CHAPTER 7

CONCLUSION AND FUTURE PROSPECTS

The main objective of the above studies was to find a suitable computational method that would help in the prediction of magnetic parameters like g-tensor, D-tensor and hyperfine coupling constant theoretically based on the coordinating environment surrounding a metal ion. We have extensively studied 1st row tansition metal ions, viz. Mn(III), Cu(II), Co(II) and NiO clusters by employing DFT levels of calculation. Also *ab initio* CASSCF method was engaged for tetradentate Co(II) complexes. In most of the cases we tried to predict the magnetic parameters and comparing them with the already established experimental results.

7.1 Concluding Remarks and Outlook

As the main objective of the proposed research work was the prediction of magnetic properties using various computational approaches in case of transition metal complexes and clusters; in this context, the thesis comprised of total seven chapters.

- In Chapter 1 we have presented a comprehensive introductory glimpse on transition metal complexes and clusters whose magnetic properties were studied by theoretical methods extensively. The key magnetic properties of the transition metal complexes and clusters were highlighted in context of g-tensor, D-tensor and hyperfine coupling constants. The extensive literature reviews on the emerging applications of the theoretical methods in magnetism were explored. Finally, the objectives of the present investigation were highlighted.
- In Chapter 2 we studied a set of Mn(III) complexes whose experimental D-tensor values are available. For the calculation of spin-orbit coupling (SOC) the Coupled Perturbed approach gives better results when compared to the Pederson-Khanna method as evident from this chapter. Here the spin-spin and spin-orbit contribution towards the total zero-field splitting was discussed briefly and it was found that the major contribution comes from the spin-orbit coupling effect of ligand environment in a given complex.
- In Chapter 3 considering the basis sets available on the ORCA program package while calculating the magnetic parameters the use of Barone's basis set EPR-III

gives better results along with hybrid functional B3LYP. EPR-II and EPR-III basis sets are exclusively used for EPR studies. This study is conducted on a set of Cu(II) complexes whose magnetic parameters are experimentally available and subsequently we have compared the result with the theoretically obtained values.

- From Chapter 4 we tried to calculate D-tensor and g-tensor of tetra-coordinated $Co[Cl_2L_2]$ complexes using DFT method and correlate their corresponding chemical reactivity with these parameters. Their FMO analysis reveals that complexes with higher chemical reactivity have higher deviation from the free electron g-value.
- Chapter 5 shows that the *ab initio* CASSCF level of calculation in cases of Co(II) with heterodentate ligands give D-tensor values closer to the accurate zero field splitting results while for calculation of hyperfine coupling constants DFT method is more suitable. There is successive increase in the magnitude of D value while coming from CoN_2X_2 to $Co(PPh_3)_2X_2$. Besides these complexes, in another two sets of seven coordinated experimentally prepared Co(II) complexes with dapbh ligand CASSCF method was employed for the study of zero-field splitting parameter. The zero-field splitting obtained by CASSCF yield fairly good results when compared to the experimental values.
- In Chapter 6 $(NiO)_n$ nanoclusters were studied. Most of the geometries exhibited D-tensor with positive values cancelling the chance of such clusters of being single molecule magnets. High magnitude of the D-tensor values is attributed to the possibility of superexchange between Ni atoms via bridging O atoms.
- The Chapter 7 is the last chapter of the thesis which discussed the concluding remarks drawn from the theoretical works with emphasis to the research contributions and its major findings together with pointing out the challenges and directions of possible future scopes which are yet to be explored.

FUTRE SCOPE

Further studies can be done to find more accurate computational methods for prediction of magnetic parameters. In future many additional challenges like treatment of the g-tensor, D-tensor or the hyperfine coupling constant in anisotropic exchange resulting from spin-orbit coupling or spin-spin coupling must be dealt with. Contribution of SOC and SS coupling to the g-tensor or ZFS is required to be predicted more accurately because in case of transition metal complexes the contribution of spin-orbit effect is significant. While employing CASSCF method for multinuclear complexes active space should be more precisely calculated for better results. In some cases the DFT method overestimates the spin-spin contribution towards the zero-field splitting or towards hyperfine coupling constants. In such scenarios multiconfigurational *ab initio* methods may come to rescue. These are some of the few areas in magnetochemistry of transition metal complexes that need more in depth research and insight.