 24.810 |
| S | 10.813 | 19.467 | 10.430 | 7.750 | 17.117 | 30.243 | 13.346 | 24.730 | 16.737 |
| OH | 16.710 | 20.290 | 13.530 | 18.500 | 22.390 | 18.210 | 4.541 | 0.314 | 14.311 |
| CO | 49.787 | 86.320 | 33.997 | 41.780 | 85.770 | 111.113 | 99.748 | 129.118 | 79.704 |
| CH3 | 124.290 | 118.990 | 119.680 | 120.370 | 124.310 | 137.410 | 172.548 | 174.224 | 136.478 |

Table 5.5 The average signed heat of formation errors (Kcal/mol) for the various transition metal bonding partners against different M0X set of functionals with LANL2DZ basis set.

| Atoms | M05 | M05-2X | M06-L | M06 | M06-2X | M06-HF | M08-SO | M08-HX | Average |
|-------|---------|---------|---------|---------|---------|----------|---------|----------|---------|
| H | 3.006 | 1.768 | 8.688 | 3.756 | 3.322 | -7.344 | 17.566 | 24.015 | 6.847 |
| N | -18.080 | -50.990 | 0.250 | -20.720 | -46.450 | -77.030 | 0.041 | -58.192 | -33.896 |
| O | -10.504 | -32.833 | 1.448 | -10.812 | -33.151 | -55.355 | -16.962 | -33.657 | -23.978 |
| F | 0.395 | -5.219 | 7.375 | -1.110 | -8.043 | -30.837 | -5.025 | 9.808 | -4.082 |
| Cl | 6.359 | 0.175 | 12.254 | 10.574 | 6.433 | 5.505 | 14.978 | 15.512 | 8.974 |
| S | -1.400 | -19.467 | 10.430 | 2.057 | -17.117 | -22.863 | -6.671 | -9.542 | -8.072 |
| OH | -16.710 | -20.290 | -13.530 | -18.500 | -22.390 | -18.210 | -4.541 | 0.314 | -14.232 |
| CO | -49.787 | -86.320 | -33.997 | -41.780 | -85.770 | -111.113 | -99.748 | -129.118 | -79.704 |
| CH3 | 124.290 | 118.990 | 119.680 | 120.370 | 124.310 | 137.410 | 172.548 | 174.224 | 136.478 |

We also find that when one moves from left to right of the first row TM series, then with the increase of *d* electrons the performance of the functionals having higher exchange correlation energies are increased. From Table 5.4, which shows average unsigned HOF errors for various TMs bonding partners against different M0X set of functionals, it is clear that for the TM-hydrides the M06-L, M06-HF, M08-SO and M08-HX functionals give the pitiable results. For -N and -O containing TM complexes the M06-L and M08-SO functionals are the best players. For -S- containing TM complexes the use of the M06 functional is suggested. Functional group -OH containing TM complexes give average performance among all the functionals, however, the use of M08-HX is recommended. Carbonyl group containing TM complexes are the poor performers with all the functionals. TMs having -CH₃ group as ligands find as the worst player among the entire coordination groups with all the functionals studied here. The performance of the M06-L functional is found to be the best at least in four out of nine cases. Nonetheless, its performances are much better than the performance of the B3LYP functional for the same complexes as obtained in earlier work.¹⁵ The signed HOF errors for various TMs bonding partners against the different M0X set of functionals are shown in the Table 5.5. A close look on the average value furnished in the Table 5.5 shows that the hydride and

fluoride ligands containing TM complexes show better performances than all other ligands, nonetheless the methyl group containing metal complexes show worst performance in predicting the same.

5.3.2 Ionisation Potential (IP)

We have taken 47 TM complexes to evaluate theoretically their IP values using eight different M0X suite of functionals in combination with LANL2DZ basis set as mentioned earlier. The detailed results of IPs for these 47 complexes are depicted in the bunch of tables named as Table 5 in appendix. We have excluded seven TM complexes from the total 54 benchmarked complex systems, viz, TiCl, VCl, VF, CoF₂, CoCl₃, CuO and CuS due to lack of experimental findings, as without experimental findings it is impossible to calculate the amount of IP errors. We compare these computed IP values with their respective experimental results obtained from the literature. Average unsigned and average signed IP errors for the entire set of TM complexes with respect to the eight M0X suite of functionals are represented with a graphical format in Figure 5.7 and Figure 5.8 respectively. Now, if we take a quick look on Figure 5.7, we can find that maximum erroneous results are shown by M06-HF functional, whereas, M06 functional shows the

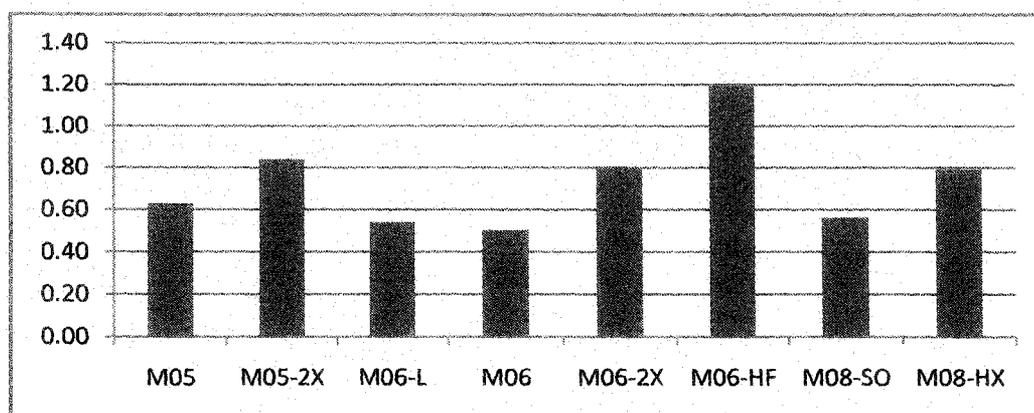


Figure 5.7 The average unsigned ionisation potential errors (eV) for the whole set of complexes with these transition metals against different M0X set of functionals with LANL2DZ basis set considered in this study.

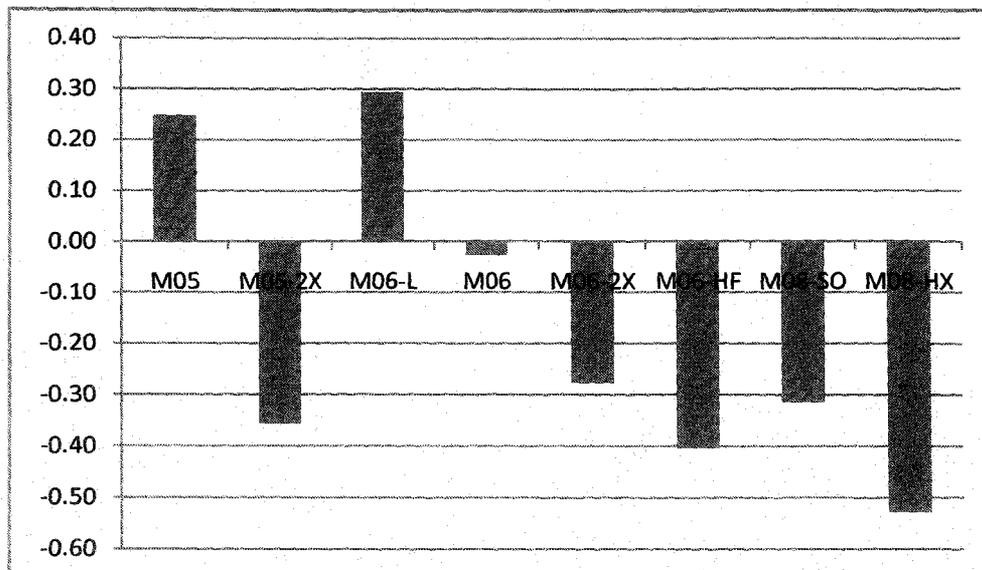


Figure 5.8 The average signed ionisation potential errors (eV) for the whole set of complexes with these transition metals against different M0X set of functionals with LANL2DZ basis set in this study.

most correct results among the eight such functionals. The second best functional is M06-L having no HF exchange correlation energy. Please be noted that, the third best is M08-SO functional, which is even better than the M05-2X, M06-2X and M08-HX functionals having almost equal HF exchange. Nonetheless, the accuracy of finding unsigned IP errors by the M06-2X and M08-HX for these TM complexes are found to be almost close to each other. From the Figure 5.8, it is clear that the functionals M05 and M06-L show the errors in positive direction which means that our theoretical calculations for these two functionals give lower values than the corresponding actual experimental results. However, the other six functionals in this family show errors in the negative direction. Although there is a huge difference in χ between the functionals M06-L with the M06-2X and M08-SO; however, their performances are almost same in predicting the signed IP errors although the errors producing by the last two functionals have opposite in sign with that of the first one. If one takes a bird's eye view to both of the Figure 5.7 and Figure 5.8, one can find that the performance of M06 functional is excellent compared to the other functionals in M0X family for the predicting the IP values for the first row TM complexes. Nonetheless, it is needless to say that the performance of M06-HF for the

calculation of unsigned IP errors and the performance of M08-HX for the prediction of signed IP errors is worst among this family of eight functionals.

The average values of the unsigned and signed IP errors of different TM systems against different M0X suite of functionals are given in Table 5.6 and Table 5.7 respectively. In first sight one should get the values of unsigned and signed errors of every individual TMs irrespective of their complexes against all eight M0X functionals from these two tables. From Table 5.6 it is clear that, The computationally low cost local functional M06-L shows overall less erroneous results compared with other meta-hybrid functionals of this family, and some cases these computed values are found to be even lower than the B3LYP errors.¹⁵ We also find a competition between the results among M06-L, M06 and M08-SO functionals, although their HF exchanges are increases sequentially. A quick look on the unsigned IP values reveals that the Ti, Ni, and Zn complexes give less correct results irrespective of all the functionals. However, Ti complexes show more deviation in unsigned IP results as χ increases with an exception for the M08 set of functionals. The highest deviation of results (2.775 eV) is obtained for Cu complexes with the M08-HX functional. The lowest deviation of results (0.11 eV) is observed for M06 functional in case of Cu complexes and also for the M08-SO functional in case of Ti complexes. If one takes all the cases then it is obvious that the worst performer is none other than M06-HF (gives huge errors in 5 out of 9 cases) with cent percent exchange correlation energy. Now, we want to discuss over the values of signed IP errors which are depicted in Table 5.7. Here, one finds that the Zn complexes are most problematic among different molecules taken for this study. The results of Zn and Ni containing complexes deviate more than 0.5 eV with 6 out of 8 functional cases. However, the Ti complexes also have shown same range of deviations in 3 cases. For Ti complexes at higher χ the results are problematic with an exception of M08 set of functionals. Highest deviation (-2.775 eV) is found for M08-HX functional in case of Cu complexes and the lowest deviation i.e. more accurate results (0.035 eV) are observed for Co in case of M06-L functional. From Table 5.7 it is also clear that the M06 functional is the best performer throughout the M0X series for calculating the signed IP errors of these TM complexes, although, the performances of the M06-L, M05 and M06-2X functionals

are also not yet to be neglected. Point to be mentioned here is that, the B3LYP results¹⁵ are found to be outperformed in many cases after calculating these physical quantities with the above mentioned Minnesota density functionals.

Table 5.6 The average unsigned ionisation potential errors (eV) for all the systems containing various transition metals against different M0X set of functionals with LANL2DZ basis set.

| Functional | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Average |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| M05 | 0.680 | 0.405 | 0.573 | 0.748 | 0.458 | 0.405 | 0.705 | 0.483 | 1.173 | 0.626 |
| M05-2X | 1.112 | 0.983 | 0.985 | 0.947 | 0.593 | 0.72 | 1.085 | 0.48 | 0.643 | 0.839 |
| M06-L | 0.454 | 0.673 | 0.503 | 0.337 | 0.267 | 0.575 | 0.552 | 0.553 | 0.932 | 0.538 |
| M06 | 0.488 | 0.275 | 0.527 | 0.640 | 0.402 | 0.393 | 0.880 | 0.11 | 0.798 | 0.501 |
| M06-2X | 1.300 | 0.795 | 0.738 | 0.657 | 0.607 | 0.708 | 1.198 | 0.458 | 0.695 | 0.795 |
| M06-HF | 1.568 | 0.965 | 1.063 | 0.948 | 1.482 | 1.275 | 1.312 | 1.280 | 0.877 | 1.197 |
| M08-SO | 0.107 | 0.079 | 0.488 | 0.231 | 1.684 | 0.847 | 0.923 | 0.422 | 0.277 | 0.562 |
| M08-HX | 0.263 | 0.266 | 0.263 | 0.242 | 0.923 | 0.863 | 1.109 | 2.775 | 0.418 | 0.791 |

Table 5.7 The average signed ionisation potential errors (eV) for all the systems containing various transition metals against different M0X set of functionals with LANL2DZ basis set considered for this study.

| Functional | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Average |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|-------|---------|
| M05 | -0.348 | 0.380 | 0.193 | 0.525 | 0.055 | -0.120 | -0.115 | 0.483 | 1.173 | 0.247 |
| M05-2X | -0.848 | -0.318 | -0.815 | -0.297 | -0.287 | -0.525 | -0.965 | 0.203 | 0.643 | -0.357 |
| M06-L | 0.322 | 0.673 | 0.207 | 0.313 | -0.133 | 0.035 | -0.065 | 0.553 | 0.742 | 0.294 |
| M06 | -0.156 | 0.100 | -0.127 | 0.243 | -0.115 | -0.298 | -0.733 | 0.045 | 0.798 | -0.027 |
| M06-2X | -1.032 | -0.050 | -0.685 | -0.093 | -0.18 | -0.548 | -0.795 | 0.205 | 0.690 | -0.276 |
| M06-HF | -1.500 | -0.510 | -1.128 | -0.712 | -0.375 | 0.655 | -1.125 | 0.400 | 0.668 | -0.403 |
| M08-SO | 0.107 | 0.079 | -0.488 | 0.231 | -1.684 | -0.847 | -0.923 | 0.422 | 0.277 | -0.314 |
| M08-HX | 0.263 | 0.266 | -0.263 | 0.242 | -0.923 | -0.863 | -1.109 | -2.775 | 0.418 | -0.527 |

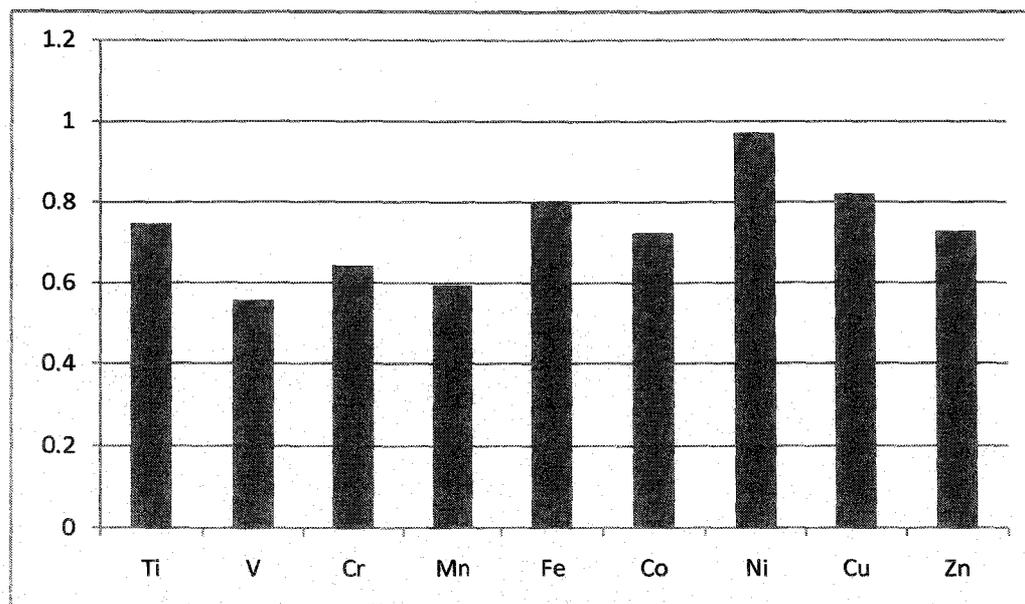


Figure 5.9 The average unsigned ionisation potential errors (eV) for the nine different transition metal systems considered in this study.

The Figure 5.9 and Figure 5.10 depict the average unsigned and signed IP errors respectively for different TM complexes which are chosen for this work. From Figure 5.9 it is clear that V containing complexes show best results among all the TM systems studied here. On the other hand, we find that the results of unsigned IP errors for Fe, Ni and Cu complexes are very large and among them the deviation made by Ni complexes is highest. Nonetheless, the unsigned IP error limits for the other TM complexes are almost in the same range. If one look at Figure 5.10, one can find that the V, Mn and Zn containing complexes show errors in the positive direction, that is the theoretically computed IP values of these complexes are below the respective experimental results and for the other six TM complexes the sign of errors are negative. The lowest signed IP errors are shown by the Mn and Cu complexes but the direction is opposite, whereas like unsigned IP errors the signed IP errors shown by Ni complexes are highest among the series.

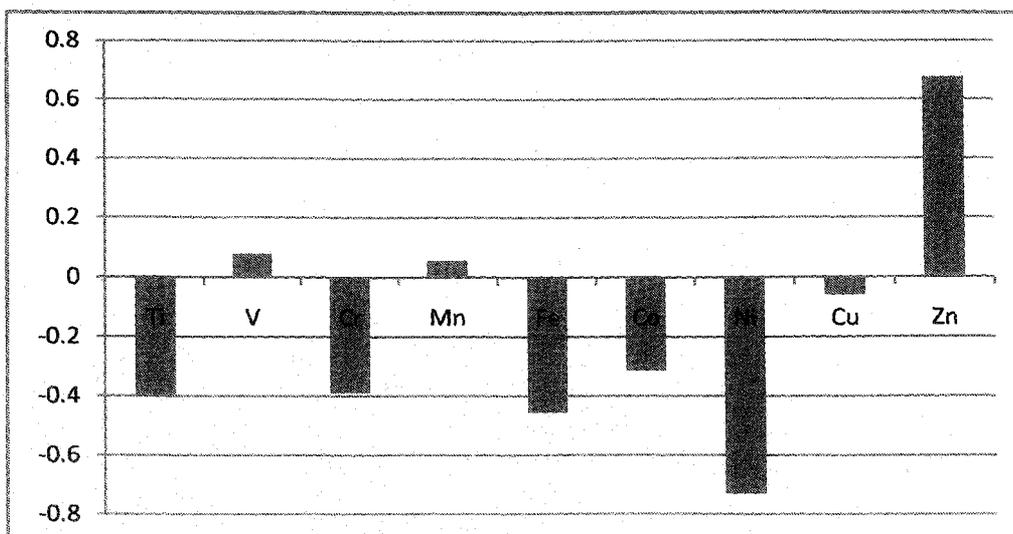


Figure 5.10 The average signed ionisation potential errors (eV) for the nine different transition metal systems considered in this study.

The Table 5.8 and Table 5.9 represent the values of unsigned and signed IP errors respectively in different M0X functionals against the different ligands which are used to form different TM complexes. One can easily understand from these two tables that how the different ligands can act in determining IP values irrespective of the different TMs. It is obvious from Table 5.8 that the functionals M05, M06 and M06-L perform well in predicting the average unsigned IP values for systems containing a particular bonding partner. It is also found from the literature that when a particular bonding ligand has more than one atom then the performance of B3LYP¹⁵ functional is increased. From the Table 5.8 it is clear that the M08-HX functional shows the lowest error (0.018 eV) with the –OH functional group among the series and the next less deviated result (0.050 eV) is shown by the M05 functional when –N acts as a ligand. On the other hand, the maximum error (2.135 eV) is observed for the carbonyl group than any other bonding partners with the M08-HX functional. Hence, one can conclude that, the highest and the lowest unsigned IP errors are furnished by the M08-HX functional with the –CO and –OH ligands respectively. On the other hand, in a quick look on the Table 5.9, we find that the M05 functional shows the lowest error (0.005 eV) with the –Cl ligand among the series and the next less deviated results (–0.007 eV) are also shown by the same functional when –CO acts as a ligand. Here, one point to be mentioned is that, for the –CH₃ ligand both of the M06-2X and M06-HF functionals give same magnitude of deviation in IP

results (0.08 eV), but they are opposite in sign. If we take an overall view on the results of Table 5.9, we find that the M05 functional performs well (out of 9 cases it gives lowest error in 3 cases). After the M05 functional the credit of accuracy goes to M06-2X functional as it shows less erroneous results in 2 cases each.

Table 5.8 The average unsigned ionisation potential errors (eV) for all the systems containing various transition metals coordinating groups against different M0X set of functionals with LANL2DZ basis set considered for this study.

| Atoms | M05 | M05-2X | M06-L | M06 | M06-2X | M06-HF | M08-SO | M08-HX | Average |
|-------|-------|--------|-------|-------|--------|--------|--------|--------|---------|
| H | 0.966 | 0.738 | 0.712 | 0.988 | 0.972 | 0.768 | 0.929 | 0.719 | 0.849 |
| N | 0.050 | 1.160 | 1.330 | 0.270 | 0.920 | 0.650 | 0.539 | 0.075 | 0.624 |
| O | 0.528 | 0.986 | 0.496 | 0.288 | 0.867 | 1.140 | 0.852 | 0.948 | 0.763 |
| F | 0.695 | 0.996 | 0.493 | 0.534 | 0.856 | 1.650 | 1.738 | 1.834 | 1.099 |
| Cl | 0.567 | 0.893 | 0.327 | 0.538 | 0.840 | 1.284 | 1.125 | 1.807 | 0.923 |
| S | 0.425 | 1.155 | 0.605 | 0.355 | 0.670 | 0.980 | 1.127 | 0.422 | 0.717 |
| OH | 0.130 | 0.080 | 0.260 | 0.140 | 0.330 | 0.170 | 0.061 | 0.018 | 0.149 |
| CO | 0.740 | 0.413 | 0.620 | 0.830 | 0.407 | 0.890 | 1.437 | 2.153 | 0.936 |
| CH3 | 0.530 | 0.170 | 0.320 | 0.150 | 0.080 | 0.080 | 0.161 | 0.264 | 0.219 |

Table 5.9 The average signed ionisation potential errors (eV) for all the systems containing various transition metals coordinating groups against different M0X set of functionals with LANL2DZ basis set considered for this study.

| Atoms | M05 | M05-2X | M06-L | M06 | M06-2X | M06-HF | M08-SO | M08-HX | Average |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|---------|
| H | 0.474 | 0.274 | 0.216 | 0.164 | -0.040 | 0.112 | 0.344 | 0.362 | 0.238 |
| N | -0.050 | 1.160 | 1.330 | -0.270 | 0.920 | -0.650 | -0.539 | 0.075 | 0.247 |
| O | 0.488 | -0.783 | 0.298 | 0.172 | -0.416 | -0.613 | -0.311 | -0.237 | -0.175 |
| F | 0.303 | -0.088 | 0.317 | 0.148 | -0.504 | -1.510 | -0.721 | -0.779 | -0.354 |
| Cl | 0.005 | -0.720 | 0.242 | -0.266 | -0.692 | -1.149 | -0.943 | -1.692 | -0.652 |
| S | -0.185 | -1.155 | 0.605 | -0.355 | -0.640 | -0.980 | -0.134 | -0.067 | -0.364 |
| OH | 0.130 | -0.080 | 0.260 | -0.140 | -0.330 | -0.170 | -0.061 | 0.018 | -0.047 |
| CO | -0.007 | 0.413 | -0.620 | -0.830 | 0.407 | 0.890 | 1.437 | 2.153 | 0.480 |
| CH3 | 0.530 | 0.170 | 0.320 | 0.150 | 0.080 | -0.080 | 0.161 | 0.264 | 0.199 |

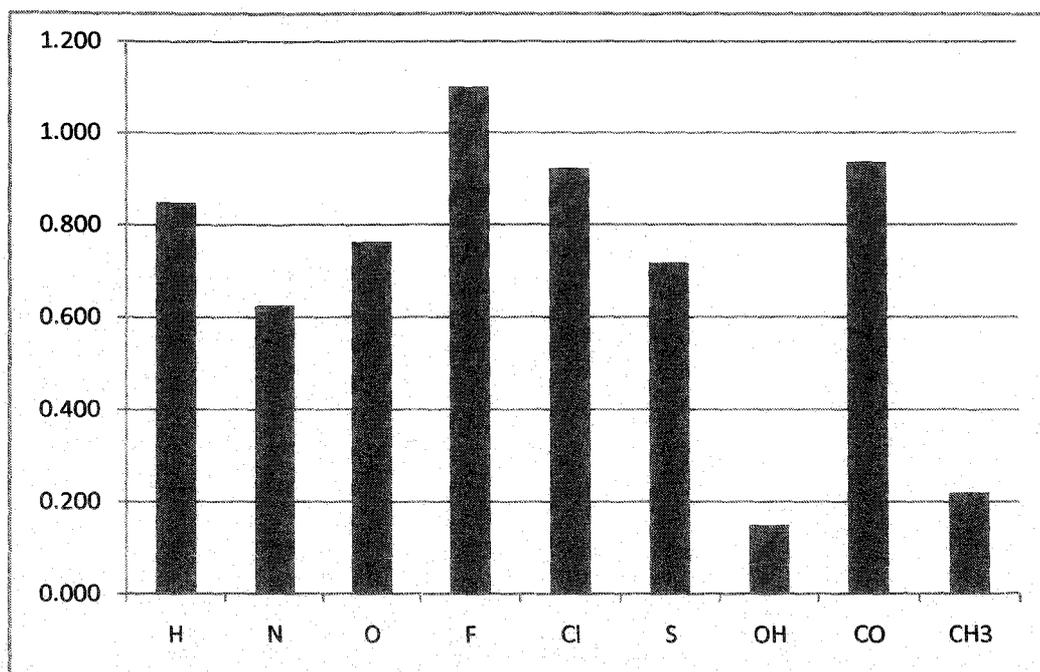


Figure 5.11 The average unsigned ionisation potential errors (eV) for different transition metal coordinating groups considered in this study.

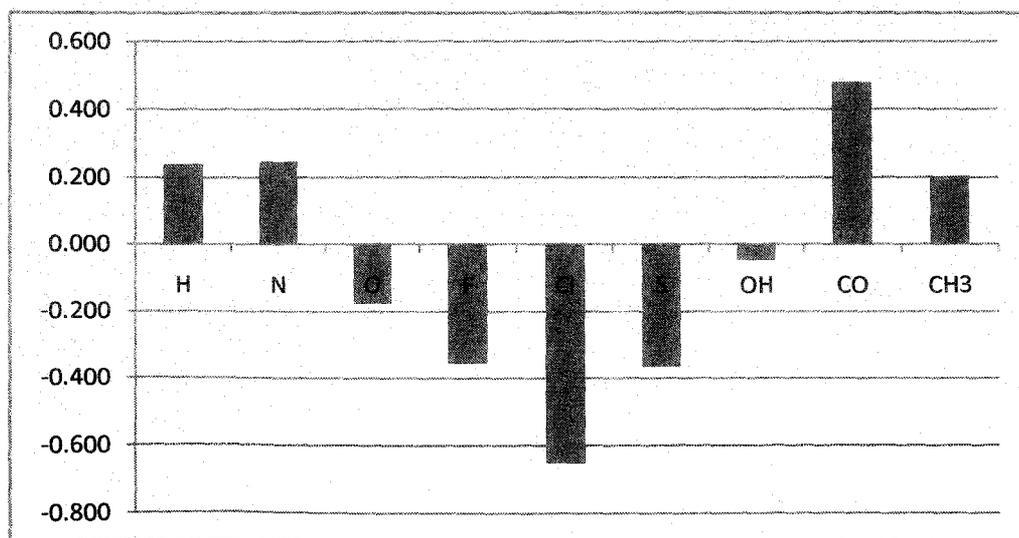


Figure 5.12 The average signed ionisation potential errors (eV) for different transition metal coordinating groups considered in this study.

The Figure 5.11 and Figure 5.12 graphically show the average unsigned and signed IP errors respectively for different coordinating groups which are used to form these benchmarked TM complexes. At a first look on Figure 5.11, one can easily find that the $-OH$ and the $-CH_3$ groups show smallest amount of errors among these series of prototype ligands, whereas the ligand $-F$ shows the highest unsigned IP error. Now, if one consider the Figure 5.12, one can readily infer that the ligands $-H$, $-N$, $-CO$ and $-CH_3$ show the signed IP errors in positive direction, whereas the rest of the five ligands which are taken in this study show the signed IP errors in the negative direction. Here, we find that the coordinating group $-OH$ shows the least error among these series of ligands but the error direction is negative. Nonetheless, the ligands $-Cl$ and $-CO$ are found to be most problematic in predicting these signed IP errors.

5.4 Summary

This work provides a benchmark study of the performance of different versions of the M05, M06 and M08 set of Minnesota density functionals with first row transition metal compounds. More precisely, in this study, we have evaluated the accuracy and reliability of eight M0X suite of functionals for the prediction of HOF and IP values of different first row transition metal complexes. We have taken 54 benchmark TM complexes for calculating the HOF values, whereas only 47 systems among these molecules are taken for evaluating IP values due to lack of experimental results. Following the procedure used by Riley and coworkers¹⁵ we have computed these molecular properties for our selected TM systems. The M06-L functional is the best average performer among the M0X series of functionals in predicting these thermodynamic parameters of different first row TM complexes, whereas the robust functional M06-HF gives the worst performance in predicting such properties confirming the recommendation of the developers of these functionals that the Minnesota density functionals with high H-F exchange should not be used for the TM compounds. Nonetheless, almost similar performance of the M06-2X, M08-SO and M08-HX functionals having closely HF exchange in treating the thermochemical parameters of the TMs is also claimed by them.^{8,11,12,14} The Fe complexes show most notorious HOF

results, whereas Ni complexes are found to be most problematic for the prediction of IP values. The discussion about the huge average HOF errors produced by the Fe complexes by our chosen eight Minnesota density functionals is due here. Notably, there are difficulties in dealing TM complexes by computational techniques due to the partial filling of *d* orbitals which is also responsible for degeneracy. Another point to be mentioned here is that, Merz and co-workers^{15a} have found that the -CO group containing TM complexes are found to be problematic in predicting the HOF errors. Riley and co-workers¹⁵ have chosen ten systems of iron, whereas we have taken only six complexes among those systems with one mono- and one bi-carbonyl complex. Secondly, they have found that the mono coordinated TM systems show best results and as the number of coordination increase the average unsigned HOF errors increases, that is the performance of the functionals decreases. It is also noteworthy that, we have taken three complexes for iron where the coordination higher than one. Nonetheless, they also have found that all the HGGA and HMGGGA methods overestimate the HOF errors for TM complexes.^{15a} Here, in this work out of eight functionals the seven functionals are HMGGGA type. In another study, Reiher and co-workers²⁷ have analysed the spin density distribution in some Fe-nitrosyl complexes in DFT framework and they have found that the satisfactory description of spin densities in such complexes are not to be properly provided. In another effort Swart²⁸ have found that the reliable prediction of accurate spin ground state energies for the Fe complexes is tricky job both for theory and experiment. On the otherhand, in case of the prediction of IP values the deviation from the experimental results is much smaller than that of HOF results. Besides M06-L functional, the M05 and M06 functionals are also to be recommended for the theoretical prediction of these thermochemical parameters for the first row TM complexes. Point to be noted is that, the non-hybrid meta GGA functional M06-L takes 5-10% less effective CPU time consumption for calculating these physical parameters of these benchmarked TM complexes than the seven other hybrid meta GGA functionals. However, this argument is true for these small systems, but it underestimates the issue for larger systems, such that when one has a system with ~100 atoms, the cost for $\chi = 0$ is more than an order of magnitude smaller than for systems with nonzero χ , and for periodic calculations the speedup becomes 2-to-3 orders of magnitude greater. From the results obtained in this

work, one can categorically extract the following points- (i) The non-hybrid meta GGA M06-L functional with zero exchange correlation energy outdo all other functionals in predicting unsigned HOF values of the respective species. (ii) In predicting the IP results the performance of the M06 functional is found to be even better than the results obtained from M06-L functional. (iii) The hybrid meta GGA M05 and M06 functionals show quite accurate results after the local one compared to the other hybrid functionals taken for this study. (iv) With the increase of exchange correlation energy the performance of the M0X group of functionals to predict these physical properties for different first row TM complexes is noticeably found to be lowered. (v) The M06-HF functional having cent percent exact exchange contribution gives huge deviated results in all the field of calculations used in this study. (vi) We conclude that the M05 and M06 functionals found to be the good alternative to the popular B3LYP functional to study the HOFs and IPs. (vii) Considering the signed and unsigned HOF and IP errors (shown in Figure 5.1, Figure 5.2, Figure 5.7 and Figure 5.8 respectively), one can find with ease that 3 out of 4 cases the performance which has made by M08-SO is considerably more accurate than its other M08 counterpart as also advocated by the developers.¹⁴ Nonetheless, this study has two quite different aspects: (a) Testing of the functionals viz. M06-L, M05 and M06 which are excellent candidates for the transition metal applications can forms a new transition metal database, and (b) Double checking the original recommendations that the functionals with $\chi > 30$ should not be used for transition metals.^{8,14} At last an interesting note is that all existing M0X family of functionals have their own strength as well as weaknesses, hence there lies a difficulty in choosing the right functional to evaluate a particular physical property. We hope that, upcoming years will see a new M0X functional with all the merits which all would exist in the today's M0X functionals.

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