Theoretical investigation of magnetic behaviour in metal-based systems

For the Award of

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Chemistry

By

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GUIDE

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DECLARATION

I declare that the thesis entitled "Theoretical investigation of magnetic behaviour in metal-based systems" has been prepared by me under the guidance of Dr. Anirban Misra, Associate Professor in the Department of Chemistry, University of North Bengal. No Part of the thesis has formed the basis for the award of any degree or fellowship previously.

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ABSTRACT

The first chapter is pervaded with the account of several possible molecule-based magnets with an emphasis on metal containing building blocks. The primary classes of magnetic status in a system are also introduced in brief. In the course of the discussion the huge potential of these new generation magnetic molecules is highlighted with reference to real life applications.

The second chapter is devoted to the different theoretical and experimental techniques to quantify the magnetic interaction in molecule-based magnets. The discussion is centred on the estimation of the exchange coupling constant (*J*), a phenomenological parameter in spin Hamiltonian, introduced by Heisenberg, Dirac and van Vleck. Among a wide variety of methodologies, the broken symmetry (BS) formalism coupled with density functional theory (DFT) is found to come up with the optimum solution for the computation of *J*.

In the third chapter, the effect of chemical composition on the inherent magnetism is put into the focus with $Cr_2O_n^-$ (n = 1,2,3) as the representative system. The presence of more than one electron in the magnetic site Cr makes the implementation of BS-DFT method intricate. Hence, a special effort is given to figure out an appropriate strategy to quantify the magnetic interaction in such cases with multiple electrons in magnetic orbitals. The exchange coupling constant is found to decrease steadily with the formation of new covalent bond due to consumption of unpaired spin.

The crux of the fourth chapter is to investigate the magnetostructural correlation in manganese systems such as neutral Mn dimer, charged Mn dimer and its oxide. Difference of exchange mechanism in these systems is also put under purview. Low value of exchange coupling constant is estimated at a very large and small distance between magnetic sites; whereas in the proximity of equilibrium bond distance the exchange interaction is found to be at its zenith.

The fifth chapter addresses the computational scheme with self contained theoretical basis to estimate the Magnetic exchange coupling constant (*J*) in systems with multiple magnetic sites (SMMS). In the first step of presently devised strategy, the spin density distribution in the ground state of SMMS is obtained. Next, on the basis of this spin mapping, exchange coupling constants between specific pairs are estimated through BS-DFT approach while keeping all other paramagnetic atoms magnetically inactive. Nonetheless, the effect of magnetically inert paramagnetic sites is already taken into account through the use of ground state spin density. We employ this technique to hypothetical benchmark systems, H_3He_3 and H_4He_4 followed by real molecules, cationic manganese trimer, 1,3,5-benzenetriyltris (N-*tert*-butyl nitroxide), and a pentanuclear manganese complex and the results are found to be concordant with the already established nature of magnetic interaction in these systems.

In the sixth chapter, a formalism is developed to quantify the interaction among unpaired spins from the ground state spin topology. Starting from a general Hamiltonian, an effective Hamiltonian is obtained in terms of spin density to compute exchange coupling constants in magnetic systems executing direct exchange. On the other hand, a perturbative approach is adopted to address the superexchange process. This process uses the stabilisation energy for site-to-site charge transfer and the spin density on the involved sites to estimate the extent of spin coupling in superexchange process. Thus, the spin topology turns into a simple and logical means to interpret the nature of exchange interaction.

The key issue of the seventh chapter is the magnetism of all metal aromatic systems (AMAS), which are the latest inclusion in the family of aromatic systems. Among the clusters under investigation, Al_4^{2-}, $Te_2As_2^{2-}$ and their Cu complexes, the molecules which are aromatic only in singlet state are found to manifest antiaromaticity in their triplet state. Hence, in such systems an antagonistic relationship between aromaticity and high spin situation is emerged. On the other hand, in case of triplet aromatic molecules, the magnetic orbitals and the orbitals maintaining aromaticity are found mutually exclusive; hence aromaticity is not depleted in high spin state. The present systems are ideal materials to exhibit nonlinear optical (NLO) behaviour, which inspires the study of NLO response in the same set of clusters with different spin states. The second hyperpolarizability is correlated with spin density, which reveals a high degree of NLO behavior in systems with excess spin density. The variance of aromaticity and NLO response with spin multiplicity is found to stem from a single aspect, the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO); and eventually the interplay among aromaticity, magnetism and NLO response in such materials is established. Such interplay is of crucial importance in tailoring novel paradigm of multifunctional materials.

The eighth chapter sheds light on the possibility of dissociating a bond with applied magnetic field. Since, singlet pairing of electrons gives rise to a covalent bond; the parallel alignment of electron spins is an antithesis to bonding. The spin- parallel situation can be facilitated by magnetic field and thus the covalent bond dissociation can be catalysed with external magnetic field. This possibility is explored theoretically in this work taking simple dimer molecules as references. At the upper vibronic levels, where the bond length is significantly longer than the equilibrium value, the high spin - low spin energy splitting is small enough to be compensated by moderate magnetic field. For example, a magnetic field of 50 Tesla is found to increase the rate of bond dissociation almost four times in Cr_2.

The concluding remarks are put in the ninth chapter. In this chapter, the objectives of the present thesis, as explained in the first chapter are harnessed with the conclusions drawn in the chapter two to eight. The significance of the present investigation on the magnetism of metals-based systems is also highlighted in the same chapter.

PREFACE

This rapidly evolving technological world requires smart materials. To fabricate such multifunctional materials, molecular magnet is a unanimous and ubiquitous choice. Once the quantum chemical origin of magnetism becomes clear, it becomes easy to tune the property or to synthesize molecules with desired degree of magnetism. Since, the magnetic status depends on the interaction among unpaired electron spins; it requires an appropriate theoretical framework to find out the mechanism of such interaction followed by its quantification. The metal-based molecules offer interesting yet intricate magnetic systems, which are awaited for a proper theoretical underpinning about the complicated interaction among their multicentre multielectronic magnetic sites. These factors inspire the need of present investigation. To start with, a proper classification of building blocks of molecular magnets seems necessary to decipher the varieties of mechanism through which the spins interact. A crisp discussion about the categories of metal-based magnetic molecules is thus made in the first chapter. There exist a plethora of theoretical frameworks through which the quantum chemical nature of magnetic interaction is unveiled. In spite of so many formalisms, there are subtle factors which inhibit the general applicability of the state-of-the-art techniques. These several theoretical constructs are illustrated in chapter 2. The bottleneck in the established methods to deal magnetism in metal-based magnetic molecules and the consequent requirement of a new theoretical approach is illustrated in this chapter. Tuning of magnetism by varying the chemical composition has been the epitome of many theoretical and experimental works. However, explanation of such behaviour through quantum chemical study is fragmentary in nature and requires attention. This issue has been addressed in the third chapter where the change in magnetic behavior of dichromium oxide anions with increasing the proportion of oxygen is put under review. In the fourth chapter magneto-structural correlation is exercised on three different manganese systems Mn_2, Mn_2^+ and Mn_2O^-.This study claims a special importance as it concludes about the controversial electronic structure of manganese clusters. Due to simultaneous existence of several magnetic exchange interactions, the estimation of magnetic interaction becomes even more complicated. The theoretical methods already in practice have many limitations, which urges for coining an easier and sound computational scheme. This task is performed in the fifth chapter. The importance of spin topology in predicting the magnetic nature of a system, as understood from the fifth chapter as well as existing references, prompts for estimating magnetic interaction in terms of spin density. The spin density is an experimentally achievable quantity. Hence, this exercise of spin density parameterization, shown in the chapter six, can aid the prediction of magnetic behavior directly from experimental data. The magnetism in any material is the total manifestation of the interaction among spins. So, other electronic properties, in case controlled by spin, can have an intimate correlation with magnetism. In this way, multiple properties can be stitched together in a single molecule making it an appropriate precursor for multifunctional material. The additional advantage in such materials is that a single switch “spin” is enough to modulate all the properties. Thus, the interplay among three important properties, aromaticity, non linear optical response and magnetism, is explored in the seventh chapter. Following the same venture, the magnetic status in a molecule is expressed as a function of the bond strength in the chapter eight. Such correlation between the bond strength and inherent magnetism can logically sermonize for the possibility of catalyzing the bond dissociation by the magnetic field. In the final chapter, the essence of preceding chapters and the significance of the present study are surmised. In spite of the ample cultivation of the topic “molecular magnets”, this study is deemed to touch a few of the shaded corners of this field of research and facilitate a clear understanding of the magnetism in metal-based magnetic systems.

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APPENDIX A: List of Publications

PUBLISHED

1. **Paul, S.**; Goswami, T.; Misra, A.; Chattaraj, P. K. Concurrent loss of aromaticity and onset of superexchange in Mg_3Na_2 with an increasing Na - Mg_3 distance, *Theor. Chem. Acc.* **2013,** DOI: 10.1007/s00214-013-1391-3.

2. Shil, S.; **Paul, S.;** Misra, A. Charge transfer induced magnetism in mixed-stack complexes, *J. Phys. Chem. C* **2013**, *117*, 2016–2023.

3. **Paul, S**.; Misra, A. Interpretation and quantification of magnetic interaction through spin topology,*J. Chem. Theory Comput.* **2012,** *8*, 843-853.

4. **Paul, S**.; Misra, A. Interplay among aromaticity, magnetism and nonlinear optical response in all-metal aromatic systems, *Inorg. Chem.* **2011,** *50*, 3234-3246.

5. **Paul, S**.; Misra, A. Exchange interactions in systems with multiple magnetic sites, *J. Phys. Chem. A.* **2010,** *114*, 6641-6647.

6. Sarkar, S.; Shil, S.; **Paul, S**.; Misra, A. On protonationa and methylation of benzene: a B3LYP DFT based study,*J. Mol. Struct. (THEOCHEM)* **2009,** *916*, 154-158.

7. **Paul, S**.; Misra, A. On magnetic nature of Mn clusters, *J. Mol. Struct. (THEOCHEM)* **2009,** *907*, 35-40.

8. **Paul, S**.; Misra, A. Magnetic properties of $Cr_2O_n^-$ clusters: a theoretical study, *J. Mol. Struct. (THEOCHEM)* **2009,** *895*, 156-160.

COMMUNICATED

1. Goswami, T.; **Paul, S.**; Misra, A. Effect of charge transfer and periodicity on the magnetism of $[Cr(Cp^*)_2][ETCE]$.

2. Sinha, B.; Goswami, T.; **Paul, S.**; Misra, A. The effect of size and symmetry on the optoelectronic properties of Cu_2O nanoclusters.

APPENDIX B: Acknowledgement

Once told by Socrates "I know that I know nothing and I don't know what I know". It is this quest for known and unknown, what makes a being "human" and I bow to thee for befitting me for such a pursuit. In this voyage of mine through the darkness of ignorance, the person who has always been lending his finger to hold on is my guide Dr. Anirban Misra. I am grateful to Dr. Misra for his never-ending patience to bear with my utopian work plans. It goes without saying, that I am indebted to my family members who kept me alive by providing all my basic needs. In this occasion, I would also like to express my gratitude to all my colleagues in Darjeeling Polytechnic for their constant support and encouragement. My fellow lab mates also deserve a warm and cordial thank, with whom I have savoured this exciting journey of anguish and ecstasy; failure and success; knowledge and ignorance. Finally, I owe to all of my teachers, who taught me not only to read the lines but also in between the lines and set my ego suitable for such a journey for scientific truth. Last but not the least; I must mention of my parents and my Dada who taught me the first lesson and without whom I could not reach this destination.

CHAPTER 1

Molecule-based magnets

Abstract:

In this chapter, different types of magnetic materials are introduced and the genesis of magnetism in such systems is briefly discussed. Starting from the ancient paradigm of magnets such as load stone, the discussion rolls down to the need of novel kind of magnetic materials. With this introduction to the field of "Molecular Magnetism", tremendous applicability of these new generation magnetic molecules is highlighted as well. The historic achievements in this field are cited with the mention of first synthesized molecule-based magnets of various kinds. The second part of the chapter deals with the several possible building blocks of molecule-based magnets ranging from organic to inorganic domain. This discussion itself advocates that large number of unpaired spins in metals causes an interesting yet complicated nature of magnetism in molecules from inorganic domain. This intricate and intense magnetism in metal-based systems need a special attention and calls for detail theoretical exploration.

1.1

INTRODUCTION

1.1.1 History

Since antiquity, magnets have been amazing for their unique properties. From the day, when lodestone was discovered, inquisitive minds are looking for the reason of such fascinating behavior of magnetic materials. Before entering into the vivid domain of magnetism, a brief discussion on the origin of magnetism might help to make the description a lucid one. The quantum mechanics of electrons is described by Dirac equation which speaks that electrons have an additional degree of freedom, known as 'spin'. The mathematical form of a "spin" is angular momentum and the genesis of magnetism is considered to be inherent within the interaction of such spins. Magnetism can be divided into two groups. In one group, either there is no net spin moment or there is no interaction between the individual spin magnetic moments and each moment acts independently of the others. Congeners belonging to these groups are referred to as diamagnets and paramagnets respectively. In the other group, the individual moment couple to one another and form magnetically ordered materials. The coupling, which is quantum mechanical in nature, is known as the exchange interaction and is rooted in the overlap of electrons in conjunction with Pauli's exclusion principle. Most of the well known magnets are based on the compounds of iron, cobalt, nickel, gadolinium etc. which are ferromagnetic i.e. having unpaired spins in parallel orientation in their bulk state. The situation, where each spin is aligned antiparallel to its nearest neighbors, gives rise to antiferromagnetism. Metal compounds, MnO, MnF_2 or NiO are the archetypes of antiferromagnetic materials. In case, the numbers of antiparallel and parallel pair of spins are different or the antiparallel aligned spins are of unequal magnitude, a remnant magnetization develops in the material. These are defined as ferrimagnets of which the best example is magnetite, Fe_3O_4. The intrinsic magnetic character of a material is manifested through its response to another external applied magnetic field. In 1839, Faraday published the first picture of the lines of magnetic flux around a magnetic material and iron was the only element which could then expected to show such flux. The change in the density of line of magnetic flux in a material in presence of magnetic field is related to the susceptibility, which is defined as the induced magnetic moment per unit magnetic field. The ferro, antiferro or ferrimagnets undergo a phase transition to the paramagnetic state where the spins are in random orientation, and the nature of magnetism is revealed from the susceptibility vs. temperature plot. The critical temperature corresponding to the inflection point of susceptibility curve is referred to as the Curie temperature (T_C) and Neel temperature (T_N) in case of ferro and antiferromagnetic materials respectively (Figure 1.1). A variety of substances is gradually explored which can exhibit spontaneous magnetization. Over the past decades, enough evidences have been accumulated which tells that some living organisms respond to the geomagnetic field.[1] In addition to the homing experiments with pigeons, Moore has reported direct visual evidence that the orientation of free-flying nocturnal migrants is affected by fluctuation of geomagnetic field.[2] This geomagnetic field governed movement, termed as magnetoreception, stems from the existence of *in vivo* magnetic particles. Under the microscope, many organisms have now been found to have at least some kind of magnetite embedded in them including homing pigeons, tuna, honey bees, dolphins, whales and green turtles.

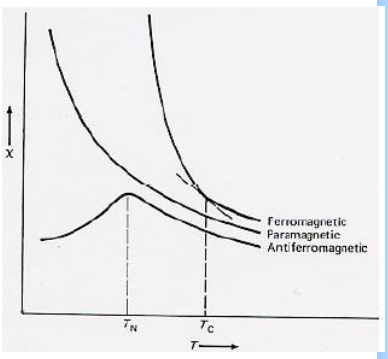

Figure 1.1 Susceptibility vs. Temperature curve for ferro, antiferro and paramagnetic materials.

However, to cope up with the necessities of rapidly evolving technological world, the human civilization sets out the quest for novel kind of materials which will have a tunable magnetism, purpose oriented design, and can be fabricated in laboratory. This endeavor to explore beyond naturally occurring magnets is ended up with the invention of molecule-based magnets. A most pragmatic picture of this topic is obtained from the definition of the Olivier Kahn who defined that "*Molecular Magnetism* deals with magnetic properties of isolated molecules and/or assemblies of molecules". The history of molecule-based magnetism started early in the year 1951 with Cu (II) acetate monohydrate (Figure 1.2).[3]

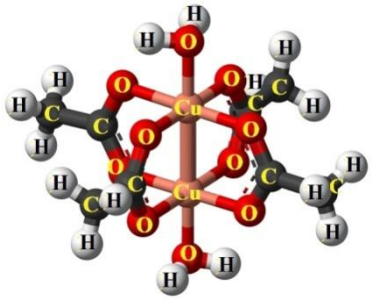

Figure 1.2 Copper Acetate Monohydrate

Research in this field soon received an impetus when Wickman and co-workers synthesized and characterized the first molecule-based magnet diethyldithiocarbamate-Fe (III) chloride compound Fe (Cl) $[S_2CN\ (C_2H_5)_2]_2$, in the year of 1972.[4] This compound was found to have ferromagnetic ordering at 2.43 K. Till then, a plethora of molecular magnets have been developed, where the building blocks are either inorganic, organic or a combination of two. The basic components in most of the inorganic building blocks are transition metals with a large number of unpaired spins which contribute to the net magnetic moment. In case, the magnet contains lanthanides, the unpaired electrons reside on metal *f* orbitals. On the other hand, in purely organic species those unpaired spins would reside in highly localized non bonding molecular orbital (NBMO) with a dominant *p* character. The synthesis and characterization of charge transfer (CT) ferromagnetic compound $[Fe(Cp^*)_2][TCNE]$ ($Cp^*= \eta^5\text{-}C_5Me_5$ and TCNE= tetracyanoethylene) by Miller et al. in 1985 is the first reported complex where the unpaired electron of *p*-orbital participates in the exchange interaction.[5] This is the first reported metallocene based magnet as well. Organic polyradicals are the common starting materials for developing purely organic magnets.[6] The first ever bulk organic ferromagnet, p-nitronyl nitroxide had been made by Kinoshita and co-workers.[7] Like conventional magnets, molecular magnets may be classified as hard or soft, depending on the magnitude of the

coercive field. The mechanism by which molecule-based magnets stabilize and display a net magnetic moment is different kind of exchanges among spins.[8] Around 1980's, when the subject *Molecular Magnetism* started to take a shape, much of the effort had been directed to grow magnets with high Curie temperature. However, with the gradual development of this area, new challenges appeared at the horizon, which include development of multifunctional magnetic materials or nanostructured magnets. To meet these requirements, knowledge in co-ordination Chemistry or in a broader sense, Inorganic Chemistry becomes almost indispensable.[9]

1.1.2 Applications

Molecule based magnets are multidimensional in their uses because of their unique properties such as light weight (plastic magnets), solubility in organic solvents, optical transparency etc. Micro electronics, electronic circuits and devices are decreasing in size and weight and will eventually reach the molecular dimension which can be made possible through spin based electronics *i.e.* spintronics. This behavior is guided by giant magnetoresistance (GMR) of magnetic multilayered structures, where two magnetic layers are closely separated by a thin spacer of the order of few nanometers.[10] These kind of materials are already being realized for application in high density data storage devices and IBM is the first one to market the hard disk based on this technology. In magnetic memory devices, logical bits (''ones'' and ''zeros'') are stored by setting the magnetization vector of individual magnetic domains either ''up'' or ''down". Information storage devices need magnets in which the magnetic moment can be oriented through an external magnetic field ("writing of information") and the orientation is retained after removal of the field ("storage of information"). Further a suitable sensor retrieves ("reading") that particular information as orientation of the magnetic moment.[11] The glorious domain of information technology is led by a quest for making storage devices smaller and smaller. Single-molecule magnets encourage a huge opportunity owing to their potential applications in high-density information storage, quantum computing, and magnetic refrigeration.[12] Electron transport through molecules conneted to two metallic leads can be manipulated with spins and thus nanoscale magnetic molecules turns out to be the appropriate materials for use in spintronics. Along with spintronics; photomagnetsim *i.e.* photo switching of magnetic properties is also being used commercially as in optomagnetic amplifier. Magneto-optical disks also have a higher data density than conventional disks. In the magneto-optical effect, the magnetization of the medium is changed when irradiated by a high power laser beam. The polarization of the region of disc can be read back by measuring the polarization of reflected light from a lower-powered laser. The degree of polarization is dependent on the magnetization of the target area. The occurrence of charge transfer in organoligand-metal fragments is found to induce a high dielectric polarization and concomitant intense nonlinear optical (NLO) response.[13] It is also worth mentioning that molecular magnetism can act as a bridge between two apparent isolated areas which are material science and biological processes as it has immersed as a newer research field known as biomagnetism. For instance, the interaction between Fe (III) and Cu (II) in cytochrome *c* oxidase is exactly of the same nature as the interaction between Mn (II) & Cu (II) ions in a ferrimagnetic chain compound exhibiting a spontaneous magnetization at low temperature. Such a biocompatibility of magnetic molecules can be well used in magnetic imaging and transducers in medical implants. Biomedicines, when tagged with magnetic nanoparticles (NPs) can be used in regioselective drug delivery.[14] The hysteresis loop recorded in the magnetic NPs shows saturation magnetization but no coercive field or remnant magnetism is observed synchronously. This behavior is termed as superparamagneism. This is due to the fact that in such a small particles, because of the

thermal fluctuation the magnetic moments are free to rotate despite the magnetic energy barrier. This characteristic allows a promising future in application of magnetic nanocomposites in biomedicine especially in magnetic resonance imaging (MRI). Gadolinium (Gd) and other paramagnetic metal ions are used in MRI contrast agents in the present medical science. However toxic effect of Gd ion due to accidental *in vivo* dissociation of the Gd chelate cannot be avoided causing renal failure of patient after MRI investigation. An alternative way is to use stable organic radicals, which are non-toxic, water soluble and more biocompatible than metals. Use of nitroxyl or aminoxyl based diradicals as organic MRI contrast agents have already been advocated experimentally and theoretically.[15] When exposed to a radiofrequency magnetic field parallel to a strong static field, ferromagnetic NPs may be energized. In this phenomenon, known as ferromagnetic resonance, the heat generated is sufficient to destroy diseased cells. This technique is recently being opted for cancer treatment and defined as hyperthermic oncology. In recent works, the field induced temperature rise in Yttrium Iron garnet has been evaluated through spin wave theory.[16] However, at present wide application of these molecular magnets is a bit difficult because of very low critical temperature. In this regard the applicability of molecular magnets resembles that of super conductors.

1.2

BUILDING BLOCKS

1.2.1 Organic Radicals

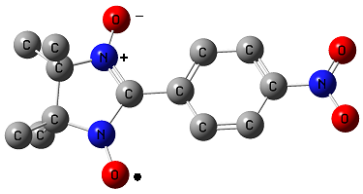

Figure 1.3 The *β*-crystal phase of *p*-nitrophenyl nitronyl nitroxide (H's are not shown for clarity)

The engineering of molecular magnets has spawned interest in organic radicals as new building blocks of molecular magnets. However, for the high reactivity of such polyradicals, only a few organic paramagnetic species have been found suitable for the design of organic molecular ferromagnets.[17] Among different types of stable organic radical, the family of nitronyl nitroxide has gained maximum popularity. The synthesis and characterization of this family had been pioneered by Ullman.[18] The search for ferromagnetic organic systems leads to the invention of *β*-crystal phase p-nitrophenyl nitronyl nitroxide (Figure 1.3) by Kinoshita and co-workers in 1991.[7] Other stable nitroxide organic radicals showing ferromagnetic interactions have been found, including those based on imino nitroxides and TEMPO [TEMPO = 2,2,6,6 tetramethyl-piperidinyl-1-oxy].[19] The nitronyl nitroxide diradical with ethylene coupler has been extensively studied by Ziessel et al.[20] Normally, the magnetic interaction between two radical centers depends on the distance and the nature of the coupler.[21] To design molecular magnets, active verdazyl moiety, which is essentially resonance stabilized hydrazyl radical, is a viable alternative to nitronyl nitroxide. Verdazyl radical was first synthesized by Kuhn and Trischmann in early 1960s.[22] Verdazyl molecule and its various derivatives have been synthesized by Gilroy et al.[23] Nevertheless, its potential as a precursor of molecular magnets remained unnoticed for long.[24] Non-Kekulé bis-oxoverdazyl diradical remains in singlet ground state with a small amount of thermally populated triplet.[25] Brook et al. have extensively studied its electronic properties and found strong antiferromagnetic coupling among unpaired spins.[26] Azidophenyl substituded verdazyls have been prepared by Serwinski et al.[27] Substitution of the

oxygen atom of oxoverdazyl moiety with less electronegative sulfur atom gives thioverdazyl radical moiety with a notable variation of electron density from its oxo-analogue. In case of phosphaverdazyls, one of the skeleton carbon atoms of verdazyl radical is replaced by phosphorus atom.[28] The intramolecular magnetic exchange coupling constants have been theoretically studied for a series of tetrathiafulvalene (TTF) and verdazyl diradical cations bridged with some aromatic and linear π-couplers by Polo et al.[29] However, all these organic diradicals are not expected to have a high degree of T_c because of less number of spins. Hence, to have a sustainable magnetism, organic polyradicals can be the potential candidates. A high T_c (16.1 K) organic system tetrakis (dimethylamine) ethylene fullerene (TDAE-C_{60}) has been synthesized by Wudl and coworkers.[30] Macrocycles based upon calyx[4]arenes have also been utilized as effective plaquette for high spin polyradicals (Figure 1.4).[31]

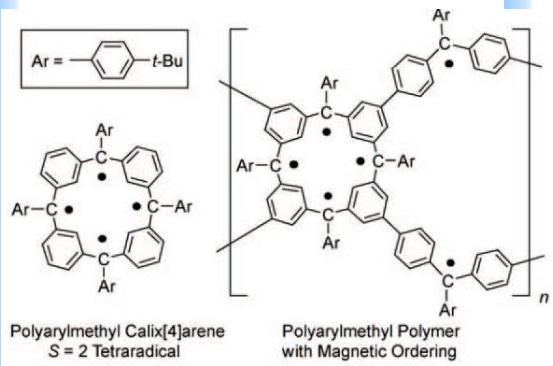

Figure 1.4 Examples of high spin organic polyradical.

1.2.2 Metal Clusters

The clusters are ensemble of bounded atoms intermediate in character and size between a molecule and a bulk solid. Their reduced dimensionality causes a significant change of energy ordering near Fermi surface due to increased surface to volume ratio and develops magnetic moment in the clusters. For this, many transition metal clusters, which are diamagnetic in their bulk phase turn into strong ferro or antiferromagnetic species at their reduced dimension. Metal clusters like Mn^{5-}, Cr_2O^{n-} are the ideal examples of this category.[32] The search for the magnetic behaviour in the so-called non-ferromagnetic transition metals became exciting with the findings by Cox et al. who observed non-zero magnetic moment for rhodium clusters.[33] Such observations were also made for manganese clusters[34] and chromium clusters.[35] Surveys at the Virginia university revealed "anomalous" magnetic ordering in clusters of nonferromagnetic transition metals, specifically V_n, Ru_n, and Pd_n.[32, 36] However, in the above cases, ferromagnetism was found to be absent in the bulk phase of such metals.[37] The magnetism in these transition metal clusters is actually size specific and grows more and more with reduced dimension.[38] In a series of molecular beam studies beginning around 1990, de Heer[38] and Bloomfield[39] demonstrated that Fe_n, Co_n , and Ni_n clusters ($n \approx 100–1000$) undergo deflections toward high field in a gradient (i.e., Stern–Gerlach Magnet). Their results showed that these clusters are superparamagnetic monodomain particles that undergo internal spin relaxation as they are passed through a magnetic field. These molecular beam studies are aimed to map out the atom-by-atom evolution of cluster magnetic moments from the molecular size domain toward the bulk limit, to investigate magnetic phase transitions in systems with reduced dimensions.

1.2.3 Bridged Metals

Coordination compounds, where the metal magnetic sites are bridged via diamagnetic ligands have been the most widely cultivated starting materials for metal-based magnets.[40] Metal binuclear compounds with a wide variety of bridging ligands such as chloro, azido, oxo, hydroxo, oxalato or more complex bridges have received much attention for their interesting magnetic properties. In this series of compounds, Cu (II) acetate hydrate dimer is the most primitive and cultivated one.[41] In the year 1952, Bleaney and Bowers were the first one to explain the antiferromagnetism of the said complex.[3] Though bridged Cu (II) dimers are usually reported to have antiferromagnetic nature, example of ferromagnetically coupled Cu (II) dimers are not entirely rare. $Cu_2Cl_4(CH_3CN)_2$, synthesized by Willett and Rundle is one such example.[42] In these compounds, not only the metals but also the bridging ligands and bridging geometry take a leading role in the overall manifestation of magnetic properties. Metal-Bridge-Metal bond angle has a profound effect on the resulting magnetism of such compounds. In a work, Staemmler and coworkers could find maximum ferromagnetism for Ni-S-Ni angle in between 85° and 100 °.[43] The same group extended their effort to understand the nature of magnetism in oxo-bridged hetero bi-metallic dimers.[44] Magneto-structural correlation for Cr (III) dimers with the double hydroxo bridge is also established.[45] Recently, some reports have been devoted to correlate the experimentally determined magnetic coupling constant to the bridging geometry of oxo-bridged Fe (III) dimers.[46] Oxo-bridged Fe (III) dimer exists *in vivo* in proteins of oxygen carriers such as ribonucleotide reductase and hemerythrins. Here, Chen et al. noted no change in magnetic interaction with the variation of Fe – O – Fe bond angle, but rather expressed the magnetic coupling as a function of Fe – O distance.[47] Magnetism of these interesting compounds is theoretically addressed by Hart et al.[48] A special class of complexes is constituted by $M[N(CN)_2]$, where M = Mn, Fe, Co, Ni, Cu, where the metal spins are neither parallel or antiparallel to each other, rather someway canted between these two directions.[49] The azido is an another versatile ligand which can bridge two metals in different coordination modes and hence effect the magnetic interaction between metal spins.[50] There are two main modes through which the azido group can bind the metals: either in a end-to-end (μ – 1,3) fashion or in a end-on (μ – 1,1) fashion. The end-to-end bridge is most commonly observed with extended ligand, as in the dinuclear oxovanadium (IV) complex, where the metals are ferromagnetically coupled through pyrimidine derivative.[51] To modulate magnetic status, this class of materials is the best option for its chemical versatility.

1.2.4 Metal – Organic radical conjugates

The interaction of transition metals with organic radicals has currently received much attention, probably due to the extra stability of organic polyradicals, when attached to metals.[52, 53] Also, organic polyradical – high spin metal conjugate are promising precursors for high T_c ferromagnets. Another driving force behind the fabrication of organomedical radicals is the existence of such systems in the active site of metalloproteins.[53] The best example having been the galactose oxidase where a Cu(II) ion is coordinated to a modified tyrosyl radical.[52] Among the other paramagnetic ligands in this regard are nitroxide and verdazyl radicals.[54, 55] The first verdazyl complexes of paramagnetic Ni ions which exhibit a strong ferromagnetic behaviour have been prepared by Hicks et al.[56] In the $CuBr_2$(TEMPO), the ligand is exceptionally bound to metal in a η_2 fashion rather than binding to oxygen only.[57] Taking an extensive series of [CpNi(dithiolene)], Fourmigu et al. demonstrated that cyclopentadienyl (Cp) ligand with significant spin density can act as a non-innocent ligand in inducing magnetic interaction.[58] This Cp ligand in metallocenes also plays a crucial role in dispensing the spin to an organic acceptor moiety. In this class of systems, the magnetic interaction is set in through such electron transfer from donor to acceptor unit. Prussian blue

related compounds[59] are old example of such charge transfer complexes.[60] Charge transfer salts of the type $MCp^*_2[TCNE]$ with a variety of transition metals (M) like Cr, Mn, or Fe are synthesized and characterized as ferromagnetic complexes.[61] In early 1990's, the 3D coordination polymer $V[TCNE]_x.yCH_2Cl_2$ was discovered which shows magnetic ordering near room temperature.[62] The ferromagnetism of such complexes was retained with different acceptors such as [DMeDCF] (DMeDCF = dimethyl dicyanofumarate), [ETCE] (ETCE = ethyl tricyanoethylenecarboxylate) and so on. Yee and coworkers developed $CrCp^*_2[DMeDCF]$, $MnCp^*_2[DMeDCF]$,[63] and analogous series of $[M(Cp^*)_2][ETCE]$ with M=Cr, Fe, Mn; all of which were found to have ferromagnetic ordering.[64] Similar systems like $[Fe(Cp^*)2][TCNQ]$ (TCNQ= dicyanoquinodimethane), and $[Mn(Cp^*)_2][DDQ]$ (DDQ= 2,3-dichloro-5,6-dicyanoquinone) exhibit metamagnetism.[65] $[BDTA]_2$ $[Cu\ (mnt)_2]$, (where BDTA = benzo – 1,3,2 – dithiazolyl and mnt = maleonitriledithiolate) has been synthesized and characterized as an ideal one dimensional Heisenberg antiferromagnetic material.[66] A similar anion $[Pt\ (mnt)_2]^-$ when stabilized with $[4\text{-R-benzylpyridinium}]^+$ cation (R = Cl, Br, NO_2) shows an interesting phase transition from paramagnetic to diamagnetic at several temperature range.[67] Cooperative magnetic properties of linear chain alternating donor/acceptor complexes have been the focus of contemporary study. Although, the mechanism of charge-transfer processes within the molecular scale has been fairly cultivated in such complexes, [68] their proper magnetic characterization is still in its infancy.

1.2.5 Single Molecular Magnets.

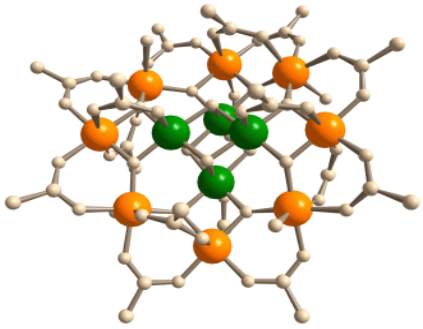

Figure 1.5 Crystal structure of single molecular magnet $Mn_{12}Ac$. Orange and green colors signify Mn(III) and Mn (IV) respectively.

Molecules with large total spin angular magnetic moment, which can be magnetized individually, belong to a very special class of magnetic materials, termed as single molecular magnet (SMM) by Hendrickson.[69] SMMs are characterized by an exceedingly slow paramagnetic relaxation at low temperature. At very low temperature, the magnetization in these molecules can be oriented in a particular direction for a long time. In 1993, the first SMM, the compound $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot\ 4H_2O\cdot\ 2CH_3CO_2H$, was discovered,[70] which contains eight Mn (III) sites antiferromagnetically coupled to four Mn (IV) sites, resulting in a S =10 ground state (Figure 1.5). The relaxation time of the magnetization in Mn_{12} is usually as long as about two months at 2 K. Consequently, magnetic hysteresis cycle for these molecules resemble to that observed in bulk magnets. Variable field magnetization and high-frequency electron paramagnetic resonance (HFEPR) data indicate that this complex has an S =10 ground state.[71] Mn_{12} based wheel was first reported by Rumberger et al.[72] The smallest molecule of this type is the tetranuclear manganese complex, reported by Beedle et al.[73] The larger wheels include the the Mn_{22} wheels,[74] Mn_{24} wheel,[75] and the Mn_{84} wheel.[76] The largest spin ground state for a wheel-shaped SMM is S = 14 for the Mn_{16} wheel reported by Manoli et al.[77] in 2007. A high spin ground state of Mn atom has thus enabled several

other research groups to enrich the realm of Mn-based SMM.[78] Next to manganese, the metal which has been widely used in forming SMM, is iron.[79] Among these, the most widely studied complex is the Fe_8 system, $[Fe_8O_8(OH)_{12}(tacn)_6]Br_8 \cdot 9H_2O$ (tacn = 1,4,7-triazacyclononane), with the same spin as Mn_{12} (S = 10).[80] Though rare, there are also instances of SMMs containing cobalt and vanadium ions.[81] An example of Co based SMM, $[Co_4(hmp)_4(MeOH)_4Cl_4]$ is reported by Yang et al.[82] Opposed to the polynuclear metal cluster, few mononuclear species are also showing the amazing ability of slow magnetic relaxations. The first of two such cases are phthalocyanine (PC) double-decker complexes with Tb (IV) and Er (III), encapsulated in a polyoxometalate framework.[83] Also, Jiang et al. reported a mononuclear Dysprosium complex $[Dy(acac)_3(H_2O)_2]$ featuring SMM behaviour.[84] The first *3d* mononuclear complex, containing tetracoordinate Fe (II) center was obtained by Long and coworkers.[85] Polymeric linear chains with paramagnetic centers are few well-known examples of molecule-based magnets having a combination of organic and inorganic molecules.[86] Mrozinski and co-workers have synthesized and characterized two dimensional polymer of formula [Cu(pyridine-2-carboxylate)Cl], where the Cu(II) ions are ferromagnetically coupled through dichloro and *syn-anti*-carboxylate bridges.[87] Last decade has witnessed an emerging interesting the fabrication of such systems with multiple magnetic sites (SMMS) beyond the limit of much cultivated systems with two magnetic sites.[88]

The foregoing discussion sheds light on the versatility of molecular magnetism. Amongst all, the metal systems emerge as significant congener in the family of moleule-based magnets. Presence of large number of unpaired electrons in metal systems makes their magnetism intense. The intricate interaction among spins entails special attention and calls upon the need of present theoretical investigation.

1.3

OBJECTIVES OF THE THESIS

Magnetism is induced in a material through the coupling of its inherent spin moments. It requires an keen attention to work out an appropriate theoretical framework to quantify the interaction among spins. Especially, in the inorganic systems, the theoretical explanation about the origin and degree of magnetism becomes further complicated due to the multicentre multielectronic magnetic sites. Keeping these factors in mind, the present thesis is aimed to cultivate the objectives, which are summarized as follows.

1) The systems with more than one unpaired spin per magnetic site leads to the possibility of several states with different spin multiplicities. Hence, it becomes important to properly select the ground state spin multiplicity prior to the estimation of magnetism. Consequently, addressing the ferro or antiferromagnetic status of that ground state also becomes complicated. Here, we make an attempt to sort out the intricacy of this problem.

2) Synthesis of molecules with multiple magnetic sites, each with large magnetic moment has made possible the genesis of single molecular magnets. The SMMS, mostly being organic polyradicals[89] or polynuclear transition metal complexes,[69, 90] have the possibility of simultaneous existance of magnetic interactions which makes the estimation of magnetic interaction much more complicated in such systems. Hence, a proper and easier treatment of the complex magnetic interactions in SMMS is attended.

3) The state-of-the-art formalisms use the expectation value of $\langle \hat{S}^2 \rangle$ in the ferro and antiferromagnetic states to estimate the degree of magnetic interaction. However, it is not always straight forward to estimate the parameter $\langle \hat{S}^2 \rangle$, especially in antiferromagnetic condition. Valero et al. concluded that this spin square term should not always be used as a reliable indicator of the success of a given calculation.[91] These facts necessitate the modification of existing methodologies for estimating the interaction among spins.

4) In the last part of this work, the effect of spin on different other properties are explored. Since, magnetism is an obvious outcome of the interaction among spins, any other property being regulated by spin can be correlated with magnetism. This correlation can be an effective guide in rational design of a smart material with multiple functionalities.

1.4

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CHAPTER 2

Quantification of Magnetism

Abstract:

This chapter is devoted to the different theoretical and experimental techniques to quantify the magnetic interaction in molecule-based magnets. The phenomenological spin Hamiltonian, introduced by Heisenberg, Dirac and van Vleck is found to be the cornerstone in all the theoretical models aimed to estimate the magnetic interaction. The parameter, exchange coupling constant (*J*) in this Hamiltonian is accepted as the best descriptor of magnetic interaction till date. For the determination of this constant, a variety of formalisms have been evolved, which are described here with their merits and demerits. The performance of different computational methodologies in deriving exchange coupling constant is also reviewed. Among these methodologies, the density functional theory is found to provide an optimum adjustment between accuracy and computational rigor. This chapter also sheds some light on several experimental methods available to extract the exchange coupling constant.

2.1

THEORETICAL METHODS

2.1.1 Spin Hamiltonian

In 1928, Heisenberg realized that the strong coulomb repulsion between the electrons does not explicitly depend upon the spins. Two electrons with parallel or antiparallel spins behave differently, even though the fundamental interaction is the same. There exists a miscellany of exchange mechanisms such as direct exchange, indirect exchange, double exchange, superexchange and so on, through which the spins can interact.[1] Direct exchange operates between spin moments, which are close enough to have sufficient overlap of their wavefunctions. It gives a strong but short range coupling which decreases rapidly as the spin sites are separated. Superexchange describes the interaction between spins on sites far apart to be connected by direct exchange, but coupled over a relatively long distance through a non-magnetic bridge. In fact this mechanism acquired the name superexchange because of the relatively large distance among the magnetic sites. The mechanism of superexchange was first introduced by Kramer.[2] Indirect exchange is the phenomenon of coupling of conduction electrons with localized spins in a metal. Indirect exchange couples spin moments over relatively large distances. It is the dominant exchange interaction in metals, where there is little or no direct overlap between neighboring electrons. It therefore acts through an intermediary, which in metals are the conduction electrons (itinerant electrons). This type of exchange is better known as the RKKY interaction named after Ruderman, Kittel, Kasuya and Yoshida. On the other hand coupling of two localized spins through an itinerant electron is defined as double exchange. In case of the mixed valence systems, where metal centers are present with different oxidation states, Anderson and Hasegawa introduced the concept of double exchange.[3] However, irrespective of the exchange mechanisms, the exchange interactions are usually quantified through the phenomenological Heisenberg-Dirac-van Vleck (HDVV) spin Hamiltonian,

$$H = -J_{ij}\hat{S}_i.\hat{S}_j \tag{2.1}$$

where, $\hat{S}_i$ and $\hat{S}_j$ are the spin angular momentum operators on magnetic sites *i* and *j* and J_{ij} is the exchange coupling constant between them. The first spin Hamiltonian in the literature was presented by van Vleck in his famous book in 1932.[4] This Hamiltonian becomes popular as "Spin Hamiltonian" since this only involves the spin degrees of freedom.

2.1.2 Estimation of exchange coupling constant (J)

There is one-to-one correspondence between the eigenvalues of Heisenberg Hamiltonian and those of the exact Hamiltonian, because both the Hamiltonian commutes with the spin square operator. For, a diradical, the possible lowest energy electronic states are singlet (S = 0) and triplet (S = 1), which are the eigen states of Heisenberg Hamiltonian. Let, in the dimer A – B, the spins are localized in the orbitals ϕ_a and ϕ_b, and the molecular orbitals (MO) formed through linear combination of these orbitals are

$$\phi_1 = \frac{1}{\sqrt{2}}(\phi_a + \phi_b)\,, \tag{2.2}$$

and

$$\phi_2 = \frac{1}{\sqrt{2}}(\phi_a - \phi_b). \tag{2.3}$$

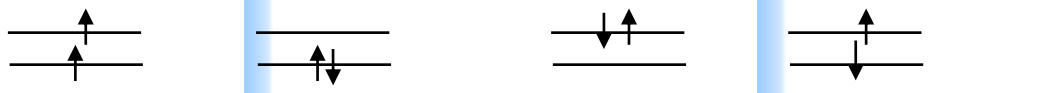

Figure 2.1 Multi-electronic configuration for two electron in two MO

There are several possibilities of electron distribution in these two MOs giving rise to following multi-electronic configurations (Figure 2.1), where, the overbar denotes the occupation with spin-down electrons. The lowest singlet state of the system (Ψ_s) is an approximately equal mixture of S_1 and S_2, while the lowest triplet state is Ψ_T. Since, S_3 is in different symmetric form compared to S_1 and S_2, this state corresponds to an excited state much higher in energy. Hence, the quantity of interest, the singlet-triplet splitting, becomes

$$E_T - E_S = J_{12} - \frac{1}{2}(J_{11} + J_{12}) + \frac{(h_1 - h_2)^2}{2K_{12}} \tag{2.4}$$

where,

$$h_i = \int \phi_i^*(1)\hat{h}\phi_i(1)dr_1$$

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2)\frac{1}{r_{12}}\phi_i(1)\phi_j(2)dr_1dr_2$$

$$K_{ij} = \int \phi_i^*(1)\phi_j^*(2)\frac{1}{r_{12}}\phi_j(1)\phi_i(2)dr_1dr_2.$$

Now, if orthogonal localized MOs are defined as $\phi_a = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$ and $\phi_b = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$, in terms of these orbitals,

$$\begin{aligned} J_{11} &= 1/2(J_{aa} + J_{ab}) + K_{ab} - 2\langle aa|bb\rangle \\ J_{22} &= 1/2(J_{aa} + J_{ab}) + K_{ab} - 2\langle aa|bb\rangle \\ J_{12} &= 1/2(J_{aa} + J_{ab}) - K_{ab} \\ K_{12} &= 1/2(J_{aa} - J_{ab}) \end{aligned} \quad ,$$

and the singlet-triplet energy splitting can be expressed in terms of the localized orbitals as,[5]

$$E_T - E_S = -2K_{ab} + \frac{(h_1 - h_2)^2}{J_{aa} - J_{ab}} = J. \tag{2.5}$$

For the degenerate case $h_1 = h_2$, the triplet state is the ground state, whereas a large energy gap between ϕ_1 and ϕ_2 will lead to a singlet ground state. The direct contribution of the first part to the

total exchange coupling constant J (eq 2.1) is always positive and referred to as "potential" exchange by Anderson.[6] On the other hand, the second part in eq 2.5 is referred to as "kinetic" exchange by Anderson, who expressed this part in the form of t^2/U, where t is the charge transfer integral and U is the onsite repulsion energy (difference between covalent and ionic configurations).[6] This splitting of the total coupling constant into ferromagnetic and antiferromagnetic part is also exercised within valence bond treatment of Heitler and London for the H_2 molecule.[7] The singlet-triplet energy splitting or the total coupling constant J is expressed as follows,[8]

$$J = K + 2\beta S \,. \tag{2.6}$$

The first part in the right hand side is the two electron exchange integral and hence is always positive. Whereas the second term, being the product of negative resonance integral and positive overlap integral, is always negative. Therefore, the overall sign of J and the concomitant nature of magnetism is an ensemble of two competitive terms.[9] Following them, Kahn and Briat derived the magnetic orbitals as the highest occupied MOs (HOMO). They obtained the expression[10]

$$J_{AF} = -\frac{2S_{AB}}{1+S_{AB}^2}; \quad \text{and} \quad J_F = 2J' - 2KS_{AB}^2 \,. \tag{2.7}$$

where, S_{AB} refers to the overlap between magnetic orbitals belonging to A and B. However, due to large energy separation between ionic and neutral singlet configurations, eq 2.5 often underestimates the kinetic part of the exchange.[11] Through an extensive dynamic correlation treatment, Malrieu and coworkers allowed the energetic ionic singlets to relax.[12] This causes a better mixing of ionic states with low-lying neutral singlet states, ultimately leading to an enhanced antiferromagnetic coupling. In a different approach Loth et al.[13] considered the energy difference between ferromagnetic and antiferromagnetic term, i.e., the eigenvalues of ψ_T and ψ_{S_3} to be equal with the potential exchange, J

$$\Delta E_0^{ST} = -2K_{ab} = -2J \,. \tag{2.8}$$

In case ψ_{S_3} corresponding to the antiferromagnetic state is only considered to represent the singlet state, the ground state will always be ferromagnetic since in Hartree-Fock theory, the ferromagnetic state is always stabilized due to positive value of K_{ab}.[14] Hence, other determinants such as two ionic states S_1 and S_2 are also required to represent the singlet state to construct a *configuration state function* (CSF). Mixing of these configurations with S_3 stabilizes the antiferromagnetic state (Figure 2.2) and refines the value of the zeroth order singlet-triplet splitting in eq 2.8. However, the ionic states which are eigenfunctions of spin square operator will occur mainly due to the kinetic energy of electrons and gives rise to the kinetic part of the exchange according to Anderson.[6] These charge transfer states are separated from the ground state by a large gap $(U = E_0 - E_{|a\bar{a}|})$, which is actually the energy of Coulomb repulsion between two electrons located at the same site.[15] Configuration interaction of these two CSFs with ψ_{S_3} leads to an energy lowering of singlet state, which can be estimated from second order perturbation theory as,

$$\Delta E_{SE}^2 = \frac{4F_{ab}^2}{E_0 - E_{|a\bar{a}|}} \,. \tag{2.9}$$

Here, F_{ab} is the Fock operator of the system. This part in eq 2.9 necessarily has a negative contribution towards the exchange coupling constant J and adds to "kinetic exchange".[16] Therefore, similar to the expression given by Hay et al. (eq 2.5), here also the total coupling constant (as in the HDVV Hamiltonian) can be represented as

$$E_{S=0} - E_{S=1} = 2K_{ab} - \frac{4F_{ab}^2}{E_0 - E_{a\bar{a}}} = 2J_{HDVV} \ . \tag{2.10}$$

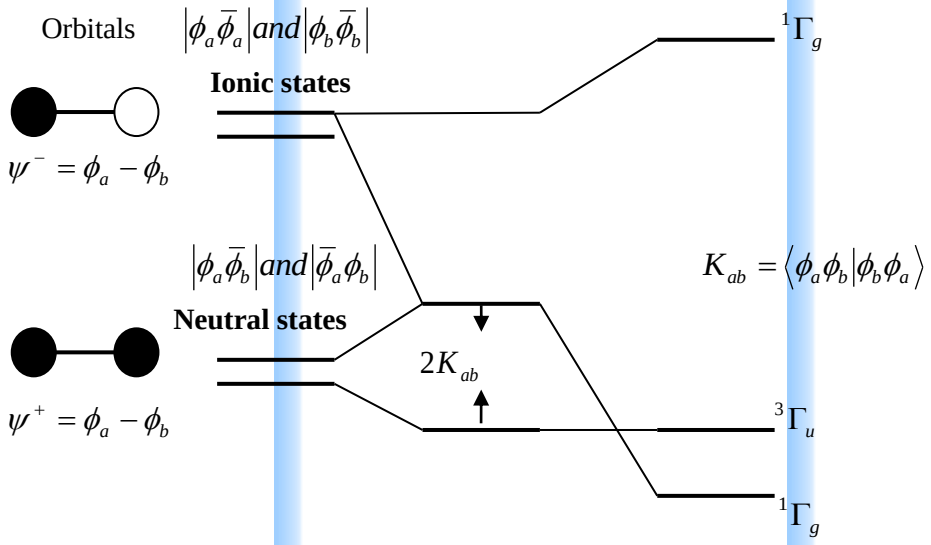

Figure 2. 2 Stabilization of antiferromagnetic state through configuration interaction of neutral and ionic state.

On the other hand, Yamaguchi and co-workers proposed an entirely different formalism, similar to that given by Ginseberg,[17] which uses *ab initio* symmetry projected unrestricted Hartree-Fock (PUHF) approximation to estimate J.[18] In UHF approximation, the singlet states (M_S = 0) of a magnetic molecule is generally given by,

$$\psi_n^{\pm} = \cos\theta_n\phi_n \pm \sin\theta_n\phi_n^* \tag{2.11}$$

where, φ_n and φ_n^* denote the n-th bonding and antibonding approximate natural orbitals. Therefore taking the superposition of (n + 1) PUHF solutions, the singlet UHF solution is

$$^1\psi_{UHF} = \left|\psi_1^+\bar{\psi}_1^-\psi_2^+\bar{\psi}_2^-..\psi_n^+\bar{\psi}_n^-\right| = \sum_{S=0}^{n} C(2S+1)^{2S+1}\phi(PUHF) \tag{2.12}$$

where, S is the total spin angular momentum of the molecule and $C(2S+1)$ and $^{2S+1}\phi(PUHF)$ are the expansion and wave function of the spin eigen state ($2S+1$). The total energy, spin eigenvalue of the total wave function in eq 2.12, thus can be expressed as

$$^1E_{UHF} = \sum_{S=0}^{n} C^2(2S+1)^{2S+1}E(PUHF) = \sum_{S=0}^{n} {}^{2S+1}E(PUHF)$$

and,

$$^{1}\left\langle \hat{S}^2 \right\rangle_{UHF} = \sum_{S=0}^{n} C^2(2S+1)\, S(S+1) = \sum_{S=0}^{n} S(S+1) \text{ , since } \quad \sum_{S=0}^{n} C^2(2S+1) = 1. \tag{2.13}$$

Now, for a dimeric system with spin angular momentums S_a and S_b at each radical site and where $S = S_a + S_b$, the spin Hamiltonian $H = -2JS_a \bullet S_b$ can be rewritten as,

$$H = -J_{ab}(\hat{S}^2 - \hat{S}_a^2 - \hat{S}_b^2). \tag{2.14}$$

Therefore using eq 2.13 and 2.14, the energy of singlet state can be written as,

$$^{1}E_{UHF} = -J_{ab}\left(^{1}\left\langle \hat{S}^2 \right\rangle_{UHF} - \hat{S}_a^2 - \hat{S}_b^2 \right) \tag{2.15}$$

and similarly the energy for the high spin state with total spin angular momentum *S*,

$$^{2S+1}E_{UHF} = -J_{ab}\left(^{2S+1}\left\langle \hat{S}^2 \right\rangle_{UHF} - \hat{S}_a^2 - \hat{S}_b^2 \right). \tag{2.16}$$

Now, since spin contamination is negligible in the high spin state, from eq 2.13

$$^{2S+1}\left\langle \hat{S}^2 \right\rangle_{UHF} \cong ^{2S+1}\left\langle \hat{S}^2_{PUHF} \right\rangle = S(S+1). \tag{2.17}$$

If the energy and spin expectation values of singlet state and (*2S+1*) eigen state is defined as those of low spin (LS) and high spin (HS) states, then from eqs 2.15, 2.16, and 2.17, the effective exchange integral J_{ab} can be described as,[18]

$$J_{ab} = \frac{E_{LS} - E_{HS}}{\left\langle \hat{S}^2 \right\rangle_{HS} - \left\langle \hat{S}^2 \right\rangle_{LS}} \quad . \tag{2.18}$$

However, in case for many magnetic centers, such as a periodic system, it is not always possible to find the eigenfunctions of HDVV Hamiltonian. In these cases, the common approach is to use the simplified version of HDVV Hamiltonian, where the total spin operators are replaced by their *z*-components,[19]

$$\hat{H}_{ISING} = -J_{ij}\hat{S}_i^z . \hat{S}_j^z . \tag{2.19}$$

This derivative of HDVV Hamiltonian is known as Ising model Hamiltonian and produces exact solutions for at least one- and two-dimensional models.[20]

2.1.3 Broken Symmetry Approach

Preceding discussion clarifies the need of interaction among different configurations with $M_S = 0$ to properly describe the open shell singlet state, i.e. antiferromagnetic state.[21] The *configuration state function* formed through several such determinants is an eigenfunction of spin square operator.[22] To obtain such multideterminantal wave functions, the best policy is to resort to correlated multireference *ab initio* approaches. However, these approaches have to encounter serious challenges

in simultaneous treatment of static and dynamic correlation in such systems.[22] Moreover, with the increase in the dimension of the system, the consideration of extended configuration interaction to account for correlation and huge basis set renders the post HF method almost unfeasible and painstakingly resource-intensive.[12] To overcome these problems of *ab initio* approaches, the best alternative has been the DFT method which in conjunction with "Broken Symmetry" (BS) formalism produces a fair estimate of spin exchange coupling constant.[23] This BS approach, coined by Noodleman, makes use of an unrestricted or spin polarized formalism, where a weak antiferromagnetically coupled system is taken as the reference to represent the singlet system.[23] Other than reducing the computational rigor, the consideration of BS state is also important from another point of view. Symmetrically equivalent magnetic sites must necessarily have equal amplitude of spin density which imposes a delocalized solution for the system. Thus, such "full-symmetry" calculations are unable to consider the weakly coupled limit, where the electrons are fully localized.[24] This necessitates the removal of all symmetry elements connecting the magnetic centers and thus enables to account for weak coupling limit. The literature shows various ways to interpret BS-DFT solution, in the estimation of coupling constant.[25] The wavefunction for a BS state is artificially constructed through two magnetic orbitals (*a* and *b*), belonging to two different irreducible representations and having different spins α and β at separate magnetic sites.[25b] These two different orbitals with maximum local m_s value are allowed to couple together to have the minimum value of total M_S. Hence, for a diradical system where there is up-spin density around the magnetic center A (having orbital *a*) and the down-spin density is concentrated on B (Figure 2.3), the guess function for the BS state can be represented as,

$$\phi_{BS}^{Guess} = \left|(core)a\bar{b}\right|. \tag{2.20}$$

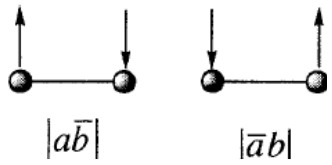

Figure 2.3 Representation of Broken Symmetry (BS) state

It is important to note that the integral of spin density over all space being equal to zero with α and β spin at different site. This spin density distribution is qualitatively wrong, since a proper singlet wave function has zero spin density at each point. The orbitals of this guess thus need to be re-optimized through variational principle.[26] At the stationary state, the true BS wave function has the form[22]

$$\psi_{BS} = \left|(core')a'\overline{b'}\right| \tag{2.21}$$

where, *a'* and *b'* are relaxed to their final form. The condition of orthogonality, as maintained by *a* and *b* is no longer applicable on these new set of optimized functions. Since, these spin-orbitals are always orthogonal by their spin part, there is no further orthogonality restriction on their space part. This flexibility is used to lower the energy of the system, leading to antiferromagnetic ground state. Noodleman and coworkers showed that the BS state can be expressed as an weighted average of the different possible pure spin states $|\psi_S\rangle$ of the system,[27]

$$\psi_{BS} = \sum_{S} A(S) \mid \psi_{S} \rangle \tag{2.22}$$

where, *A (S)* is the Clebsh-Gordon coupling coefficient. Now, from eq 2.1 and 2.22, the energy splitting between the highest spin state and BS state appears as,[27]

$$E(S_{\max}) - E(BS) = \left[S_{\max}(S_{\max}+1) - \sum_{S} A(S)S(S+1) \right] \frac{J}{2} \ . \tag{2.23}$$

Using $\sum_{S} A(S)S(S+1) = S_{\max}$, the following expression was obtained for orthogonal magnetic orbitals by Ginseberg, Noodleman and Davidson[27]

$$J_{GND} = \frac{E_{BS} - E_{HS}}{S^2_{\max}} \ . \tag{2.24}$$

For $S_A \neq S_B$, the above expression changes into

$$J_{GND} = \frac{E_{BS} - E_{HS}}{2S_A S_B} \ . \tag{2.25}$$

However, eq 2.24 and 2.25 are constructed assuming magnetic orbitals to be orthogonal. Taking the overlap of magnetic orbitals into account, the above expression is corrected as,[27]

$$J = \frac{E(S_{\max}) - E(BS)}{2S_A S_B (1 + S^2_{AB})} \ . \tag{2.26}$$

Noodleman and Davidson also showed that in the context of spin-polarized configuration interaction (CI) treatment, the coupling constant can be separated into the sum of terms, $J = J_F + J_{AF} + J_{LSP} + J_R$, where J_F is the ferromagnetic contribution, J_{AF} is the contribution from superexchange, J_{LSP} is due to ligand spin polarization and J_R takes the other contributions into account. They further claimed that the coupling constant estimated through eq 2.24 includes all of the J_F, J_{AF} and J_{LSP} terms.[27] However, the possibility of overlap between magnetic orbitals is dealt in a different fashion by localizing two unpaired electrons at two different atoms in antiparallel alignment (Figure 2.3).[28] Using these localized orbitals *a* and *b*, Noodleman defined the BS state as,[23]

$$\phi^1_{BS} = \left| a\bar{b} \right| \ \text{ or } \ \phi^2_{BS} = \left| \bar{a}b \right| \tag{2.27}$$

Though, BS wave functions are not the eigen function of spin square operator, an adequate singlet function $\phi_{\left|S=0,M_S=0\right\rangle}$ can be formed through their combination as follows,[28]

$$\phi_{\left|S=0,M_S=0\right\rangle} = \frac{\phi^1_{BS} - \phi^2_{BS}}{\sqrt{2 - 2\left\langle \phi^1_{BS} \middle| \phi^2_{BS} \right\rangle}} \ . \tag{2.28}$$

Another possible combination of these two BS wave functions gives the M_S = 0 component of the triplet state (T') is,

$$\phi_{|S=1,M_S=0\rangle} = \frac{\phi_{BS}^1 + \phi_{BS}^2}{\sqrt{2+2\left\langle \phi_{BS}^1 \middle| \phi_{BS}^2 \right\rangle}} \ . \tag{2.29}$$

By subtracting the energies (E_{BS} and $E_{T'}$) of the above wave functions (eq 2.28 and eq 2.29), the following expression for J results in,[28]

$$J = \frac{2\left(E_{BS} - E_{T'}\right)}{1 + S_{ab}^2} \tag{2.30}$$

where, S_{ab} is the overlap integral between the spatial parts of spin polarized α and β orbitals in the BS solution. If spin polarization is neglected for core electrons, the overlap integral can simply be regarded as that between two singly occupied molecular orbitals (SOMOs) a and b.[28a] However, Matteo et al. obtained the same expression for J as in eq 2.30 by considering the BS state as a weighted average of several possible spin multiplets, as suggested by Noodleman.[27] In case of a diradical, the BS wave function can be expressed as the average of triplet (Ψ_T) and singlet (Ψ_S) wave functions; [27, 28]

$$\psi_{BS} = a\left|\psi_T\right\rangle + b\left|\psi_S\right\rangle \tag{2.31}$$

and, analogously the energy and expectation value of the spin square operator will be,

$$E_{BS} = a^2\left|E_T\right\rangle + b^2\left|E_S\right\rangle \quad \text{and} \quad \left\langle \hat{S}^2 \right\rangle_{BS} = a^2\left\langle \psi_S \middle| \left\langle \hat{S}^2 \right\rangle \middle| \psi_S \right\rangle + b^2\left\langle \psi_T \middle| \left\langle \hat{S}^2 \right\rangle \middle| \psi_T \right\rangle . \tag{2.32}$$

Now, since $a^2 + b^2 = 1$ and therefore $a = b = 1/\sqrt{2}$; the singlet-triplet energy gap (if denoted as $2J$),[21] can be written as

$$2J = E_S - E_T = \frac{\left(E_{BS} - E_{T'}\right)}{1 - b^2} \ . \tag{2.33}$$

Now, putting the expectation value of the spin square operators for the pure singlet and triplet state as 0 and 2 in eq 2.32, we get $b^2 = \frac{1}{2}\left\langle \hat{S}^2 \right\rangle_{BS}$; with which eq 2.33 turns into,

$$J = \frac{\left(E_{BS} - E_T\right)}{2 - \left\langle \hat{S}^2 \right\rangle_{BS}} \ . \tag{2.34}$$

To proceed further, it can be recalled that for a singlet state, [29]

$$\left\langle \hat{S}^2 \right\rangle = M_S\left(M_S + 1\right) + N_\beta - \sum_{i,j}^{N_\alpha, N_\beta} \left(S_{ij}^{\alpha\beta}\right)^2 \tag{2.35}$$

Where, $S_{i,j}^{\alpha,\beta}$ is the overlap between the spin orbitals referring to opposite spins. Neglecting all the overlap between spin orbitals other than magnetic spin orbitals $|a\rangle$ and $|b\rangle$,

$$\left\langle \hat{S}^2 \right\rangle_{BS} = 1 - S_{ab}^2 \ , \tag{2.36}$$

with which eq 2.34 takes the following form,

$$J = \frac{\left(E_{BS} - E_T\right)}{1 + S_{ab}^2} . \tag{2.37}$$

as given by Noodleman, Norman,[23, 27] and Caballol et al.[28a] However, use of BS solution to get a proper estimate of the energy of singlet state, is a crucial problem. Meanwhile, two propositions from Baerends and Perdew et al. lead the way to escape this problem. Baerends showed that the single determinant wave function includes all the electron correlation contributions to the energy,[30] while Perdew, Savin and coworkers suggest that the energy of singlet state can be approximated through the BS single determinant state (eq 2.27) in DFT calculation.[31] They further showed that such a BS state can produce accurate electron and electron pair density even if the spin density distribution is unrealistic. With this lead, Ruiz et al. developed an alternative method where they used the broken symmetry approach, coined by Noodleman in the platform of DFT.[28b, 32] In this method, the exchange coupling constant for a system with local spins S_1 and S_2 (where, $S_2 < S_1$) is expressed as,

$$J = \frac{\left(E_{BS} - E_T\right)}{2S_1S_2 + S_2} \tag{2.38}$$

where non-spin-projected energies are used. With the assumption, $S_1 = S_2$ and $S_{max} = S_1 + S_2$, the above expression changes into

$$J = \frac{2\left(E_{BS} - E_T\right)}{S_{\max}(S_{\max} + 1)} \ . \tag{2.39}$$

In spite of the variety in approaches to estimate the exchange coupling constant, it becomes obvious from the preceding section that the applicability of these equations depends on the appropriate choice of overlapping limit.[33] Illas et al. have shown that the most adopted trend to consider larger degree of delocalization of magnetic orbitals obtained from DFT as opposed to UHF is not fully justified.[33a] This problem of taking the appropriate weight of overlap between magnetic orbitals can be tackled by slight modification of eq 2.18, which is developed through approximate spin projection technique of Yamaguchi. In this formalism, eq 2.12 is similar to the construction of BS state by Noodleman et al. (eq 2.31). This fact, along with Perdew's prescription that the singlet state can be represented by single determinantal BS state within DFT framework, helps to rewrite eq 2.18 as,[34]

$$J = \frac{E_{BS}^{DFT} - E_{HS}^{DFT}}{\left\langle S^2 \right\rangle_{HS} - \left\langle S^2 \right\rangle_{BS}} \ . \tag{2.40}$$

Clark and Davidson used a similar kind of expression to define J_{ab} (eq 2.41),[35] which obviously reduces to eq 2.40 through cancellation of local spin operators $\hat{S}_a$ and $\hat{S}_b$,

$$J_{ab} = \frac{E_{BS} - E_{HS}}{2\left(\langle S_a \bullet S_b \rangle_{HS} - \langle S_a \bullet S_b \rangle_{BS}\right)} \quad . \tag{2.41}$$

However, the expression of J_Y given by Yamaguchi (eq 2.40) has an appealing aspect which can be understood through the dependence of $\langle \hat{S}^2 \rangle$ of a Slater determinant on the overlap of magnetic orbitals (eq 2.35).[29, 36] In case of the overlap among all pairs of α and β orbitals, the sum in eq 2.35 is reduced to a summation over N^{β} with individual terms all equal to 1. Therefore, the sum equals N^{β} and the total spin expectation value indicates a pure spin state with $<S^2>_{BS}$= 0, and the denominator in eq 2.40 transforms to S_{HS} (S_{HS}+*1*) which resembles eq 2.39. On the other hand, if magnetic orbitals do not overlap (BS determinant), the sum in eq 2.35 becomes $N_{\beta} - 2S_A$, where S_A is the sum of α and β magnetic orbitals. In this weakly coupled limit, $<S^2>_{BS} = 2S_A = S_{HS}$ and resembles Noodleman's original expression (eq 2.24). Thus eq 2.40 is superior to others in fair description of magnetic interaction. Yamaguchi et al. further claims that eq 2.24 or eq 2.39 does not work well for large magnetic systems,[37] whereas the approximate spin projected technique (eq 2.40) reliably deals the magnetic properties of systems with trinuclear or even larger clusters, linear or annular.[38] In fact they gave another expression for magnetic exchange coupling constant, which is specifically applicable for polynuclear magnetic systems,[39]

$$J_{ab} = \frac{E_{BS} - E_{HS}}{4(N-1)S_a.S_b} \quad . \tag{2.42}$$

2.1.4 Level of Computation

It should be noted that the high spin-low spin energy difference and corresponding coupling constant are usually several orders lower that the total energy, which urge for the use of robust theoretically methods like multideterminantal approaches.[28b] The intersite magnetic coupling is found to originate from local electronic interaction between two specific magnetic sites.[40] This opens up the possibility of accurate estimation of spin state energies and hence *J*, using ab initio methods. However, the UHF approach produces only 30% of the experimental value of *J*.[41] The complete active space configuration interaction (CASCI) with magnetic orbitals as the active space also behaves in a similar manner in estimating *J*. This similarity is not surprising since, UHF wave functions are merely the effective approximation to the CASSCF or CASCI wave function.[42] This underestimation of *J* in UHF or CAS methods is generally attributed to the disregard of the effects like ligand-spin polarization, dynamic spin polarization, double spin polarization etc. which are important physical mechanisms contributing to the exchange phenomenon.[43] Yamaguchi suggested the need of configuration interaction methods such as UCCSD (T), UQCISD (T) or CASSCF techniques to reproduce experimental values of *J*.[44] One can find these effects in the second-order terms or diagrams and hence calls for second order perturbation theory based upon the UHF wave function.[43] The UMP2, being this kind of method, is found to significantly improve the value of *J*; though the magnitude is still one-half the experimental value. Another similar method, complete active space second-order perturbation theory (CASPT2), which imposes second order correction to the CAS wave functions, is also found useful in producing *J* close to experimental values.[45] The second order correction applied to contracted CASSCF wave function is not enough to include all important

dynamic correlation effects. Hence this problem can be solved by enlarging the complete active space (CAS). However, enlargement of active space causes a significant loss of interpretive power.[45c] The method can further be refined by considering "external correlation" through multireference configuration interaction (MRCI) tools,[46] among which the difference dedicated CI (DDCI) approach by Miralles et al. has been particularly successful to produce the desired degree of accuracy.[47] Different variants of DDCI wave function have also been formulated which can account for second order mechanisms such as double spin polarization, kinetic exchange etc.[48] However, the main limitation of DDCI is its demand for high basis set without which the value of *J* is found to be underestimated.[49] The computational rigor for such *ab initio* computation urged the requirement of new technique, which can estimate *J* with less rigor and comparable accuracy as that of first principle calculations.

The BS ansatz is indeed a very clever idea to simulate the effects of configuration interaction without actually resorting to this expensive calculation. However, the Achilles' heel of DFT has been the proper choice of exchange correlational (XC) functional during estimation of any electronic property.[50] Apart from the selection of proper XC functional, the unrestricted formalism used in DFT brings about an additional problem of spin contamination, particularly in the BS state.[51] Local spin density approximation (LSDA) such as VWN is found to underestimate the spin localization as evidenced from very low value of spin population in the magnetic site. This causes a huge high spin-low spin energy gap and hence overestimates *J*.[32] Though, the generalized gradient approximation (GGA) is a little improvement over LDA functional, the problem of overdelocalization cannot be avoided which again gives out overestimated exchange coupling constant.[33a] Hybrid DFT functional are believed to impose marked improvement over LSDA or GGA functional. In general, spin-unrestricted Kohn-Sham Slater functional with correlation corrections (X=P86, PL, VWN, LYP) followed by an approximate spin projection technique of Yamaguchi gives a reasonable account of singlet-triplet splitting.[52] In fact, UB3LYP with 25% of Fock exchange is claimed by Ruiz et al. to be most accurate in estimation of exchange coupling constant.[32a] However, at the same time, the value of coupling constant is found sensitive towards the percentage of Fock exchange in the hybrid XC functional.[53] While comparing the performance of pure and hybrid functionals, BLYP and B3LYP are found to predict the reverse sign of effective exchange integral, at least in case of *m-phenylene* coupled ferromagnetic interaction.[54] In this regard, UB2LYP is found reasonable, probably because this functional can properly take the spin-polarization and spin-delocalization effects into account.[55] Martin and Illas noted that a 50% admixture of Fock exchange (UBHandHLYP) appears necessary to get a reasonable agreement in *J* value with experiment.[41] Zhao and Truhlar have developed a suite of M06 functionals which borne the facility to change the fraction of HF exchange from 0 to 100%.[56]Among four different functionals of this suite, M06, which contains 27% HF exchange produces *J* value closer to the experimental value.[57] Not only the exchange effect but also the electron correlation effects play a crucial role in describing the magnetic coupling. To confront the short range and long range interelectronic interaction, another new suite of range separated functional has been introduced by Scuseria and coworkers.[58] Regarding the estimation of *J*, long range corrected range separated hybrids appear as the better performer than usual hybrid functionals.[58a, b] The coupling constant also shows sensitivity to the range separation parameter in the weight function of the range separated hybrids.[58c]

2. 2

EXPERIMENTAL TECHNIQUES

Since, no such theoretical methods has still been proved sound and flawless in estimating exchange coupling constant; it becomes necessary to use as many experimental techniques to obtain an reliable insight of magnetic properties.[59] The coupling constant, extracted from different experimental methods which include susceptibility measurement, EPR spectroscopy at X- and Q-band frequency, Raman scattering etc.[60] is found to have a long range of magnitude from a few Kelvin to about 1500 K.[61] Among all the experimental techniques, the most primitive to evaluate *J* has been the simulation of the susceptibility-temperature curve. The relation between the susceptibility (χ) and exchange coupling constant (*J*) was first suggested by Bleaney and Bowers,[62]

$$\chi = \frac{Ng^2\beta^2}{kT\left[3+\exp\left(-J/kT\right)\right]} \qquad 2.43$$

where, *N*= Avogadro number, *g* = gyromagnetic ratio, *k* = Boltzman Constant and *T* = Temperature. However, *g* is in principle isotropic and equal to 2.00023. The value of *J* is obtained from the best fit of χ vs *T* plot using eq 2.43, simulated against the experimental one. Use of the EPR spectra in interpreting magnetism has been incepted with the explanation of triplet spectra of copper acetate monohydrate.[62] The EPR also played an important role in proving the ferromagnetic coupling in organic polyradicals like polycarbenes.[63] For a system with two unpaired spins on two different magnetic sites, two electron spin resonance lines are expected in absence of any exchange interaction in between the paramagnetic sites. On the other hand, in presence of exchange coupling between them, a single resonance broad line is obtained instead of several hyperfine-split lines and this process is referred to as the *exchange narrowing*.[64] Anderson, and Kubo and Tomita used stochastic methods and a second order perturbation theory to analyze the exchange narrowing effect.[65] The change in the peak-to-peak linewidth (ΔH_{pp}) due to the presence of exchange coupling is obtained by Yokota and Koida, and by Levstein et al. as, [66]

$$\Delta H_{pp} = \frac{(2\pi/3)^{1/2}\left[g_A(\theta,\phi)-g_B(\theta,\phi)\right]^2\omega_0^2\hbar}{4g^3(\theta,\phi)\omega_{ex}\mu_0} \qquad 2.44$$

where, g_n is the angle dependent gyromagnetic ratio of paramagnetic site *n*, ω_0 is the microwave frequency of the experiment, ω_{ex} is a characteristic modulation frequency produced by the spin Hamiltonian in eq 2.1, and the squared *g* factor measured for magnetic field **B** applied along **b** = **B**/|**B**| = (sinθcosφ, sinθsinφ, cosθ) in the xyz system.[67] However, this is a second order contribution towards the peak to peak line width and hence is very small at *X* band. The magnitude of this contribution is thus increased at *Q* band. The difference of the line width in the *X* band and *Q* band is then least square fitted to get the ω_{ex} through the following equation,[68]

$$\Delta H_{pp}(Q)-\Delta H_{pp}(X)=\frac{(2\pi/3)^{1/2}\left[g_A(\theta,\phi)-g_B(\theta,\phi)\right]^2\left[\omega_0^2(Q)-\omega_0^2(X)\right]\hbar}{4g^3(\theta,\phi)\omega_{ex}\mu_0} \qquad 2.45$$

where, usually $\omega_0(X) = 2\pi \times 9$ and $\omega_0(Q) = 2\pi \times 33$ are Larmor frequencies. The exchange frequency ω_{ex} is associated with the exchange parameter *J* of eq 2.1 as[66a]

$$\omega_{ex} = \frac{2\pi}{\hbar} \sum_i Z_i J_i^2 \qquad 2.46$$

where the J_i are acting along the chemical path *i* among magnetically equivalent pairs and Z_i is the number of nearest such pairs. However, the EPR-study of high spin magnetic clusters is largely disturbed by the presence of zero field splitting, [69] which can be avoided by using high frequency-high field EPR spectroscopes. Another recently developed technique to measure *J* is high-field (pulsed) magnetization measurement, where the energies of low-lying magnetic levels can be obtained. In this technique, when an external magnetic field *H* is applied parallel to *Z*-direction on a antiferromagnetic ground state, the energy of *S = 0* component remains unaffected. Whereas, the energy of the component $M_S = n/2$ (*n* is the number of total unpaired electron in a system) of the low-lying high spin state is decreased as $-g\mu_B H$. Hence, the energy difference between the low spin ground state and low-lying excited high spin state is given by

$$\Delta = J - g\mu_B H \,. \qquad 2.47$$

At some critical field (H_C) where these two states become degenerate, the magnetization rapidly grows from zero to the saturation value for *S = n/2*, provided the temperature is kept sufficiently low. At this crossover field, the value of exchange coupling constant can thus be obtained as

$$J = g\mu_B H_C \,. \qquad 2.48$$

Though, requirements of very low temperature and very high magnetic field delimits the applicability of this technique; recently available pulsed fields as high as 700 – 800 Tesla can dilute the constrain.[70] Another EPR based technique, pulsed electron-electron double resonance (PELDOR or DEER) which is a well-established method for measuring distances between spin centers, is also being used to get exchange coupling constant. In the analysis of PELDOR data, normally the isotropic exchange coupling constant (*J*) is ignored compared to the strong anisotropic dipolar coupling υ_D

$$\upsilon_D = D\left(1 - 3\cos^2\theta\right) \qquad 2.49$$

where,

$$D = \frac{\mu_0 h g_A g_B}{4\pi r^3} \,. \qquad 2.50$$

Here μ_0 is the vacuum permeability, *g* is the gyromagnetic ratio on spin sites A and B, *h* is the Planck constant, *r* is the distance between the spin sites and θ is the angle between *r* and the external magnetic field B_0. Now, for a non-zero value of *J*, this term can be included in the eq 2.49 as

$$\upsilon_D = D\left(1 - 3\cos^2\theta\right) + J \,, \qquad 2.51$$

which enables determination of the magnitude and sign of *J*.[71] Raman scattering has also been found to give important spin related informations and especially from two-magnon Raman scattering it is

possible to obtain exchange coupling constant, evolution of spin order with magnetic fields or temperature etc. in spin-ordered systems. From the energy of the two-magnon band, an estimate of the nearest neighbor exchange coupling parameter *J* can be made. If *S* is the spin on any magnetic site and *n* being the number of nearest neighbour to that site and spin deviations are created on the adjacent sites, the two-magnon energy is given by 2*JnS* in the following way.[72] For a ferromagnetic system with spins localized at lattice sites, the Hamiltonian is

$$H = -2J\sum_{\langle i,j\rangle} S_i.S_j - g\beta H_o\sum_i S_i^z \qquad 2.52$$

where the H_0 is the static magnetic field applied in *Z* direction. Through the Holestein-Primakoff transformation of spin operators and subsequent diagonalization of the Hamiltonian through standard Bogolyubov transformation, above equation transforms into [73]

$$H = \sum_k E_k a_k^{\dagger} a_k \qquad 2.53$$

where, $a_k^{\dagger}$ and a_k are boson creation and annihilation operators and E_k is the energy of magnon,

$$E_k = \hbar\omega_k = g\beta[H_E(1-\gamma_k) + H_0] \qquad 2.54$$

and

$$\gamma_k = n^{-1}\sum_j \exp[ik(r_i - r_j)]. \qquad 2.55$$

In the above expression H_E is the exchange field and ω_k is the frequency associated with stokes-scattering process. Similarly, for antiferromagnetic system,[73]

$$E_k = \hbar\omega_k = g\beta H_E\left[\left(1+\frac{H_A}{H_E}\right)^2 - \gamma_k^2\right]^{1/2} \qquad 2.56$$

where, H_A is the z-directed anisotropy field. A Physical interpretation of the stokes-scattering process is that the incident photon excites one electron to a virtual state, with simultaneous spin flip of it and a neighbouring electron to conserve spin angular momentum. The excited electron then returns to the orbital ground state emitting the scattered photon and leaving both the spins in excited state.[74] In understanding the mechanism and extent of exchange, the spin topology in a molecule becomes of utmost importance. For example, the spin density on formally diamagnetic ligand indicated superexchange mechanism, while the sign of the spin density on two neighboring magnetic sites predict the nature of magnetic coupling.[75] Along with EPR and NMR techniques, inelastic neutron scattering (INS) has recently been included in the list of potential tools which can map the polarized spin density in the ground state. Both EPR and NMR use magnetic nuclei as local probes, which makes these techniques unsuitable for systems having nonmagnetic nuclei. Further the determination of the sign of the unpaired spin density is extremely difficult in EPR, while NMR can easily provide the sign. An alternative approach to these techniques is to use neutrons for reconstructing the polarized spin density of magnetic clusters. In the experimental condition, the nuclear spins are not polarized and thus the nuclear scattering is independent of neutron spin; while the interaction of neutron with the magnetization density is spin-dependent. At the first step of the experiment, the precise structure of crystal is determined using conventional unpolarized neutron diffraction techniques. This gives the knowledge of nuclear density (F_N) in the crystal. In the second step, a magnetization density is induced in the paramagnetic single crystal by strong magnetic field and also

exposed to polarized neutron beam. The induced magnetization density ($F_{M\perp}$) has also the same periodicity as nuclear density and thus the entire coherent elastic scattering occurs at Bragg positions. In practice one measures the *flipping ratio* (*R*) which is the ratio of scattered intensities for up (parallel to the field) and down (antiparallel) polarizations of the incident beam.

$$R = \frac{F_N^2 + F_{M\perp}^2 + 2F_N F_{M_Z\perp}}{F_N^2 + F_{M\perp}^2 - 2F_N F_{M_Z\perp}} \quad . \qquad 2.57$$

Here, F_M is the *z* component of magnetization density, $F_{M\perp} = F_M \, Sin\, \alpha$ and $F_{M_Z\perp} = F_M \, Sin^2 \alpha$, α being the angle between scattering vector and *z*. In as early as 1949, Shull and Smart had carried out a neutron diffraction study to demonstrate that MnO is an antiferromagnet.[61] The technique has recently been applied on a cluster $[Fe_8O_2(OH)_{12}(tacn)_6]Br_8$, (tacn= 1,4,7,-triazacyclononane), where each of the 8 Fe atoms containing five unpaired spins are antiferromagnetically coupled to each other. The neutron diffraction study reveals the spin topology in the cluster as shown in the following figure (taken from the reference).[76] However, the use of polarized neutron techniques is not limited to metal-based magnetic systems, rather can also be applied on organic radicals.

Figure 2.4 Representation of spin density in a Fe_8 network, where dark and grey spots correspond to positive and negative spin density respectively

2.3

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CHAPTER 3

Chemical control of magnetism

Abstract:

The effect of chemical composition on the inherent magnetism is put into the focus with $Cr_2O_n^-$(n = 1,2,3) as the representative system. The result shows that though Cr_2 is strongly antiferromagnetic, insertion of oxygen can turn it into ferromagnet. The ground state of all the systems corresponds to the highest possible spin multiplicities such as 10, 10 and 8 respectively. To estimate the intra-molecular ferromagnetic exchange coupling constant in these systems, the approximate spin projection technique is used. However, more than one electron per magnetic site in Cr makes the proper description of the broken symmetry state difficult which in turn limits the application of spin projection technique. This problem is sort out through the prescription of Dai and Whangbo, who give a simple and elegant description of the broken symmetry state in systems with multiple electrons in magnetic orbitals. The coupling constant values, evaluated in this way describe ferromagnetic coupling between Cr atoms. The magnetic interaction is mediated through bridging oxygen. The prevailing super-exchange mechanism in present systems is validated through spin density alteration and molecular orbital analysis. The exchange coupling constant is found to decrease steadily with increasing number of oxygen atoms, which is attributed to the consumption of majority spin through covalent bonding of Cr with oxygen.

3.1

INTRODUCTION

Recent theoretical studies have paid attention in the alteration in the magnetic properties by means of chemical reaction or composition. For example, by inserting two nitrogen atoms in the antiferromagnetic Cr_2 molecule, the distance between Cr atoms can be increased. This increased distance can keep away the Cr magnetic orbitals from overlapping and thus the system Cr_2N_2 turns ferromagnetic.[1] The magnetism in Cr_2O_n is found to vary similarly with the number of oxygen atom in it.[2] The effect of oxygen on the magnetism and superconductivity of three $Gd_{2-x}Ce_xRuSr_2Cu_2O_{10-\delta}$ (x = 0.5) samples have also been investigated through doping oxygen into the crystal at high pressure.[3] The magnetic ordering temperatures of the Ru spin moments are found to vary with doping concentration and Gd/Ce ratio as well. In fact it has been a traditional approach to obtain ferromagnetism by doping a 3*d* element in a semiconductor.[4] Doping 2*p* elements like B, C, or N in MgO is also found to cause half metallic ferromagnetism in it.[5] Wu et al. has achieved spontaneous magnetization in BN nanotubes by C substitution.[6] In a similar fashion, the non-magnetic BeO is turned magnetic by replacing O sites with B, C and N.[7] A theoretical study by Yadav et al. also revealed that O replacement with B, C or N in antiferromagnetic MnO semiconductor can turn the system into a ferromagnetic one.[8] Along with the chemical composition, the dimension of the system also poses significant effect on the inherent magnetism. The non-zero magnetic moment in rhodium,[9] manganese,[10] and chromium[11] clusters is found to be absent in their bulk phase.[12] The magnetism in these transition metal clusters is actually size specific and grows more and more with reduced dimension.[10c] However, among all the systems we find chromium oxide clusters to be ideal in the present context. In fact Cr_2O_n at both the neutral and anionic state, have been a topic of current research interest.[1,2a, 13] Different properties of neutral chromium oxide clusters have been correlated with electronic structure by Pandey and coworkers.[13a, b] On the other hand, the variation of their electronic structure as well as the magnetic property as a function of oxidation and composition have been discussed by Zhai et al.[13c] and Reddy et al.[2a] respectively. Kondow and coworkers showed that ferromagnetism can be induced in antiferromagnetic dimeric chromium anion by forming clusters with oxygen atoms.[14] Lau et al. also addressed the magnetic nature of higher analogues of the same cluster series $Cr_2O_n^-$(n = 4−6).[15] Such a development makes this $Cr_2O_n^-$ cluster series attractive for theoretical investigation.

The tuning of magnetism by varying the chemical composition has been the epitome of many theoretical and experimental works. However, explanation of such behaviour through quantum chemical study is fragmentary in nature and requires attention. Thus, the main objective of this work is set to find out the chemical origin of the change in magnetic behaviour of dichromium oxide anions with increasing the proportion of oxygen. The chosen systems viz. Cr_2O^-, $Cr_2O_2^-$ and $Cr_2O_3^-$ can have several spin states due to large number of unpaired system in Cr. Tono et al. have investigated the magnetic properties of these clusters through photodissociation spectra and found them ferromagnetic.[14] They further claimed to have super exchange mechanism operative in these systems. In the present work, we carry out quantum chemical investigation to explain their ferromagnetism. The mechanism of super exchange through which the systems develop the intrinsic magnetism is also verified through molecular orbital analysis. The extent of magnetism in these systems is quantified in terms of exchange coupling constant (J). Evaluation of exchange coupling constant in such systems with large spin quantum number seems challenging, since related studies mostly deal with the computation of J in the diradicals, where the possible spin states are singlet and triplet.

3.2

THEORETICAL AND COMPUTATIONAL FRAMEWORK

The magnetic coupling between spins on different radical centres *a*, *b*, etc., in a molecule is normally described by the phenomenological Heisenberg spin Hamiltonian as discussed in the previous chapter (eq 2.1),

$$H_{ex} = -2 \sum_{a<b} J_{ab} \hat{S}_a \bullet \hat{S}_b \tag{3.1}$$

The utility of the "Broken Symmetry" (BS) formalism within density functional theory (DFT) to calculate the exchange coupling constant has been elaborately discussed in the second chapter. To implement the BS method of Noodleman,[16] different spins (α and β) is to be polarized on different sites which can be done in unrestricted Hartree-Fock (UHF) method. However, the spin contamination is a major problem of UHF method, which can be overruled by the use of restricted open-shell Hartree-Fock (ROHF) method. On the other hand, the spin polarization is not adequately represented in ROHF. Moreover, Huyser et al. showed that the ROHF and two-configuration self-consistent field (TCSCF) calculations generally fail to produce the correct relative energies and geometries for diradicals.[17] This is a result of the so-called doublet instability problem in ROHF which is most severe when the basis set is small. Hence, in the present work the unrestricted Hartree-Fock (UHF) method is opted for a reasonably correct description of triplet and open-shell singlet states. The problem of spin contamination in UHF calculations can be generally overcome by a multi-configurational treatment. However, these techniques become progressively more difficult to afford computationally once the size of the system increases. Though for the high spin state the spin contamination is not too high, the BS state is largely suffered from the elevated expectation value of spin square operator. In this respect, the spin-projected method developed by Yamaguchi is the best resort to eliminate the effect of spin contamination from the energy of the BS state.[18]

$$J_{ab} = \frac{{}^{HS}E_{DFT} - {}^{BS}E_{DFT}}{{}^{BS}\langle \hat{S}^2 \rangle_{DFT} - {}^{HS}\langle \hat{S}^2 \rangle_{DFT}} . \tag{3.2}$$

The superiority of this approximate spin projected method of Yamaguchi to estimate *J* over other methods has already been discussed in the second chapter. The limitation of so-called Ginsberg, Noodleman and Davidson (GND) spin projected equation[19] or similar expressions obtained by Martin and Illas, Bencini et al., and Ruiz et al. [20] makes eq 3.2 an automatic choice for estimation of *J*. When the systems contain large number of electrons, correlation corrections can be quite time consuming and resource intensive. In that case one can rely on the DFT, which produces a good estimate of the exchange-correlation energy. However, the use of eq 3.2 to estimate *J* in the present system turns complicated from the computational point of view. The state-of-the-art computational suits require a primary input of spin multiplicity to calculate the spin state energies and spin square values. In a dimer A – B, with local spin angular momentums $\hat{S}_a$ and $\hat{S}_b$ and total spin angular momentum $\hat{S}$, the spin square value of high spin state is simply $S(S+1)$. However, the BS state is a weighted average of all possible spin states with spin quantum number $S = |S_a - S_b|, |S_a - S_b|+1, \ldots, (S_a + S_b)$, which makes it complicated to assign the correct multiplicity for the BS state. This fact stands as an obstacle to determine the spin square value of the BS state, which is a compulsory parameter to estimate *J* from

eq 3.2. To resolve this issue, we find the work of Dai and Whangbo to be the best solution.[21] In the dimer A – B, if there are *M* and *N* unpaired spins on A and B, there occurs the possibility of (*M*+1) (*N*+1) spin states. The spin stats of the dimer can be represented by $|SM_S\rangle$. Now, the each wave function $|SM_S\rangle$ of the dimer can be expanded as a linear combination of product functions $|S_a M_{Sa}\rangle|S_b M_{Sb}\rangle$ as shown below

$$|SM_S\rangle = \sum_{S=S_a-S_b} A(S)\times|S_a M_{Sa}\rangle|S_b M_{Sb}\rangle \tag{3.3}$$

where, *A(S)* is the Clebsch-Gordon coefficient (eq 2.22). Now, with *M* and *N* unpaired spins on A and B, the BS state can be written as

$$|BS\rangle = \sum_{S=\frac{M-N}{2}}^{\frac{M+N}{2}} A(S)\times\left|\frac{M}{2}\frac{N}{2}\right\rangle_A\left|\frac{N}{2}\frac{-N}{2}\right\rangle_B . \tag{3.4}$$

With this expression of the BS state, the expectation value $\langle\hat{S}^2\rangle_{BS}$ can be written as

$$\langle\hat{S}^2\rangle_{BS} = \langle BS|\hat{S}^2|BS\rangle = \left(\frac{M-N}{2}\right)^2 + \left(\frac{M+N}{2}\right). \tag{3.5}$$

Hence, from the grounds state spin configuration, the spin multiplicity of the BS state can easily be predicted from the eq 3.5. With this preconceived spin square value, now a reliable estimate of energy of the BS state is possible, which in turn facilitates the application of eq 3.2 to estimate *J*. In the present work, all the computations and visualizations are performed using the quantum chemical packages Gaussian 03W[22] and Hyperchem 7.5.[23]

3.3

RESULTS AND DISCUSSION

The geometries of the members of $Cr_2O_n^-$ (n = 1, 2, 3) series are optimized with the unrestricted Becke 3 parameter exchange and Lee, Yang, Parr correlation functional (UB3LYP)[24] and split valence triple zeta basis functions. The optimized structures of Cr_2O^- and $Cr_2O_2^-$ are in agreement with the findings by Tono et al. (Table 3.1).[14]However, the optimized planar geometry of $Cr_2O_3^-$ deviates from the slightly puckered structure reported by Tono et al. Among several possible spin states, the chromium oxide cluster anions Cr_2O^-, $Cr_2O_2^-$ and $Cr_2O_3^-$ are found to be most stable for the total spin quantum numbers 9/2, 9/2 and 7/2 respectively (Table 3.1). The lower spin states have these values somewhat higher than expected, indicating large spin contamination (Table 3.1).

Table 3.1 Geometries of (a) Cr_2O^-, (b) $Cr_2O_2^-$ and (c) $Cr_2O_3^-$ at different possible spin states, optimized at UB3LYP level using 6-311+g(3df) basis set.

(a) Cr_2O^-

S	$\langle \hat{S}^2 \rangle$	Cr(1,2)-O (Å)	Cr1-Cr2 (Å)	Cr1-O-Cr2 (º)	E (a.u)
9/2	24.926	1.813	2.984	110.714	-2164.2261
7/2	16.974	1.811	2.818	102.211	-2164.2019
5/2	10.405	1.689	3.081	118.320	-2164.1553
3/2	3.761	1.820	1.758	57.755	-2164.1079
1/2	0.757	1.940	1.593	48.476	-2164.0710

(b) $Cr_2O_2^-$

S	$\langle \hat{S}^2 \rangle$	Cr(1,2)-O(1,2) (Å)	Cr1-Cr2 (Å)	Cr(1,2)-O(1,2)-Cr(1,2) (º)	E (a.u)
9/2	24.956	1.850	2.520	85.747	-2239.5102
7/2	16.640	1.840	2.460	83.749	-2239.4977
5/2	9.964	1.830	2.590	89.845	-2239.4964
3/2	6.036	1.810	2.560	87.157	-2239.5051
1/2	3.982	1.731	2.526	86.227	-2239.4970

(c) $Cr_2O_3^-$

S	$\langle \hat{S}^2 \rangle$	Cr(1,2)-O(1,2) (Å)	Cr2-O3 (Å)	O(1,2)-Cr2-O3 (º)	Cr1-Cr2 (Å)	Cr(1,2)-O(1,2)-Cr(1,2) (º)	E (a.u)
9/2	24.914	1.870	1.990	132.850	2.516	85.120	-2314.7458
7/2	15.843	1.790	1.621	133.860	2.652	91.365	-2314.8542
5/2	9.113	1.728	1.631	131.260	2.588	89.317	-2314.8273
3/2	4.706	1.727	1.601	131.489	2.584	89.620	-2314.8272
1/2	3.066	1.724	1.629	130.440	2.518	85.862	-2314.8277

The high-spin members of Cr_2O^-, $Cr_2O_2^-$ and $Cr_2O_3^-$ are relatively stabilized from their spin-1/2 analogues by the extent of 0.155, 0.013 and 0.027 a.u respectively (Table 3.1). The extra stability gained by the high-spin Cr_2O^- in comparison with the other two members is ascribed to the large separations between metal centres. On the contrary the Cr-Cr distance is reduced in the high-spin isomer from that in the low-spin state in $Cr_2O_2^-$ and $Cr_2O_3^-$. However the overall stability of the high-spin members can be attributed to the covalent interaction between Cr and O valence orbitals, which in turn indicates the existence of super exchange interaction as justified by Tono et al.[14] To comprehend super exchange mechanism in these clusters, spin density distribution becomes a useful

tool as advocated by Trindle and et al.[25] The spin density on chromium atoms indicates partially filled *d* orbitals which can accommodate the up-spin electrons from the valence pair of oxygen anion. This spin transfer leaves major spin densities on Cr atoms and a minor opposite spin density on oxygen atom (Figure 3.1) and hence causes spin density alternation. The delocalization of electrons from bridging oxygen to metals can also be understood from the molecular orbital analysis (Table 3.2). The highest occupied molecular orbital in all of the three clusters are composed from an equitable participation of the orbitals of the bridging atom and the metals. In a similar way it can be shown that super exchange is also operative for the other members of the cluster series.

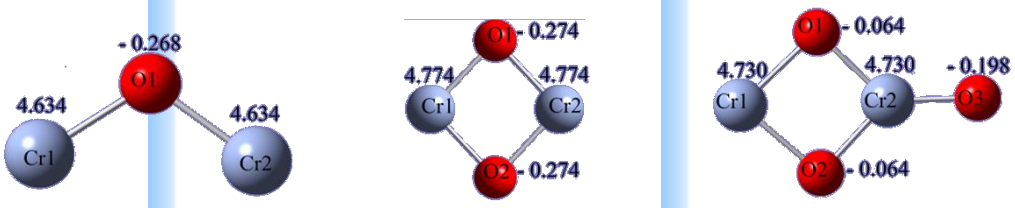

Figure 3.1 Spin mapping in the ground state of $Cr_2O_n^-$, obtained from Mulliken population analysis at UB3LYP/ 6-311+g (3df) level of theory.

Table 3.2 Molecular Orbital (MO) analysis showing the delocalization of the electrons (A.O. refers to the atomic orbital and C_i is their corresponding coefficient, $C_i \leq 10\%$ has not been considered.).

Species	α M.O	Orbital energy(a.u)	Atom	A.O.	C_i
Cr_2O^-	32	-0.02355	Cr1	d_{-2}	0.556
				p_x	0.104
			Cr2	p_x	0.104
			O	p_x	0.766
$Cr_2O_2^-$	36	0.00022	Cr1	d_{-2}	0.817
				p_x	0.327
			Cr2	d_{-2}	0.826
			O1	p_y	0.250
			O2	Nil	Nil
$Cr_2O_3^-$	38	-0.06842	Cr1	d_{+2}	0.916
			Cr2	s	0.371
				d_0	0.486
			O1	p_x	0.222
			O2	Nil	Nil
			O3	Nil	Nil

Now, in order to estimate the exchange coupling constant, the broken symmetry calculation on each species is performed on their ground states. This calculation is so adjusted that $<S^2>$ values close to that prescribed by Dai and Whangbo can be achieved.[21] The calculated *J* values are found to be decreasing steadily with increase in the number of oxygen atoms in the cluster series (Table 3.3). The lowering in *J* values from Cr_2O^- and $Cr_2O_2^-$ to $Cr_2O_3^-$ is explained by the decrease in the number of unpaired spins from nine to seven. This annihilation of the majority spin, centred on Cr2 is caused by covalent bonding with O3 (atomic labels are denoted in Figure 3.1). However, the decrease in *J* value from Cr_2O^- to $Cr_2O_2^-$ cannot be explained in a similar way, because they contain the same

number of nine unpaired electrons. Molecular orbital analysis serves the aid to explain this lowering of *J* in this case. The 32nd MO of $Cr_2O_2^-$ (Table 3.4) has contribution from p_x orbital of O2, and 3*d* orbital from Cr1 and Cr2. This indicates the covalent interaction between α-electrons of Cr2 and unpaired *β*-electron of O2. The remaining *β*-type electron in O2 atom can be spread over the 3*d* orbital of Cr1 and hence diminishes the overall major spin density. Another explanation of this gradual decrease of *J* value in the series Cr_2O^-, $Cr_2O_2^-$ and $Cr_2O_3^-$ can be given by the analogy of Hoffmann et al.[26] From extended Huckel calculations they suggested that if the energy difference (ΔE_{SS}) between two consecutive singly occupied molecular orbitals (SOMO) be less than 1.5 eV, electrons will occupy the nearly degenerate orbitals leading to a parallel alignment of spins. Recently few other investigators carried out DFT calculations on similar problem and have shown that the critical value of ΔE_{SS} is different for different systems.[27] However, increasing value of ΔE_{SS} would induce spin pairing. Our calculated average values of ΔE_{SS} are 0.199 eV, 0.368 eV and 0.467 eV for respectively. This gradual increase in ΔE_{SS} will show a net effect of decreased magnitude of ferromagnetic exchange coupling constant through the cluster series.

Table 3.3 Magnetic exchange coupling constant (*J*) computed at UB3LYP/6-311+g (3df) level of theory using the optimized geometries of ground states.

Species	State	Energy(a.u)	$<S^2>$	*J*(e.V)
Cr_2O^-	HS	-2164.2261	24.926	0.167
	BS	-2164.1023	4.723	
$Cr_2O_2^-$	HS	-2239.5102	24.956	0.103
	BS	-2239.4319	4.265	
$Cr_2O_3^-$	HS	-2314.8542	15.843	0.004
	BS	-2314.8527	5.724	

Table 3.4 Molecular Orbital (M.O) analysis of $Cr_2O_2^-$

Species	**α M.O**	**Orbital energy(a.u)**	**Atom**	**A.O.**	**Coefficient**
$Cr_2O_2^-$	32	-0.05820	Cr1	d_0	0.202
				d_{+2}	0.643
				s	0.126
			Cr2	d_0	0.214
				d_{+2}	0.642
				s	0.134
			O1	Nil	Nil
			O2	p_x	0.461

3.4

SUMMARY

The current theoretical study sheds light on the chemical control of magnetism in the representative system $Cr_2O_n^-$(n = 1, 2, 3). The members of $Cr_2O_n^-$ series are found to have ferromagnetic ground states, which is achieved by the superexchange interaction between chromium spins through bridging oxygen atoms. The existence of superexchange mechanism is validated through the spin density alternation and MO analysis. The intra-molecular magnetic exchange coupling constants are quantified by DFT calculations using BS approach. In this evaluation the

correct BS state is obtained by the prescription of Dai and Whangbo. The calculated *J* values are so large compared to *kT* that all the species is expected to sustain their ferromagnetism at room temperature. The value of coupling constant shows a monotonic decrease with increase in the oxygen content. This observation is explained by the dispersal of minor spin density in the magnetic orbitals. A drastic decrease in the *J* value of $Cr_2O_3^-$ is attributed to the consumption of unpaired spin, centred on Cr2, by covalent interaction with terminal oxygen atom.

3.5

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CHAPTER 4

Distance-dependence of magnetic interaction

Abstract :

Study of magnetostructural correlation is important for designing molecules with desired strength of magnetic interaction. Systems containing manganese with number of unpaired electrons turn out to be an interesting system for such study. In this work, neutral Mn dimer, charged Mn dimer and its oxide are chosen to decipher the effect of distance between two magnetic sites on their net magnetism. The magnetic characteristics of the chosen systems have been quantified in terms of intramolecular exchange coupling constant. The computation is performed in the framework of density functional theory using broken symmetry approach. We obtain positive values of magnetic exchange coupling constants for all these three species and hence their ferromagnetic ground states are recognized. Direct exchange or superexchange of spins between the sets of *d*–electrons in the metals is found responsible for the ferromagnetic behavior of these clusters. The distance-dependence of exchange coupling constant on intermetallic distance reveals a maximum value of coupling constant in the proximity of equilibrium bond distance.

4.1

INTRODUCTION

Magnetostructural correlation is important in designing molecule-based magnets and understanding spin exchange mechanisms. Study of such correlation has been incepted with bridged Cu(II) dinuclear complexes by Hatfield and coworkers,[1] and has been widely cultivated till then.[2] In planar dihydroxy-bridged copper dimers, the exchange coupling constant J is found to vary in parallel from + 172° to − 509° with the Cu – O – Cu bridging angle (Φ) from 95.6° to 104.1°. This led Crawford et al. to draw a linear correlations between J and Φ as follows,[1]

$$J(cm^{-1}) = -74\Phi + 7270\,. \tag{4.1}$$

Similar type of correlations are found to exist in μ_4-oxo-bridged tetrameric Cu (II) complexes,[3] μ-phenoxo-bridged Cu (II) complexes with exchangeable exogenic ligands,[4] as well as dimeric hydroxo-bridged Cr (III) complexes.[5] It is interesting to note that the critical bridging angle, where does occur the magnetic phase transition (AFM to FM), is more or less same (97.5 ± 1°). In the μ-hydroxo compound, due to the lengthening of the Fe – O bonds in the Fe – O – Fe linkage, the spin density delocalized from the metal towards the bridge is strongly reduced and the AFM interaction is reduced in consequence.[6] Gorun and Lippard have been able to establish a semi-empirical correlation on the basis of magnetic and structural data for dinuclear oxygen-bridged Fe (II) complexes.[7] They have shown that the magnitude of J is correlated with a single structural parameter P,

$$J(cm^{-1}) = A \times \exp(B \times P) \tag{4.2}$$

where, $A = -8.76 \times 10^{11}$ cm^{-1} and $B = -12.66$ cm^{-1} and P corresponds to the half of the length of the shortest Fe – O – Fe bridge in the complex. For oxo-bridged dimers, Weihe and Gudel developed another semi-empirical equation which considers both the bridging angle Φ and Fe – O distance r,[4]

$$J = 1.337 \times 10^{8} (3.536 + 2.488\cos\phi + \cos^2\phi) \times \exp(-7.909r)\,. \tag{4.3}$$

This expression demonstrates that the angular dependence of J is not as strong as it depends on r. Generally, the magnetic interaction in bridged complexes is executed through superexchange, for which the ligand to metal charge transfer is also an important parameter to account for the resulting magnetism. Keeping this in mind, Werner et al. incorporated the radial as well as angular dependence of transfer integral for the symmetrically bridged Fe dimers.[8] In cases the isotropic interaction between remote magnetic centers is mediated through long extended bridges, Coffman and Buettner proposed an equation relating to the limiting distance beyond which the interaction is feeble. The limiting value of J (J_{lim}) is related with the distance (r) between two spin – ½ sites as,[9]

$$J_{\text{lim}}(cm^{-1}) = -1.35 \times 10^{7} \exp(-1.80r) \tag{4.4}$$

Plenty yet conflicting results on the magnetostructural correlation draw our attention to exercise similar study on the manganese dimer which is reported to show a AFM to FM phase transition with elongation of bond.[10] On the basis of *ab initio* calculation, Lopez et al. showed that the

antiferromagnetic ground state of manganese dimer switches into a ferromagnetic one when inter-atomic distance changes from 2.89 Å to 3.06 Å.[11] A tentative relationship between the magnetism of Mn_2 cluster and its dimension is also revealed elsewhere.[12] A preliminary study of magnetism of manganese clusters is credited to Nesbet who predicted an antiferromagnetic $^1\sum_g^+$ ground state of Mn dimer,[13] which is subsequently confirmed by several experiments.[14] Experimental study produces a value of –9±3 cm^{-1} for intramolecular magnetic exchange coupling constant (J) in case of Mn_2 which gets further confirmation from UV absorption data.[15] Bauschlicher, through CASSCF approach, also found Mn_2 to have J = –7 cm^{-1} at short bond distance.[14] A number of theoretical studies were conducted on Mn_2 and came out with contradictory results.[15] For example, Gutsev and Bauschlicher found $^{11}\Pi_u$ ground state for Mn_2,[16] similar prediction has also been made by Khanna and coworkers.[17] On the contrary Wang and Chen obtained a singlet ground state for CASPT2 calculations using relativistic effective core potential.[18] A new relativistic model core potential was developed by Mon et al. and calculation at CASSCF and MCQDPT2 level revealed again a $^1\sum_g^+$ ground state for Mn_2.[19] Using state-averaged complete active space self-consistent field method, followed by second-order quasidegenerate perturbation theory Yamamato et al. predicted manganese dimer to be a van der Waals molecule with antiferromagnetic coupling.[20] Nevertheless, three main predictions about the ground state of Mn_2 is antiferomagnetic singlet state,[21] a triplet state[22] and ferromagnetic 11-tuplet state.[17,23] Pederson et al. also suggested a multiple magnetic and structural minima for manganese dimer.[23c] Instead of this controversial theoretical prediction of ground state of Mn_2, almost all the experimental results stick to the antiferromagnetic ground state of manganese dimer. However, the experimental data are in most of the cases obtained from a fitting of the magnetic susceptibility data to the expression obtained using a model Hamiltonian that includes several fitting parameters, that is, the very empirical nature of experimental J value makes this comparison inconsequential. The contradictory results about the magnetic status of the Mn_2 as apparent from the preceding discussion are summarized in Table 4.1.

Table 4.1 Experimental and Calculated equilibrium bond length (r_e) and corresponding ferromagnetic (FM) or antiferromagnetic (AFM) state of neutral manganese dimer.

References	r_e(Å)	State
11a	2.89	AFM
11b	3.06	FM
12	3.40	AFM
13a	2.91	AFM
13b	3.44	FM
14	2.88	AFM
15a	2.66	FM
16	2.68	FM
17a	2.62	FM
17b	2.70	AFM
18a	3.64	AFM
18b	3.79	FM
19a	3.13	AFM
19b	3.47	FM
20	3.30	AFM
12a	2.52	AFM
22	2.27	AFM
23a	3.55	FM
23c	2.61	FM

Contrary to the neutral Mn_2, the magnetic nature of its positively charged congener Mn_2^+ is free from such opposing experimental and theoretical results. DFT study on Mn_2^+ by Desmaris et al. predicts a ferromagnetic ground state for the species.[17] Application of higher level multiconfigurational method by Wang and Chen on dimanganese cation concludes the same.[24] Ferromagnetism in Mn_2^+ is also reported by Terasaki and co-workers.[25] In this case theoretically predicted magnetic behavior is found to be concordant with EPR study, previously made by van Zee and Weltner.[26] Both the work shows a $^{12}\sum_g^+$ ground state for Mn_2^+. When an oxygen atom is attached with Mn_2^+, strong ionic and covalent Mn – O bond is formed as exemplified by Tono et al.[27] By electronic structure analysis they further concluded a ferromagnetic ground state for Mn_2O^-. They have also studied the change in magnetic nature of metal dimer with oxidation in case of Cr.[28] In, Mn_2 and Mn_2^+ localized *3d*-electron spins are coupled through either direct or indirect exchange mechanism. However, in case of Mn_2O^-, Tono et al. opined super exchange to be responsible for its bulk ferromagnetism.[27]

The controversial electronic structure of manganese clusters, especially that of neutral manganese dimer, arouses us to take into account their magnetic behavior within DFT framework. Moreover, in this work we have focused on the change in the degree of magnetism in three types of manganese clusters, which are Mn_2, Mn_2^+ and Mn_2O^-. In one of our recent work we also found super exchange mechanism to be operative between the set of metal *d*-electrons in Cr_2O^-, similar to Mn_2O^-.[29] Hence, present study also provides us the scope to compare the exchange mechanisms in Mn_2O^- and Cr_2O^-. To account for the variation in the exchange coupling constant in these three types of Mn clusters, a detail electronic structure analysis is performed. Coupling constants in three manganese clusters are measured varying intermetallic separation (*r*), which is the central issue of the present chapter.

4.2

THEORETICAL AND COMPUTATIONAL BACKGROUND

To describe magnetic interaction, the best model so far been developed is that of the Heisenberg-Dirac-van Vleck (HDVV). This model quantifies the magnetic interaction through a non relativistic energy operator, popularly known as HDVV Hamiltonian

$$\hat{H} = -2 \sum_{i>j} J_{ij} \hat{S}_i \bullet \hat{S}_j \qquad (4.5)$$

where, the symbol (i, j) indicates summation over all *i* and *j* neighboring magnetic centers and J_{ij} is the effective exchange coupling constant between them. Coupling constants describe the interaction among local spins. The eigen functions of the above Hamiltonian are basically spin functions. A proper mapping between eigen states of the exact Hamiltonian and HDVV Hamiltonian is made through the complete active space (CAS) configuration interaction (CI) based wave function. However, this methodology is resource- intensive and difficult to deal with the systems having multiple magnetic centers with elevated spin moments. An alternative yet efficient method to measure the exchange coupling constant is provided through broken symmetry approach implemented through density functional theory.[30] Perdew et al. also propose that the solution of BS single determinant wave function corresponds to the energy of pure singlet states in spite of its wrong expectation value for

total spin quantum number.[31] In this work, we have used spin-projected technique of Yamaguchi to evaluate the energy of BS state.[32]

$$J = \frac{E_{HS} - E_{BS}}{\langle S^2 \rangle_{BS} - \langle S^2 \rangle_{HS}} \qquad (4.6)$$

In this expression E_{HS}, E_{BS} and $<S^2>_{HS}$, $<S^2>_{BS}$ imply the energies and spin expectation values of high-spin and broken symmetry spin states respectively. This formalism of Yamaguchi is found to be approximately valid over the whole coupling strength span, both weak and strong. However, in a recent work Ruiz et al. have shown that if spin projection is applied for the calculations without the self interaction correction (SIC),[33] it may produce an overestimated *J* value and spin projection should be included in case of SIC energy of BS state. This is also the suggestion of Cremer and coworkers for reproducing the full CI value for *J*.[34] They also argued that hybrid functionals like B3LYP corrects the self interaction energy (SIE) to a significant extent.[35] Spin projected technique may thus be employed with this partial SIC-DFT functional. The performance of various exchange-correlational functionals to describe the magnetic exchange coupling was extensively studied by Illas and group, who concluded the value of coupling constant to be functional-dependent.[36] Ruiz and coworkers also prescribed that unrestricted B3LYP functional is the best performer in evaluating the value of magnetic exchange coupling constant in dinuclear complexes.[33,37]

4.3

RESULTS AND DISCUSSION

Table 4.2 Geometry optimization of different spin states of Mn_2

Multiplicity of pure spin states	Energy(a.u)	$\langle \hat{S}^2 \rangle$	Mn –Mn (Å)
11	-2301.6096	30.106	2.622
9	-2301.5839	21.038	2.588
7	-2301.4845	13.069	2.181
5	-2301.4284	8.037	2.173
3	-2301.3618	3.026	2.018
1	-2301.4268	0.000	1.674

Table 4.3 Geometry optimization of different spin states of Mn_2^+

Multiplicity of pure spin states	Energy(a.u)	$\langle \hat{S}^2 \rangle$	Mn – Mn (Å)
12	-2301.3885	35.774	2.991
10	-2301.3815	24.805	2.503
8	-2301.2846	15.809	2.129
6	-2301.2032	8.773	1.864
4	-2301.1884	5.778	2.108
2	-2301.0984	2.916	2.457

Table 4.4 Geometry optimization of different spin states of Mn_2O^- (Atoms' labeling is shown in Figure 4.2)

Multiplicity of pure spin states	Energy(a.u)	$\langle \hat{S}^2 \rangle$	Mn – Mn (Å)	Mn(1,2) – O(Å)
12	-2376.9667	35.811	2.986	1.865
10	-2376.9611	25.279	3.639	1.825
8	-2376.9156	17.093	2.641	1.824
6	-2376.8588	10.170	2.210	1.794

All the computations in this work have been carried out with hybrid density functional and Density-Gauss (Dgauss) local spin density (LSD) double zeta valence plus polarization basis function.[38] Performance of this basis set in evaluating electronic properties of typical organic and small inorganic molecules is found to be comparable with that of correlated Hartree-Fock optimized basis sets.[39] Geometry optimization of different possible spin states of Mn clusters with this DGDZVP2 basis set predicts that the state with highest spin multiplicity is the ground state. Energies of lower spin multiplets of Mn_2O^- can not be achieved because of triplet instability problem, which arises due to very small energy gap of 4.026 eV between HOMO and LUMO.[40] Desmaris et al. obtained relative stabilization energies of Mn_2^+ spin states ranging from S = 4.5 to S = 0.5 with respect to the ground state S = 5.5 to be non-monotonic.[17] On the other hand, in our calculation we obtain steadily increasing values 0.189, 2.826, 5.043, 5.444 and 7.894 eV for similar spin state ordering. This nature of relative stability is in accordance with the results obtained by Bauschlicher by CASSCF (CISD) calculations.[14] Long bond between manganese atoms in their respective ground states facilitates the decoupling of *d*-electrons and produces high expectation value of the total spin angular momentum operator (Tables 4.2, 4.3 and 4.4). Nevertheless, Bauchlicher[14] and Lopez et al.[11] have obtained a ferromagnetic ground state even at longer bond distance in case of manganese dimer, through ab initio calculation. This disparity in the measure of bond distance may be attributed to different theoretical approach, viz. DFT and ab initio, in determining molecular properties. Even, within DFT framework, Nayak and Jena reported a very long bond distance of 3.55 Å in ferromagnetic Mn dimer.[23] This fact of different value of interatomic separation in Mn_2 may also find an explanation from the work of Scheiner et al. who have shown that three parameter functionals are more sensitive in determining molecular parameters than other to the size of basis function.[41] Although, according to ab initio or DFT calculation,[11, 14, 23] at the interatomic separation of around 3.4 Å manganese dimer behaves ferromagnetically, experimental study by Baumann et al. reports an antiferromagnetic state at the same distance.[12] Nonetheless, in the present study the intermetallic bond distance increases in the charged Mn dimer from that of the neutral analogue. This fact can be attributed to the loss of one of the β-electrons from the bonding molecular orbital (MO) of neutral manganese dimer as can be evidenced from the natural bond orbital (NBO) analysis of both types of manganese dimers (Table 4.5).

Table 4.5 Natural bond order (NBO) analysis for Mn clusters

Molecular units	Bond between atoms	Occupancy of α electrons	Occupancy of β electrons
Mn_2 (high-spin)	Mn1 – Mn2	Nil	1.000
	Mn1 – Mn2	Nil	1.000
Mn_2^+(high-spin)	Mn1 –Mn2	Nil	1.000
	Mn1 –Mn2	Nil	0.995
	Mn1 –O	Nil	0.962
Mn_2O^-(high-spin)	Mn1– O	Nil	0.937
	Mn2– O	Nil	0.962

Table 4.6 Magnetic exchange coupling constant with the optimized geometry of the high-spin (HS) state

Species	State	Energy(a.u)	$\langle \hat{S}^2 \rangle$	J(cm^{-1})
Mn_2	HS	-2301.6096	30.106	668.436
	BS	-2301.5350	5.636	
Mn_2^+	HS	-2301.3885	35.774	1562.482
	BS	-2301.1681	4.820	
Mn_2O^-	HS	-2376.9667	35.811	953.703
	BS	-2376.8331	5.071	

The exchange coupling constants for all three species, which are reported in Table 4.6, have been evaluated using the standard approach by Yamaguchi.[29,32] The increase of J value in charged manganese dimer from that of the neutral species can be explained by NBO analysis (Table 4.5). It shows a loss of one minority-spin electron from the bonding orbital which eventually increases the relative majority-spin density and hence J increases. Increment of J in Mn_2O^- from Mn_2 is an obvious outcome of increase in the number of unpaired electrons from 10 to 11. However, the decrease in J value in Mn_2O^- from that in Mn_2^+ is not very evident as both have same number of unpaired electrons. This can be explained from the delocalization of oxygenic minority-spin into the orbitals of metal atoms. This delocalization can be verified from the NBO analysis of Mn_2O^- (Table 4.5). It shows existence of significant β-electron occupancy in between Mn atoms and oxygen. Mulliken spin density matrix is also found to have β-electron spin density in between those pair of atoms (Table 4.7). Dispersal of minority spin density of bridging oxygen into metal d-orbitals can be further verified from the MO analysis (Table 4.8), where most of the singly occupied molecular orbitals have significant contribution from d-electrons of two metal atoms and oxygen p-electrons.

Table 4.7 Mulliken spin density matrix for high-spin Mn_2O^-

	Mn1	Mn2	O
Mn1	5.872	-0.428	-0.084
Mn2	-0.428	5.872	-0.084
O	-0.084	-0.084	0.447

Table 4.8 Molecular orbital analysis of high-spin Mn_2O^- (A.O. refers to the atomic orbital and C_i's are their coefficients, $C_i \leq 10\%$ has not been considered.)

α	M.O	Atom	A.O.	C_i
		Mn1	s	0.196
			d_{-2}	0.135
	35		p_y	0.104
		Mn2	s	0.859
			d_{-2}	0.135
		O	p_x	0.568
	34	Mn1	s	0.563
			p_x	0.351
			d_{+2}	0.136
		Mn2	s	0.561
			d_{+2}	0.136
			d_{-2}	0.161
		O	p_y	0.470
		Mn1	p_z	0.131
			d_{+1}	0.322
	33	Mn2	p_z	0.131
		O	p_z	0.930
			d_{-2}	0.417
		Mn1	s	0.358
	32		d_0	0.174
			d_{+2}	0.108
		Mn2	s	0.226
		O	p_x	0.620
			s	0.230
	31	Mn1	d_{+2}	0.361
			s	0.230
		Mn2	d_{+2}	0.361
		O	p_y	0.704
		Mn1	d_0	0.322
	29		d_{+2}	0.246
			d_{-2}	0.529
		Mn2	d_0	0.323
			d_{-2}	0.241
		O	p_y	0.146

To investigate the dependence of ferromagnetic exchange coupling constant on intermetallic bond distance we have calculated *J* varying Mn – Mn separation (*r*) in their high-spin states. The plot of *J* vs. r (Figure 4.1a - d) shows a similar trend in all the four cases. The plot of Mn_2O^- has been obtained by varying both of Mn – O and Mn – Mn distance. We have studied the effect of Mn – Mn distance on *J*, first at longer and optimum Mn – O bond distance of 1.86 Å (Figure 4.1d) and second at shorter Mn – O bond distance of 1.80 Å (Figure 4.1e). Although first case produces a plot (Figure 4.1d), similar to Figure 4.1a, b and c, but the second variation leads to a curve of different nature as

can be seen from Figure 4.1e. All the plots in Figure 4.1 follow a Gaussian type of fitting, and thus for any arbitrary value of *r* the value of *J* can be obtained from these plots.

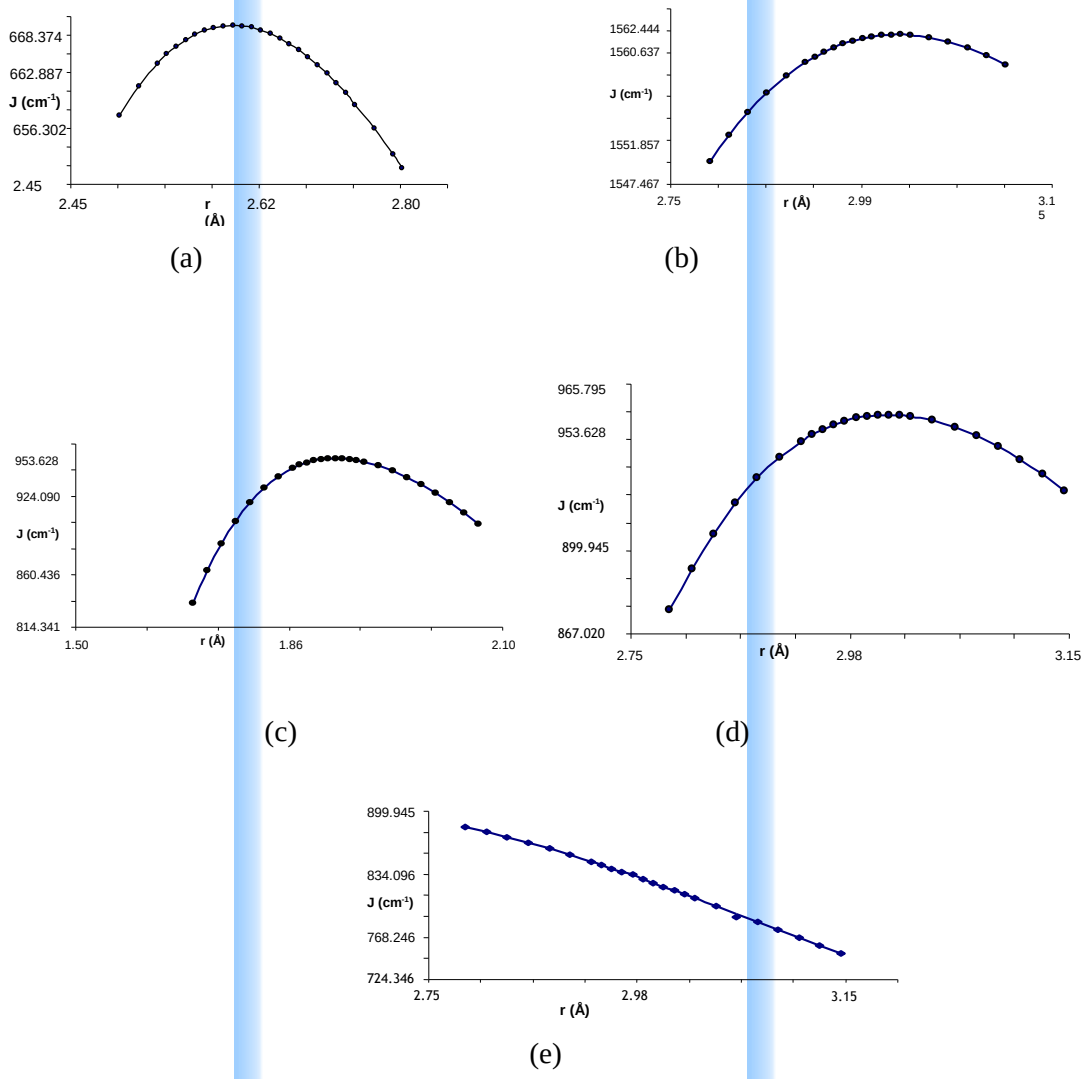

Figure 4.1 Variation of exchange coupling constant with (a) Mn – Mn distance in Mn_2 (b) Mn – Mn distance in Mn_2^+ (c) Mn – O distance in Mn_2O^- (d) Mn – Mn distance in Mn_2O^- (Mn (1, 2) – O bond distance kept unchanged at 1.86 Å) (e) Mn – Mn in Mn_2O^- (Mn (1, 2) – O bond distance kept unchanged at 1.80 Å).

Similarity of first four figures (4.1a – d) indicates the even nature of exchange mechanism in three types of Mn clusters. For first two entities, the possible exchange mechanisms are direct exchange and indirect exchange. However, for indirect exchange hopping of electrons between localized states is crucial. As the hopping integral decays exponentially with the distance between magnetic centers, we may disregard the plausibility of indirect exchange in the ground state for these widely separated Mn-couples in Mn_2 and Mn_2^+. Henceforth, considering the probability of direct exchange only, the magnetic exchange coupling constant can be related with the energy difference between the high-spin and low-spin states at zeroth order perturbation level in the following manner,[42]

$$J_0 = E_{HS} - E_{LS} = 2K_{ab} \qquad (4.7)$$

where E_{HS} and E_{LS} are energies of high and low-spin states and K_{ab} is exchange integral,

$$K_{ab} = \left\langle \phi_a(1)\phi_b(2) \left| \frac{1}{\hat{R}_{ab}} \right| \phi_a(2)\phi_b(1) \right\rangle . \qquad (4.8)$$

ϕ_a and ϕ_b are orthogonalized magnetic orbitals in the above expression. This relation, originally derived for two local doublets, is well extendable for more than one electron per magnetic site.[43] However, eq 4.7 corresponds to a case without any antiferromagnetic contribution.[44] In spite of this unrealistic correspondence, it has been used because all the manganese clusters have been found to be strongly ferromagnetically coupled and as a result the ferromagnetic contribution towards magnetic exchange coupling constant becomes dominant. This relation of magnetic exchange coupling constant and exchange integral is depicted through the plots. The *J* value is found to be lower at large Mn – Mn distance which expectedly increases with decrease in intermetallic separation. The *J* value reaches a maximum near equilibrium bond distance. If the intermetallic separation is further decreased below the equilibrium bond length, the magnetic orbitals come closer to each other and spin annihilation starts which are obvious from the plots (Figure 4.1a – d). From the scrutiny of variation in energy of single determinantal function for magnetized and unmagnetized states with increasing internuclear separation, Slater had drawn similar conclusion which states that the energy difference between magnetized and unmagnetized state is zero at long distance, goes through a maximum finally decreasing to zero and changes sign at small internuclear distances. Slater also expected similar behavior for the Heisenberg exchange integral, which in turn correlates to the energy difference between the magnetized and unmagnetized state.[45] This fact of maximum extent of ferromagnetic interaction is analytically proved by Mielke et al. through the one electron Hubbard model.[46] However, the plot in Figure 4.1e obtained at shorter Mn – O distance becomes comprehensible with the symmetry consideration of the orbitals. From the molecular orbital analysis the fact of strong interaction between metal and oxygen atoms is obvious (Table 4.8). This interaction becomes stronger with diminished Mn – O distance. With increasing distance between Mn atoms and at constant Mn – O separation, oxygenic orbital comes in between the metal-based magnetic orbitals and hinders direct exchange (Figure 4.2); as a consequence a continuous decrease in *J* value takes place. On the other hand, in Figure 4.1d, larger Mn – O separation produces a usual pattern for weak interaction of metal and oxygenic orbital.

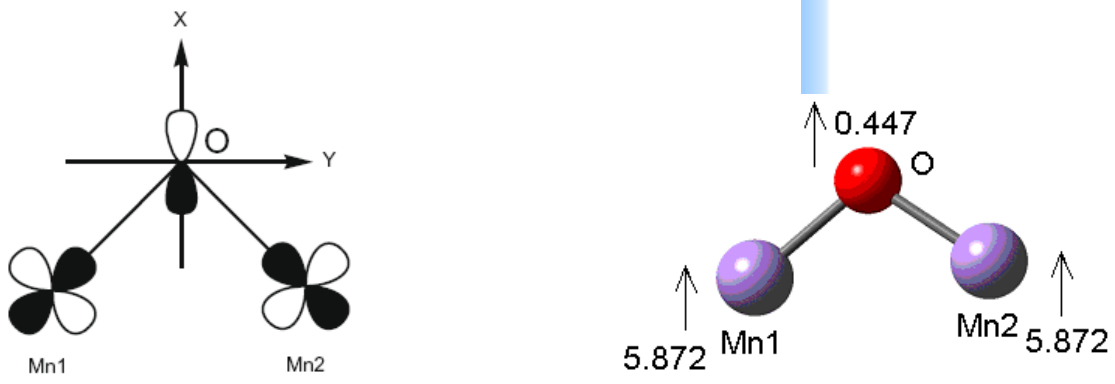

Figure 4.2 (a) Average orbital interaction in singly occupied molecular orbitals (c.f Table 4.7) and (b) Spin density from Mulliken population analysis in Mn_2O^-.

As far as the exchange mechanism in Mn_2O^- is concerned, the presence of diamagnetic bridging group opens a possibility for super exchange mechanism along with direct exchange. So, the question comes which one of them or the both are operative in this case. In one of our recent work we extensively studied a similar system, Cr_2O^- where we found super exchange mechanism to be operative.[29] Alternate spin density on adjacent atoms of Cr_2O^- fortified the super exchange mechanism. On the contrary, Mn_2O^- apparently does not show any spin alternation (Figure 4.2b) which indicates that the mechanism of super exchange is somewhat different from that in Cr_2O^-. The negative spin density on oxygen atom of Cr_2O^- indicates the delocalization of positive spin density between Cr and O atom. On the other hand, in the present case, the positive spin density is reserved on the O atom of Mn_2O^- and dispersal of negative spin density in between Mn and O atoms becomes certain (Table 4.7). Now the question arises that what causes this difference in super exchange in manganese oxide anion. In Cr_2O^-, for the partial vacancy in the band of metal *d*-orbital, the majority-spin electron from the ligand can be delocalized, keeping their alignment parallel to metal unpaired electrons.[47] This causes the spin density alternation in Cr_2O^- and causes it to have ferromagnetic ordering. Anderson also showed that Kramers' idea of super exchange gives rise to ferromagnetic interaction between cations with less-than-half-filled *d*-orbitals.[47] Thus the difference of super exchange in Mn_2O^- can be attributed to the unavailability of vacant *d*-orbitals, which contain a total number of 11 unpaired electrons. For the occupied α-MOs in Mn_2O^-, only the dispersal of β-electrons is feasible, which is ascertained on the basis of time-dependent density functional response theory (TD-DFT). The results (Table 4.9) show that the lowest energy transitions take place in all the clusters preferentially from the β-molecular orbital. Low value of ionization energy of the β-electrons may be ascribed to the higher polarizability of smeared out β-electron density. On the contrary α-electrons show a strong adherence to their respective MOs.

Table 4.9 Lowest transition energies (A/B= α/β MO)

Species	MOs	Transition energy (eV)
Mn_2	20B→ 22B 20B→ 33B 20B→ 42B	0.020
Mn_2^+	29A → 33A 19B→ 21B 19B → 22B	1.431
Mn_2O^-	24B → 25B 24B → 26B 24B → 32B	1.275

All the calculations and visualizations in this work have been performed by GAUSSIAN G03W[48] and HYPERCHEM 7.5[49] suit of quantum computational packages.

4.4

SUMMARY

In the present work, the magnetic interaction in neutral, charged manganese dimer and its oxide is quantified through DFT-BS approach. The investigation results in positive value of exchange coupling constants indicating ferromagnetic interaction in all the three species. A weak interaction between Mn atoms in the neutral and charged clusters causes localization of unpaired electrons in

their respective orbitals. The localized majority-spins are exchanged through space to produce a high positive value of exchange coupling constant. On the other hand, in Mn_2O^-, apart from the direct exchange between metal spins, a superexchange also operates through the orbital of bridging oxygen. Nevertheless, the mechanism of superexchange in Mn_2O^- is somewhat different from that in Cr_2O^- which is attributed to the more than half filled and less than half filled metal *d*-orbitals in Mn_2O^- and Cr_2O^- respectively. The differing occupation also causes the variation of spin density distribution in Mn_2O^- and Cr_2O^-. Finally, the variation in the coupling constant against the intermetallic separation is investigated. A plot of *J* as a function of intermetallic distance reveals weak ferromagnetism at a very small and long internuclear separation, whereas the ferromagnetism is found to reach its zenith near the equilibrium bond distance.

4.5

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CHAPTER 5

Exchange interactions in systems with multiple magnetic sites

Abstract:

Magnetic exchange coupling constant (*J*) in systems with two magnetic sites is reliably estimated using Heisenberg-Dirac-van Vleck (HDVV) model through broken symmetry approach (BS) within density functional theory (DFT) framework. However, in case of systems with multiple magnetic centers, exchange coupling constants, evaluated through state-of-the-art techniques are often found inadequate to produce a correct fingerprint of the nature of magnetic interactions therein. Hence, in this chapter we suggest a new scheme to estimate exchange coupling constants in such systems. In this strategy, distribution of spins on magnetic sites in the ground state of systems with multiple magnetic centers is computed. On the basis of this spin mapping, exchange coupling constants between specific pairs are estimated through BS-DFT approach while keeping all other paramagnetic atoms magnetically inactive. Nonetheless, the effect of magnetically inert paramagnetic sites is already taken into account by the process of spin mapping, which is further justified through expressing the HDVV Hamiltonian in terms of spin density operators. We employ this technique to hypothetical benchmark systems, H_3He_3 and H_4He_4 followed by real molecules, cationic manganese trimer, 1,3,5-benzenetriyltris (N-*tert*-butyl nitroxide), and a pentanuclear manganese complex. Results are found to be concordant with the already established nature of magnetic interaction in these systems. This strategy is different from the most popular scheme to compute *J* in systems with multiple magnetic centers in the sense that it avoids the formation of a large matrix out of different spin configurations and thus provides a reliable and computationally economic way to address the magnetic interactions in non isotropic systems with multiple magnetic sites.

5.1

INTRODUCTION

Last decade has witnessed an emerging interest in the fabrication of magnetic molecules of desired magnetic characteristics with complex functionality. This endeavor eventually thrusts into the investigation of magnetic characteristics of systems with multiple magnetic sites (SMMS) beyond the limit of much cultivated systems with two magnetic sites.[1] SMMS, mostly being organic polyradicals[2] or polynuclear transition metal complexes,[3] have the possibility of simultaneous existance of magnetic interactions and so may happen that ferromagnetic (FM) interaction prevails along a particular direction while antiferromagnetic (AFM) interaction dominates along the other. This direction dependent magnetic behavior gives rise to non isotropic magnetic interactions in such systems. Isolated magnetic interactions along three mutually perpendicular axes have been addressed through spin wave treatment.[4] However, this approach is only applicable for crystalline systems of high symmetry and a more generalized analysis of magnetic interactions in non isotropic magnetic systems is called for. First generation SMMS, such as Mn and Fe cluster based systems have attracted substantial attention of the researchers due to their high anisotropy barrier.[5] High energy barriers of these systems resist their magnetization to alter with increasing temperature and their multifarious applications are possible in diverse conditions.[6] Suitably designed nanoscale organic polyradicals appear promising in biomedical applications as in hyperthermic oncology, regioselective drug delivery etc.[7] Synthesis and characterization of nanomagnetic materials are instrumental in the field of high density data storage devices.[8] SMMS are also ubiquitous in metalloproteins and enzymes.[9] Ultimately, a proper understanding of magnetic interactions in such non isotropic systems becomes a prerequisite to obtain information about the coordination environment of metals or reactivity - structure correlation of active sites in large bio-molecules and organic polyradicals.[10] As anisotropy in exchange interaction is found to form a barrier of magnetization reversal,[11] tailoring of newer materials with high anisotropic barrier also needs an estimation of magnetic exchange interaction in SMMS.

In most of the experimental works,[2,3] the nature of magnetic interaction is understood through the product of magnetic susceptibility and temperature ($\chi_m T$) versus temperature (T) plot. This plot is simulated by a Bleaney-Bowers type of equation[12] to obtain the best-fit value of magnetic exchange coupling constant (J). Presence of multiple magnetic sites makes the system over parameterized and the fitting procedure becomes meaningless.[13] In this regard, theoretical methods can be foreseen as a valuable tool to rule out those experimentally fitted values of exchange coupling constants. From theoretical point of view, estimation of J requires a proper description of spin multiplets in any magnetic system. This can be achieved by correlating magnetic electrons through configuration interaction method. However, huge demand for computational resource for such treatment on SMMS limits its application. On the other hand, DFT based treatments are excellent compromise between resource and applicability. As an alternate method to correlate magnetic electrons, Noodleman and Norman[14] suggested formalism based on broken spin and space symmetry single determinant wave function for describing low spin states. This BS state is not a pure spin state, but a weighted average of them. Nevertheless, from the energy differences of the BS states to the high spin state, the estimation of spin exchange coupling constants is possible. This formalism became very popular immediately and found wide applications in different types of magnetic systems.[15]

However, estimation of exchange coupling constant in SMMS becomes much more complicated due to simultaneous existence of several magnetic exchange interactions. A method to evaluate *J* in such systems was initially proposed by Noodleman et al. with application in Fe_3S_4 system.[16] Later on, Ruiz and coworkers extensively used this method to evaluate *J* in polynuclear transition metal complexes.[17] In this method, energies of $n+1$ spin states of a system with *n* number of magnetic sites are first evaluated. Then from the energy difference, which is correlated to the diagonal terms of the Hamiltonian matrix, *n* different coupling constants are estimated. Nonetheless, this process becomes progressively complex with increasing size of the system because a system with *n* paramagnetic sites, each with spin *S*, requires diagonalization of a $(2S+1)^n \times (2S+1)^n$ matrix.[18] To reduce the rigor of diagonalization, least square fitting is also used by Ruiz and coworkers in the estimation of exchange coupling constants in Mn clusters.[19] In an alternative method, all the magnetic centers except concerned pair are replaced by diamagnetic ions.[13,17a] However, this approach is found to produce erroneous value of exchange coupling constant due to participation of the diamagnetic group in super exchange interaction.[13]

A good estimate of exchange coupling constant is usually obtained with the employment of hybrid functionals and Gaussian functions. Nevertheless, use of this method is also limited due to high resource requirement, particularly for large SMMS. Ruiz et al. made an attempt to overcome this difficulty by employing numerical basis sets instead of Gaussian functions. Although, this approach has been found effective in reducing computation time, results were not as accurate as with hybrid functionals.[17b] Hence, we stick to hybrid functional and Gaussian functions in this work. Crux of the present work lies in the determination of a general strategy to calculate exchange coupling constants in SMMS within BS-DFT framework in a reliable yet economical way. Small hypothetical benchmark systems, viz. H_3He_3 and H_4He_4, are chosen to apply the strategy and to judge the performance of the methodology; calculated coupling constants are also compared with those obtained by post Hartree – Fock (HF) methods.[17a] Finally, the same technique is applied to more realistic systems with multiple magnetic centers of both inorganic and organic origin. All the calculations are implemented through GAUSSIAN 03W suit of quantum chemical package.[20]

5.2

METHODOLOGY

Magnetic nature of any system depends upon the exchange interaction between paramagnetic centers, which can be quantified through the phenomenological Heisenberg-Dirac-van Vleck (HDVV) Hamiltonian

$$\hat{H} = -2\sum_{i=1}^{n}\sum_{\substack{j=1 \\ (i>j)}}^{n} J_{ij} S_i \cdot S_j \qquad (5.1)$$

where, (i, j) indicates summation over all *i* and *j* neighboring magnetic centers and J_{ij} is the effective exchange coupling constant between them. S_i and S_j are spin angular momentum operators on respective sites. The nature of the Hamiltonian clearly tells that whatever the number of magnetic centers within a molecule may be, the isotropic interaction term always involves pairs of local spins.[21] As for example, in case of a triangular system with local spin quantum number ½ at each site, one will get three values of *J* (Figure 5.1). High spin situation of this system can be represented by $|\alpha\alpha\alpha\rangle$; spin flip at site *c* will give rise to $|\alpha\alpha\beta\rangle$ and so on, where α and β designate up and down spins

respectively. The *J*'s can thus be estimated by simply comparing the energy differences among these states.[14-19] Nevertheless, the problem of this process, associated with diagonalization of large matrix generated from energy differences among several spin multiplets, is already discussed in the previous section.

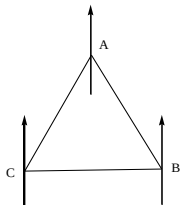


Figure 5.1 Equilateral triradical model system with spin expectation values S_1, S_2 and S_3=1/2 at radical sites A, B and C.

To overcome the difficulties discussed above, we propose a new approach to evaluate *J*. In this approach, we avoid calculation of total energy differences for several spin configurations, which originate by flipping spins at different magnetic sites. Rather, we first carry out spin mapping in the ground state of the system to obtain spin densities on each magnetic site. Then, we compute the energy difference between only high spin and broken symmetry spin states for any two magnetic sites, defining all other paramagnetic centers as dummy atoms. Computation of the energy difference for a specific paramagnetic pair is performed using the pre-calculated spins and charges on those active magnetic centers. This technique is comparable with representing atoms distant from a reactive center by "sparkles" which are point charges.[22] Nevertheless, sparkles differ from the dummy atoms which are completely devoid of any charge and electronic environment. Dummy atoms are kept in the molecular structure to maintain the ground state geometry. This approach is advantageous compared to the method of diamagnetic replacement of the magnetic sites whose limitation has already been discussed in the previous section.[13,17a]

In this approach, one uses ground state spin and charge distribution to figure out the magnetic coupling constant values between a specific pair of magnetic sites, keeping all other magnetic sites inert. Spin densities of these two magnetic sites only directly participate in computation of exchange coupling constant between this pair. At a first glance, it may appear that as the paramagnetic centers other than a specific pair are made dummies; they will not have any effect on the active magnetic pair. On the contrary, the effect of dummy magnetic sites on the active paramagnetic pair is inherent in the use of ground state spin and charge density distribution, which results only when interactions among all the spins are already set in equilibrium. This rationale can also be understood by expressing the interaction among neighboring spins in terms of spin-density operators in the HDVV Hamiltonian as described below. Rewriting eq 5.1 in terms of different components of spin operators, we get

$$\hat{H} = -2\sum_{i=1}^{n}\sum_{\substack{j=1 \\ i\rangle j}}^{n} J_{ij}\left(\hat{S}_{ix}.\hat{S}_{jx} + \hat{S}_{iy}.\hat{S}_{jy} + \hat{S}_{iz}.\hat{S}_{jz}\right). \tag{5.2}$$

Now, the Jordan-Wigner transformation[23] relates fermion creation and annihilation operators $f_i^{\dagger}$, f_i and spin raising and lowering opearators S_i^{+}, S_i^{-} as

$$S_i^{+} = S_{ix} + iS_{iy} = f_i^{\dagger} e^{i\pi\phi_i} \tag{5.3}$$

$$S_i^{-} = S_{ix} - iS_{iy} = f_i e^{-i\pi\phi_i} \tag{5.4}$$

where, the phase operator ϕ_i contains the sum over all fermion occupancies at sites to the left of i^{th} site. Now, eq 5.2 can be given by

$$\hat{H} = -2\sum_{i=1}^{n}\sum_{\substack{j=1 \\ i\rangle j}}^{n} J_{ij}\left(\frac{1}{2}\left(f_i^{\dagger} f_i + f_i f_i^{\dagger}\right) + \hat{S}_{iz}.\hat{S}_{jz}\right) \tag{5.5}$$

Again, z component of spin operator is related to spin density operator as

$$\hat{S}_{iz} = \sum_{i=1}^{n}\left\langle \hat{S}_{iZ} \right\rangle \rho_i(\vec{r})dr \tag{5.6}$$

where, $\rho_i(\vec{r})$ is the spin density operator at the i^{th} site.[24] Using this relation and anticommutation relation of fermionic operators, the Hamiltonian in eq 5.5 takes the form

$$\hat{H} = -2\left\langle \hat{S}_z \right\rangle^2 \sum_{i=1}^{n}\sum_{\substack{j=1 \\ (i\rangle j)}}^{n} J_{ij}\rho_i(\vec{r})\rho_j(\vec{r}) \tag{5.7}$$

From the above, it is obvious that the spin Hamiltonian describing the interaction between a specific pair is not directly dependent upon the spin densities from other magnetic sites. Now, say for the system in Figure 5.1, spin densities on magnetic centers *A*, *B* and *C* are obtained as n_A, n_B, and n_C through a single point calculation on the ground state of the system. In the next step, when we calculate J_{AB} between magnetic site *A* and *B*, the Hamiltonian given in eq 5.7 suggests us to keep site *C* inert. Nevertheless, the values of ground state spin densities on site *A* and *B* are very much dependent on that of site *C*. So, when we use residual spins n_A, n_B to assign the spin multiplicities of high spin and broken symmetry spin states, the effect from site *C* is also taken into account in an indirect way.

Finally, we use Yamaguchi expression to evaluate exchange coupling constants for a specific pair from the energy difference of their high spin and broken symmetry spin state in DFT framework,[25]

$$J_{ij} = \frac{E_{HS} - E_{BS}}{\left\langle \hat{S}_{BS}^2 \right\rangle - \left\langle \hat{S}_{HS}^2 \right\rangle} \tag{5.8}$$

where $\left\langle \hat{S}_{BS}^2 \right\rangle$ and $\left\langle \hat{S}_{HS}^2 \right\rangle$ are the expectation values for BS and high spin states respectively. This is the well known expression which is applicable both in weak and strong coupling regime. Use of this expression solves the problem of assigning a proper delocalization limit for BS state as described by Illas and coworkers.[26] To evaluate spin expectation values of BS states, prescription of Dai and Whangbo has been followed.[27]

5.3

RESULTS AND DISCUSSION

(a) (b)

Figure 5.2 Spin topology of (a) H_3He_3 and (b) H_4He_4.

We have chosen H_3He_3 and H_4He_4 (Figure 5.2) as benchmark systems in order to verify the applicability of the above mentioned computational strategy for evaluating magnetic exchange coupling constant in SMMS, calculated *J* values for these hypothetical compounds at UB3LYP/6-311++G(d,p) level are compared with those of post HF calculations carried out by Ruiz et al.[17a] Following our strategy we calculated exchange interaction J_{23} between H2 and H3 by disregarding the contributions from H1 (Figure 5.2a) and H1 and H4 (Figure 5.2b) and so on. All the magnetic interactions in H_3He_3 (Table 5.1a) and H_4He_4 (Table 5.1b) are found to be in good agreement with the results obtained by Ruiz et al.[17a] However, in case of H_4He_4, CASSCF results predict ferromagnetic coupling between diagonal hydrogens, whereas results obtained at other levels solicit for AFM interaction. Our computed value of *J* follows the common trend and matches well with CASPT2 level value. All the spins in H_3He_3 and H_4He_4 are found to be antiferromagnetically coupled (Table 5.1) and in this situation it is never possible for all the spins to align oppositely to each other. This constraint gives rise to topological spin frustration.[21, 28] The frustrated spins simultaneously cannot align oppositely with rest of the spins and take some intermediate direction. Spin frustration in these two systems can be visualized from the spin topology of low spin states of H_3He_3 and H_4He_4; available from Mulliken spin population analysis (Figure 5.2). Spin topology in these two systems shows parallel spin orientations in magnetic couples H2-H3 in H_3He_3 (Figure 5.2a), and H1-H3, H2-H4 in H_4He_4, which is in stark contrast with antiferromagnetic nature of magnetic interaction between those couples as shown by the computed *J* values in between them (Table 5.1). In a molecule of C_{2v} symmetry like H_3He_3, magnetic interaction between H2 and H3 (J_d) is much weaker than that between H1-H2 and H1-H3 (J_n), due to the largest distance between H2 and H3. Whereas in H_4He_4 with D_{4h} symmetry, there exist two sets of equivalent *J*'s; one set (J_n) includes H1-H2, H2-H3, H3-H4 and H4-H1 spin pairs, i.e., the nearest neighbor interactions, and the other set (J_d) describes the interaction between diagonal hydrogens H1-H3 and H2-H4. In these cases, as both J_n and J_d are negative, spin topology of the ground state will depend on the ratio $\rho = J_d / J_n$.[28] It means that the strongly coupled spins become the fixed spins and set the orientation of spins on all magnetic centers. For this reason, strong antiferromagnetic interaction between H1-H2 and H1-H3 polarizes the spins on H2 and H3 parallel, instead of antiferromagnetic interaction between H2 and H3. Similarly in H_4He_4, as the distance between the diagonal hydrogens are much longer than that between apical ones in H_4He_4, exchange interactions along the sides of the square are dominant. This makes the value of this ratio ρ much less than one (Table 5.1b). Hence, stronger AFM interactions in H1-H2, H2-H3, H1-H4 and H3-H4 spin pairs will ferromagnetically polarize the H1-H3 spins despite their antiferromagnetic interaction. In this context, it is interesting to note that, although we are making all other paramagnetic sites inactive during computation of *J* between specific pairs; magnetic effects from those apparently inactive paramagnetic sites are also existent in the form of spin frustration.

Table 5.1 Magnetic exchange coupling constants in (a) H_3He_3 and (b) H_4He_4 [#]Reported values are at CASPT2(large)/6-311g(d,p) level in ref. 17a.

(a) H_3He_3	Dummy atom	J (cm^{-1})	J (cm^{-1})[#]
	H1	J_{23}= − 137	− 195
	H2	J_{13}= − 152	
	H3	J_{12}= − 152	

(b) H_4He_4	Dummy atoms	J (cm^{-1})	J (cm^{-1})*
	H1 and H2	J_{34}= − 467	− 521
	H2 and H3	J_{14}= − 467	
	H3 and H4	J_{12}= − 467	
	H4 and H1	J_{23}= − 467	
	H1 and H3	J_{24}= − 8	− 5.2
	H2 and H4	J_{13}= − 8	

5.3.1 Mn_3^+

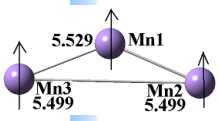


Figure 5.3 Spin distribution in cationic manganese trimer, obtained at UB3LYP/6-311+G(3df) level.

We estimate the coupling constant values in cationic manganese trimer (Figure 5.3), which has previously been investigated by Terasaki et al.,[29] where optimization of the structures of all the spin states with multiplicities of 1 through 21 revealed 17-tuplet state to be its ground state. Ferromagnetic nature of this trimer is due to the weak binding among constituent atoms and strong 3d-4s exchange interaction among manganese atoms. We perform optimization of this 17-tuplet ground state geometry using UB3LYP exchange-correlation functional and 6-311++G (3df) basis set. An isosceles triangle is resulted, which is in agreement with reported structure.[29] Population analysis shows an average spin density of 5.5 per magnetic site. With these available spins on magnetic sites, we deduce the magnetic exchange coupling constants (Table 5.2). The Mn1-Mn2 and Mn1-Mn3 distances being equal, we obtain equal values of J in between these two pairs; this is in accordance with one of our recent work where we discussed the distance dependence of J values in metallic systems.[30]

Table 5.2 Magnetic exchange coupling constants in Mn_3^+

Dummy atom	J (cm^{-1})
Mn1	J_{23}= 1641
Mn2	J_{13}= 1517
Mn3	J_{12}= 1517

5.3.2 1,3,5-benzenetriyltris (N-tert-butyl nitroxide)

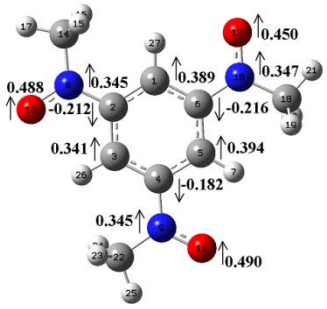


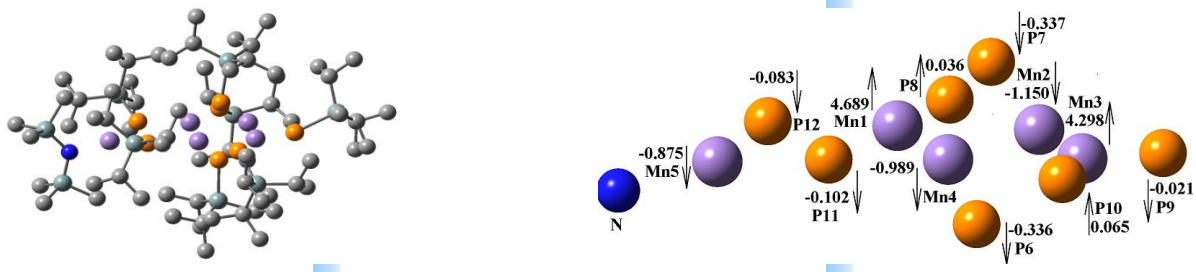
Figure 5.4 Optimized structure of 1,3,5-benzenetriyltris (N-methyl nitroxide) (Red=O, Ash=C, White=H, Blue= N) and spin distribution obtained at UB3LYP/6-311++G(d,p) level.

The 1,3,5-benzenetriyl framework has been extensively used as a coupling unit for connecting unpaired electrons ferromagnetically to construct super high-spin organic molecules.[31] Such a stable organic triangular spin system, 1,3,5-benzenetriyltris (N-*tert*-butyl nitroxide) (Figure 5.4) and its derivatives were prepared by Kanno et al.[32] Magnetic measurement of this compound with a Faraday balance reveals a quartet ground state. Electron paramagnetic resonance and magnetic susceptibility measurements suggest a ferromagnetic interaction among the spins arranged at the corners of an equilateral triangle. We have simplified the structure by replacing the *tert*-butyl groups with methyl for the sake of computational convenience and optimized its ground state geometry at UB3LYP/6-311++G(d,p) level. Spin populations on the atoms show that the unpaired spins are not centralized on either of N and O; rather the single spin ½ is delocalized on both N and O. This observation is in agreement with the well-established fact that spin remains localized at the N-O bond.[33] Ferromagnetic coupling between these unpaired spins is induced through the alternate spin polarization of π-electrons on the *m*- phenylene unit which can be verified by the spin density plot (Figure 5.4). Spin density alternation rule given by Trindle et al. further justifies this argument.[34] Quantification of magnetic interactions between three paramagnetic pairs yields positive values for exchange coupling constant, indicating FM interactions between all the pairs (Table 5.3). Calculated exchange coupling constants are equal so do the sides of the triangle connecting the radical centers. The value of *J* is within the range of the previously reported results.[32]

Table 5.3 Magnetic exchange coupling constants in 1,3,5-benzenetriyltris (N- methyl nitroxide) #Range of experimental values as in ref. 32

Dummy atom	J (cm^{-1})	J (cm^{-1})#
O1	J_{12}= 334	
O2	J_{23}= 334	139-348
O3	J_{12}= 333	

5.3.3 $Mn_5\{N(SiMe_3)_2\}\{\mu_4\text{-}Psi(iPr)_3\}_2\{\mu\text{-}P(H)\text{-}Si(iPr)_3\}_5$



(a) (b)

Figure 5.5 (a) Crystal structure and (b) Spin density distribution (computed at UB3LYP/6-311+G (3df) level) in $[Mn_5\{N(SiMe_3)_2\}\{\mu_4\text{-}PSi\mathit{i}Pr_3\}_2\{\mu\text{-}P(H)\text{-}Si\mathit{i}Pr_3\}_5]$; (Violet=Mn, Orange=P, Ash=C, Steel blue= Si, Deep blue= N, H atoms are not shown to avoid complexity of the structure).

Recently Hanisch et al. synthesized a unique manganese-phosphorous complex (Figure 5.5) and studied its magnetic property in detail.[35] They reported a sextet ground state of the molecule through quantum chemical calculations. Their attempt to model the magnetic susceptibility directly with classical spin Heisenberg model failed due to coexistence of multiple spin couplings. This failure

led them to use DFT calculations to evaluate the exchange coupling constants. For this evaluation, Hanisch et al. followed the technique put forward in refs. 16 and 17, however, the limitation of this method has already been discussed. They found antiferromagnetic interactions among the magnetic sites therein. The coupling constants values obtained by them reasonably simulate the experimentally measured temperature dependence of the magnetic susceptibility.[35] To compute its magnetic exchange coupling constants through our approach, first we retrieve its structure from crystal structure database. The molecule is truncated by elimination of fragments which do not belong to probable exchange coupling pathways and hence are expected not to affect magnetic interactions. Hydrogen atoms are introduced into the structure to saturate valencies (Figure 5.5b). Single point calculation on the ground state of the molecule at UB3LYP/6-311+G (3df) level produced alternating surplus of up-spin and down-spin electron densities in the Mn1-Mn2-Mn3-Mn4 quadrangle (Figure 5.5b). From these residual spin and charge values on individual magnetic sites, we calculate the exchange coupling constants between specific pairs, making other magnetic sites dummy. As the high spin states are almost free from spin contamination, guess orbitals for single point calculations are generated from these states. Measures have been taken to produce a reliable estimate of $<S^2>$ values. Computations involving only nearest neighbor interactions produce negative *J* values for the pairs in Mn1-Mn2-Mn3-Mn4 quadrangle and hence are in parity with experimentally measured antiferromagnetic nature of Mn_5 complex (Table 5.4). We obtain positive *J* value for Mn4-Mn5 pair which is in agreement with the ground state spin map (Figure 5.5b), where similar spins reside on Mn4 and Mn5. However, Hanisch and coworkers found antiferromagnetic spin coupling between this pair in spite of a similar ground state spin density distribution.[35] Comparison of exchange coupling constant values in between J_{14}, J_{15} and J_{45} (Table 5.4) shows the strongest interaction is in between Mn4 and Mn5. Thus, it can be concluded that a strong FM coupling between Mn4 and Mn5 polarizes the spin on Mn1 antiferromagnetically with respect to the spins on Mn4 and Mn5. It has been argued in ref. 35 that spins on Mn atoms are coupled by super exchange through bridging atoms. This necessitates the enquiry about the equivalency of all possible exchange pathways in Mn1-Mn2-Mn3-Mn4 quadrangle; due to the existence of several possible spin exchange pathways therein. Spin densities in apical bridging P6 and P7 atoms are much larger than in equatorial P8, P9 or P10, and hence it can be predicted that spin exchange occurs through apical bridging P atoms and not through the equatorial P atoms.

Table 5.4 Magnetic exchange coupling constants between nearest neighbours in $[Mn_5(NH_2)\{\mu_4\text{-}PH\}_2\{\mu\text{-}PH_2\}_5]$ [#] Reported values at B3LYP/def2-TZVP level in ref. 35.

Dummy atoms	J (cm^{-1})	J (cm^{-1})[#]
Mn3,Mn4 and Mn5	J_{12}= − 187	−192.3
Mn2,Mn3 and Mn5	J_{14}= −20	−79.1
Mn2,Mn3 and Mn4	J_{15}= − 115	−12.7
Mn1,Mn4 and Mn5	J_{23}= − 941	−219.8
Mn1,Mn2 and Mn5	J_{34}= − 836	−182.6
Mn1,Mn2 and Mn3	J_{45}= 857	−13.3

5.4

SUMMARY

Systems with non isotropic magnetic interactions can be characterized by nonequivalent values of exchange coupling constants in systems with multiple magnetic sites. In this work, we aim at describing a new technique for calculating exchange coupling constant values in SMMS by using broken symmetry approach in DFT framework. In this scheme, we perform spin mapping on the ground state of the SMMS. With this spin distribution, exchange coupling constants for a specific pair of magnetic sites in polynuclear magnetic systems are calculated. In this process the other paramagnetic sites are kept inert. This is rationalized by writing the HDVV Hamiltonian in terms of spin density operator. However, magnetic effects of disregarded atoms on concerned paramagnetic pair are not ignored as they are primarily taken into account in the use of the ground state values of spins and charges in course of estimation of *J*.

Application of this computational strategy on the benchmark systems yields the value of exchange coupling constants very close to the results obtained through post Hartree-Fock treatments. Negative *J* values for all the magnetic pairs in both the benchmark systems give rise to competing spin interaction which makes the system topologically spin frustrated. Application of the same scheme to three real systems, viz., Mn_3^+, 1,3,5-benzenetriyltris (N-tert-butyl nitroxide), and $Mn_5\{N(SiMe_3)_2\}\{\mu_4\text{-}PSi\textit{i}Pr_3\}_2\{\mu\text{-}P(H)\text{-}Si\textit{i}Pr_3\}_5$ reproduced the known nature of magnetic interactions between the spin pairs in all the three systems. Electron spins are found to be ferromagnetically coupled in first two systems, whereas a coexistence of ferromagnetic and antiferromagnetic interactions is found in the pentanuclear manganese complex. The proposed technique significantly reduces the computation rigor by skipping the computation of energy differences among all possible spin states and subsequent diagonalization of a large matrix becomes unnecessary. Moreover, as in this strategy, electronic environment of disregarded atoms is nullified by assigning them as dummies, computation time is also decreased. Although, estimated values of magnetic exchange coupling constants in some of the cases seem to be overestimated, the sign of *J* between magnetic sites is concordant with the spin density distribution and are in agreement with reported nature of magnetic interactions. Thus, independent estimation of each coupling constant by considering only two paramagnetic centers seems to be an economical and rational approach, irrespective of systems and nature of magnetic interactions.

5.5

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CHAPTER 6

Interpretation and Quantification of Magnetic Interaction through Spin Topology

Abstract :

This work develops a formalism to quantify the interaction among unpaired spins from the ground state spin topology. Magnetic systems where the spins are coupled through direct exchange and superexchange are chosen as references. Starting from a general Hamiltonian, an effective Hamiltonian is obtained in terms of spin density which is utilized to compute exchange coupling constants in magnetic systems executing direct exchange. The high spin-low spin energy gap, required to extract the coupling constant is obtained through the broken symmetry approach within the framework of density functional theory. On the other hand, a perturbative approach is adopted to address the superexchange process. Spin transfer in between the sites in the exchange pathway is found to govern the magnetic nature of a molecule executing superexchange. The metal-ligand magnetic interaction is estimated using the second order perturbation energy for ligand to metal charge transfer and spin densities on the concerned sites. Using the present formalism, the total coupling constant in a superexchange process is also partitioned into the contributions from metal-ligand and metal-metal interactions. Sign and magnitude of the exchange coupling constants, derived through the present formalism, are found to be in parity with those obtained using well-known spin projection technique. Moreover, in all the cases the ground state spin topology is found to complement the sign of coupling constants. Thus, the spin topology turns into a simple and logical means to interpret the nature of exchange interaction. The spin density representation in the present case resembles McConnell's spin density Hamiltonian and in turn validates it.

6.1

INTRODUCTION

Magnetism is induced in a material through the coupling of its inherent spin moments. There exists a miscellany of exchange mechanisms such as direct exchange, indirect exchange, double exchange, superexchange and so on, through which the spins can interact. A rigorous analysis of this exchange interaction is a prerequisite for clear understanding of magnetic nature of any system. However, irrespective of their mechanisms, the exchange interactions are usually quantified through the phenomenological Heisenberg-Dirac-van Vleck (HDVV) spin Hamiltonian,

$$\hat{H} = -\sum_{i<j} J_{ij}\hat{S}_i \bullet \hat{S}_j, \tag{6.1}$$

where, $\hat{S}_i$ and $\hat{S}_j$ are the spin angular momentum operators on magnetic sites *i* and *j* and J_{ij} is the exchange coupling constant between them. Since, this Hamiltonian is simply related to spin eigenfunctions, it becomes necessary to map the eigenvalues and eigenfunctions of an exact nonrelativistic Hamiltonian into this HDVV Hamiltonian. Moreira and Illas have shown that for an interaction between two spin-1/2 sites, it is possible to map the Heisenberg eigenstates to the triplet and singlet *N*-electron states and the coupling constant can be derived from the singlet-triplet energy difference.[1] However, sometimes the energy difference is equated with twice the exchange integral because of the occasional appearance of an extra factor of two in the Heisenberg Hamiltonian.[2] The intersite magnetic coupling is found to originate from local electronic interaction between two specific magnetic sites.[3] This opens up the possibility of accurate estimation of spin state energies and hence *J*, using ab initio methods. Compared to computationally demanding ab intio techniques for estimation of *J*, the density functional theory (DFT) based approaches have emerged as the best compromise between computational rigor and accuracy.[4] In this DFT framework, one can relate *J* to the energy difference between the high spin ferromagnetic (FM) and the broken symmetry (BS) solution for open shell singlet. This BS approach, primarily proposed by Noodleman, makes use of an unrestricted or spin polarized formalism.[5] However, the main limitation with DFT has been the proper choice of exchange correlational (XC) functional during estimation of any electronic property.[6] The value of coupling constant is also found sensitive towards the percentage of Fock exchange on the XC functional.[7] Apart from the selection of proper XC functional, the unrestricted formalism used in DFT brings about an additional problem of spin contamination, particularly in the BS state.[8] To avoid this, usually following spin-projected methods are adopted, [5, 9]

$$J_{GND} = \frac{E_{BS}^{DFT} - E_{HS}^{DFT}}{S_{\max}^2},$$
$$J_{BR} = \frac{E_{BS}^{DFT} - E_{HS}^{DFT}}{S_{\max}(S_{\max}+1)}, \tag{6.2}$$
$$J_{Y} = \frac{E_{BS}^{DFT} - E_{HS}^{DFT}}{\left\langle S^2 \right\rangle_{HS} - \left\langle S^2 \right\rangle_{BS}}.$$

The applicability of above equations depends upon the degree of overlap between the magnetic orbitals. Ginsberg, Noodleman and Davidson derived J_{GND} in case of a weak overlap between magnetic orbitals. This is further modified by Bencini and Ruiz to get J_{BR} which describes the situation of strong overlap between magnetic orbitals. However, the third of this series, J_Y is given by Yamaguchi which can be applied in all overlap limits. The expressions above are widely employed on organic diradicals and dinuclear inorganic complexes with one or more than one electron per magnetic site.[1, 10] On the other hand, in systems with multiple magnetic sites, such as in single molecule magnets, there are several exchange interactions. For such systems, spin topology can become a reliable alternative to predict their magnetic status, albeit in a qualitative way.[11] In one of our recent works, the ground state spin density distribution has been utilized to estimate exchange coupling constant in systems with multiple magnetic sites.[12] The importance of spin topology in explaining the magnetic behavior had been highlighted by McConnell early in 1963.[13] On the basis of the HDVV Hamiltonian, he proposed the following spin density representation of exchange interaction,

$$\hat{H} = -\hat{S}^A \bullet \hat{S}^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B . \tag{6.3}$$

This Hamiltonian elucidates the exchange interaction between two aromatic radical fragments *A* and *B*, where $\hat{S}^A$ and $\hat{S}^B$ are the total spin operators for *A* and *B*; ρ_i^A and ρ_j^B are the π-spin densities on atoms *i* and *j* of fragments *A* and *B* respectively. In this expression, the exchange integral, which is evaluated in the context of valence bond theory,[14] usually considered as negative. As a consequence, ferromagnetic exchange interaction is found to be associated with the negative value of the spin density product.[15] This model to predict the nature of magnetic interaction based on spin density has been popularly known as McConnell-I model. In an effort to find out the effect of non-orthogonality in the broken symmetry approach, Caballol et al. expressed the coupling constant *J*, which takes the following expression with the same form of HDVV Hamiltonian as used for eq 6.2,

$$J = \frac{\left(E_{BS} - E_{T'}\right)}{1 + S_{ab}^2} . \tag{6.4}$$

where, E_{BS}, $E_{T'}$ are the energies of unrestricted BS and triplet state and S_{ab} is the overlap integral between the magnetic orbitals of the broken symmetry solution.[16] They could find that the overlap term in the denominator of eq 6.4 is related to the spin density of magnetic center, ρ_A as

$$S_{ab}^2 = 1 - \rho_A^2 . \tag{6.5}$$

This relation is further modified by Boiteaux and Mouesca as

$$S_{ab}^2 = \rho_{HS}^2(Cu) - \rho_{BS}^2(Cu) , \tag{6.6}$$

and used to quantify the antiferromagnetic (AFM) contribution to the exchange coupling between metal spins in ligand bridged Cu (II) dimers.[17] Ruiz et al. suggested that this difference of spin densities at metal atoms in the high spin and BS state can be a good alternative to the direct calculation of overlap integral.[18] All these facts suggest a link between exchange coupling constant and spin density and hence validates spin topology based interpretation of the magnetic nature. In fact,

the McConnell-I model is long being used in designing high spin organic ferromagnets.[19] In inorganic regime also, comprehension of spin density distribution is foreseen as a useful tool for designing FM or AFM interaction between paramagnetic centers in systems with multiple magnetic sites.[12, 20] Besides intramolecular magnetic interaction, the nature of intermolecular spin exchange has also been predicted from the polarized spin density of separate molecular units.[15, 21]

The foregoing discussion highlights the importance of spin topology in predicting the magnetic nature of a system. However, in the state-of-the-art formalisms (eqs 6.2, 6.4) any kind of such a direct correspondence between coupling constant and spin density is absent. Although, in few of the earlier works it have been shown that the exchange coupling constant is related to the spin density; the relation has not widely been adopted for estimation of *J*. The oldest model in this concern is the McConnell-I model. Its validity has been confirmed through the ESR data obtained for [2.2] paracyclophane isomers.[22] This analogy with experimental observation as well as the agreement with the results of ab initio computations on model systems has made the McConnell-I model a reliable tool in predicting magnetic nature.[23] In spite of this, McConnell-I model is questioned for its "ad hoc" way of proposition based on eq 6.1.[24] Novoa and coworkers enquired about the validity of eq 6.3 by comparing it with Heisenberg Hamiltonian and could find a direct correspondence between the spin density product and two electron exchange density matrix elements.[24a] However, they stated this correspondence to be partly accidental. In an alternative model, the equality in eq 6.6 correlates coupling constant with spin density. However, this model applies only to symmetric binuclear complexes with one unpaired electron per paramagnetic center.[18]All these aspects invoke serious doubt for general applicability of existing spin density based models and call upon the necessity of this work.

In the present work, an effort is put to correlate the spin topology with the exchange coupling constant in case of two different types of exchange mechanisms viz., direct exchange and superexchange. To quantify direct exchange, the exchange part of a general many body Hamiltonian is modified in terms of spin density to set the required correlation. Whereas, in dealing with the superexchange mechanism, Anderson's pioneering work appears as a good starting point.[25] In this model, Anderson described the system to be perturbed by the intersite electron transfer and expressed the exchange energy in terms of second order perturbation energy. Here, we recast this expression with spin density. Such obtained spin density representations of the exchange interactions are applied on few previously studied magnetic systems to estimate the exchange coupling constants therein. The formalism for direct exchange is first verified with simple neutral and cationic Cr, Mn dimers followed by three large organic diradicals. The magnetic nature of Cr and Mn dimers has already been the subject of several theoretical and experimental investigations.[26] Desmaris et al. suggested a change in the magnetic nature of Cr_2 upon ionization whereas ferromagnetic ground state is reported for Mn_2 in its neutral as well as cationic state.[26a] The MRCI techniques predict the singlet ground state of Mn_2 whereas a number of DFT based computations conclude an 11-tuplet state as the ground state.[26b] This elusive nature of Mn_2 has long been the subject of debate and addressed in one of our previous works.[26c] A recent synthesis of ferromagnetic ultrathin Mn nanosheet by Mitra et al. solicits for its high spin ground state.[26d] Among the organic diradicals chosen, widely cultivated 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-biverdazyl (bisoxoverdazyl) is selected from the popular open shell database of representative systems, used by Valero et al.[27] and later on Rivero et al.[28] to judge the performance of M06 and range separated functionals in accurate estimation of *J*. The biverdazyl diradical consists of one unpaired electron on the π-system of each ring which couple antiferromagnetically.[27,28,10a] Such organic radicals, when coupled through azobenzene exhibit a photoinduced change in magnetism and constitute an interesting class of materials.[10b] This spin

crossover is attributed to the change in the conformation of these systems from trans to cis around the double bond. Loss of planarity in the cis form makes the intervening exchange path unavailable for the spins and the radical sites execute through space direct exchange. Here, two such cis azobenzenes, one linked with nitronyl nitroxide (azobenzene-nno) and the other with verdazyl radical (azobenzene-ver) are also included as model systems. On the other hand, to deal with superexchange, anionic oxides of Cr and Mn are selected from one of our previous works, where they appeared as ferromagnets.[26c, 29] Apart from these, three other Cu binuclear complexes are selected from the open shell database,[27] which include $Cu_2Cl_6^{2-}$, $[\{Cu(phen)_2(\mu\text{-}AcO)(\mu\text{-}OH)\}](NO_3)_2\cdot H_2O$ and $[\{Cu(bpy)(H_2O)(NO_3)\}_2(\mu\text{-}C_2O_4)]$. The first of this list, $Cu_2Cl_6^{2-}$ exhibits antiferromagnetism in its planar configuration.[16, 27] In the second complex, referred to as YAFZOU in the database, the Cu (II) atoms are reported to be ferromagnetically coupled. The third candidate, BISDOW is known to have an antiferromagnetic ground state. Since, in these systems the exchange interaction is mediated through the diamagnetic bridging ligand, the total coupling constant in a superexchange process should have contributions from the metal-ligand and metal-metal interactions. Earlier studies pointed out two such contributions to the magnetic coupling; $J = J_F$ (For FM interaction) + J_{AF} (For AFM interaction) = $2K_{ab} - 4t_{ab}^2/U$, where K_{ab} describes direct exchange between magnetic orbitals and generally considered as ferromagnetic contribution.[25] The second part, including the hopping integral t_{ab} and the on-site Coulomb repulsion, U, is usually termed as kinetic exchange in Anderson's interpretation and antiferromagnetically contributes to the total coupling constant.[25] In their seminal works Calzado et al. applied CI techniques to compute these individual contributions to the magnetic coupling constant using effective Hamiltonian theory.[30] They have shown that, it is also possible to extract these three parameters K_{ab}, t_{ab} and U using different solutions of Kohn-Sham equations.[30b] The present spin density based formalism also enables one to partition the total coupling constant in a superexchange process into the contributions from the metal-ligand and metal-metal interactions. However, the variant magnetic systems opted for numerical validation can be categorized into four classes. The first group contains simple transition metal dimers executing direct exchange with more than one electron per magnetic site. Three large organic diradicals with dispersed spin in the ring are also taken as test systems for direct exchange in the second category. As the exhibitors of superexchange, systems with a single atomic ligand bridged metal dimers are taken to constitute the third group. The candidates in the fourth category also execute superexchange mechanism, but the metals are linked via extended bridging ligands in this case. In each of these categories, both the ferromagnetic and antiferromagnetic representatives are addressed. Numerical analysis with such wide spectrum of reference systems provides the opportunity to verify the general applicability of the present formalism.

6.2

THEORY

6.2.1 *Direct Exchange*

Let us consider a system of N atoms, localized on n lattice sites. In compliance with the unrestricted formalism, separate set of orbitals with different space parts are assigned for up-spin and down-spin electrons. Here, $\sum_{a=1} n_i^a$ set of electronic orbitals in atom A at site i is considered to represent such unrestricted MOs, occupied by a particular type of spin λ or λ'. Electronic interactions in such a system can be described by the Hamiltonian,

$$\hat{H} = \sum_{i,a} \frac{p_{n_i^a}^2}{2m} - \sum_{i,a} \frac{Z_i e^2}{|r_i^a - R_i|} + \sum_{\substack{i<j \\ a,b}} \frac{e^2}{|r_i^a - r_j^b|}. \qquad (6.7)$$

Many electron wave function representing the above system can be expanded in terms of the products of single particle wave functions which in its turn are the orthonormal spin-orbital components of a Slater determinant. This complete orthonormal set of spin orbitals can be expressed in terms of single particle Wannier function $\phi_{n_i^a \lambda}(r - r_i^a)$, which are used to expand the field operator ψ_λ,[25b, 31]

$$\psi_\lambda = \sum_{i,a} \phi_{n_i^a \lambda}(r - r_i^a) f_{n_i^a \lambda}(r_i^a) \qquad (6.8)$$

where, $f_{n_i^a \lambda}$ is the fermion annihilation operator which annihilates a λ spin in the orbital n_i^a. Using this second quantized form of the operator, the expectation value arising from the third term of the Hamiltonian in eq 6.7 describes the exchange interaction [25, 31]

$$E_{DX} = \sum_{\substack{i<j \\ a,b \\ \lambda,\lambda'}} J_{n_i^a n_j^b} f^{\dagger}_{n_j^b \lambda'}(r_j^b) f^{\dagger}_{n_i^a \lambda}(r_i^a) f_{n_j^b \lambda}(r_j^b) f_{n_i^a \lambda'}(r_i^a) \qquad (6.9)$$

where,

$$J_{n_i^a n_j^b} = \left\langle \phi^*_{n_j^b \lambda'}(r - r_j^b) \phi^*_{n_i^a \lambda}(r - r_i^a) \left| \frac{e^2}{|r_i^a - r_j^b|} \right| \phi_{n_j^b \lambda}(r - r_j^b) \phi_{n_i^a \lambda'}(r - r_i^a) \right\rangle. \qquad (6.10)$$

Now, it is known that the direct exchange involves only the electrons in magnetic orbitals. Between the spatially different up-spin and down-spin unrestricted MOs, the MO which does not have any population in its counterpart is considered as the magnetic orbital. However, the population status of the molecular orbitals (MOs) is not sufficient to determine their singly or doubly occupied nature. In order to determine the occupancy status of any orbital one has to check whether there is any overlap between an up-spin orbital and its corresponding pair down-spin orbital.[32] A zero overlap between an occupied up-spin MO and its corresponding pair down-spin MO can ascertain the singly occupied nature of the up-spin MO. In the present treatment, n_i^a or n_j^b set of unrestricted MOs are considered to have such singly occupied nature, only which participate in the direct exchange mechanism. Assuming one specific type of spin for one magnetic site and applying the fermion anticommutation rule as follows,

$$\left\{ f^{\dagger}_{n_i^a \lambda}, f_{n_j^b \lambda'} \right\} = \delta_{ij} \delta_{\lambda\lambda'}, \qquad (6.11)$$

eq 6.9 can be simplified to represent the direct exchange as,

$$E_{DX} = -\sum_{\substack{i<j \\ a,b \\ \lambda,\lambda'}} J_{n_i^a n_j^b} f^{\dagger}_{n_j^b \lambda'}(r_j^b) f_{n_j^b \lambda'}(r_j^b) f^{\dagger}_{n_i^a \lambda}(r_i^a) f_{n_i^a \lambda}(r_i^a). \tag{6.12}$$

Now, as the n_i^a state is singly occupied by λ spins only, the number operator $\hat{N}_{n_i^a \lambda}(r_i^a)$ can also be regarded as the spin density operator $\hat{\rho}\ (r_i^a)$, and thus

$$f^{\dagger}_{n_i^a \lambda}(r_i^a) f_{n_i^a \lambda}(r_i^a) = \hat{N}_{n_i^a \lambda}(r_i^a) = \hat{\rho}(r_i^a). \tag{6.13}$$

Hence, with this form of spin density operator, it becomes straightforward to express eq 6.12 in terms of spin density

$$E_{DX} = -\sum_{\substack{i<j \\ a,b}} J_{n_i^a n_j^b} \rho\ (r_j^b) \rho\ (r_i^a). \tag{6.14}$$

Eq 6.14 delineates the dependence of direct exchange interaction on the spin density of magnetic sites. Although, this expression includes the effect of spin density in the Hamiltonian similar to the form proposed by McConnell in eq 6.3; this is obtained from HDVV Hamiltonian through a sequence which has been absent in the formulation of McConnell's spin density Hamiltonian.[24]

6.2.2 *Superexchange*

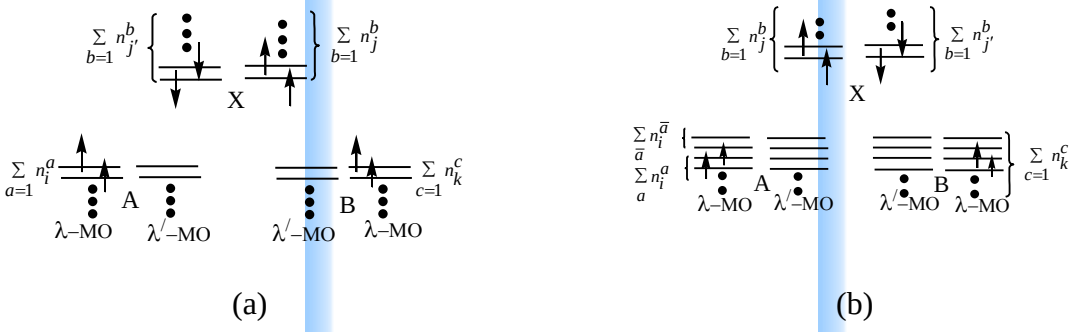


Figure 6.1 Representation of electronic arrangements in the model system *A-X-B* undergoing superexchange with (a) "both more than half full" and (b) "less than half full" *d*-states as described by Anderson.

The extent of direct exchange between magnetic sites gradually weakens with the increase in their distance,[26c] as can also be understood from the presence of $e^2 \left| r_i^a - r_j^b \right|^{-1}$ term in the exchange parameter (eq 6.10). However, the unpaired electrons in remote magnetic sites still may interact via

diamagnetic bridging group, which is defined as superexchange.[25] This necessitates a nonorthogonal condition among the valence MOs of magnetic sites and the intervening diamagnetic ligand. Kramers applied perturbation theory to obtain the effective exchange resulting from this mechanism.[33] Anderson reformulated Kramers' theory by including the ligand wave function which is the covalent admixture of cation and anion wave functions.[25b] To parameterize superexchange with spin density, a model system *A*-*X*-*B* is taken, where *A* and *B* are remote magnetic centers, intervened by a diamagnetic bridging group *X*. The active MOs in *A* and *B* are taken to be the set of $\sum_{a=1} n_i^a$ and $\sum_{c=1} n_k^c$ orbitals respectively, singly occupied by λ or λ' type of spins (Figure 6.1). In compliance with unrestricted formalism, different set of orbitals, (for example, $\sum_{b=1} n_j^b$ and $\sum_{b=1} n_{j'}^b$ in *X*) are assigned for λ and λ' type of spins respectively.[32] Now, the magnetic orbitals in *A* or *B* may be fully or partially occupied which is described by Anderson as "both more than half full" and "less than half full" cases.[25] Since, in Anderson's model an electron transits without spin flip; [25b] a change in the occupancy status of MOs discriminates the nature of interaction. In case of the full occupancy of λ-orbitals on *A* or *B*, it becomes possible for λ' spin only to enter the set of λ'-MOs on *A* or *B* from $\sum_b n_{j'}^b$ on *X*. The second order perturbation energy associated with such an electron transfer is expressed as,[25b]

$$\Delta E = \sum_{\substack{i',j' \\ a,b}} \frac{t^2_{r_i^a r_{j'}^b}}{U}\left(\frac{1}{2} + 2\hat{S}_{n_{i'}^a}(r_{i'}^a)\bullet\hat{S}_{n_{j'}^b}(r_{j'}^b)\right), \tag{6.15}$$

where, $t_{r_i^a r_{j'}^b}$ is the hopping integral which carries an electron from *X* to *A* and *U* is the single ion repulsion energy. Now, the spin momentum operators can be split into different components as,

$$\hat{S}_{n_i^a}\bullet\hat{S}_{n_j^b} = \hat{S}^x_{n_i^a}\bullet\hat{S}^x_{n_j^b} + \hat{S}^y_{n_i^a}\bullet\hat{S}^y_{n_j^b} + \hat{S}^z_{n_i^a}\bullet\hat{S}^z_{n_j^b}. \tag{6.16}$$

Using the Jordan-Wigner transformation,[34]

$$S^+_{n_i^a} = S^x_{n_i^a} + iS^y_{n_i^a} = f^{\dagger}_{n_i^a}\exp\left(i\pi\sum_{x<a} n_i^x\right) \quad \text{and}$$

$$S^-_{n_i^a} = S^x_{n_i^a} - iS^y_{n_i^a} = f_{n_i^a}\exp\left(-i\pi\sum_{x<a} n_i^x\right) \tag{6.17}$$

and following form of spin density operator [35]

$$\hat{\rho}_{n_i^a} = 2\hat{S}^z_{n_i^a}\delta(r - r_i^a), \tag{6.18}$$

where, $\hat{\rho}_{n_i^a}$ is the spin density operator at the state n_i^a; eq 6.16 can be written as

$$\hat{S}_{n_i^a} \bullet \hat{S}_{n_j^b} = \frac{1}{2}\left(f_{n_i^a}^{\dagger} f_{n_j^b} + f_{n_j^b} f_{n_i^a}^{\dagger} \right) + \frac{1}{4} \rho_{n_i^a} \bullet \rho_{n_j^b} . \tag{6.19}$$

Applying the anticommutation rule in eq 6.11, the first term within the parenthesis in eq 6.19 vanishes. Inserting this simplified form in eq 6.15, the interaction between *A* and *X* can be expressed as

$$\Delta E = \frac{1}{2} \sum_{\substack{i',j' \\ a,b}} \frac{t^2_{r_{i'}^a r_{j'}^b}}{U} \left(1 + \rho_A \bullet \rho_X \right), \tag{6.20}$$

where ρ_A is the overall spin density at *A*. While, this dispersal of λ' spins from $\sum_b n_{j'}^b$ orbitals on *X* goes on, there operates a direct exchange among localized spins on *A* and *B* (Figure 6.1a), which is expressed through eq 6.14. Therefore, the total energy in a superexchange process for all these magnetic interactions among *A*, *X* and *B* can be written as,

$$E_{SX} = \frac{1}{2} \sum_{\substack{i',j' \\ a,b}} \frac{t^2_{r_{i'}^a r_{j'}^b}}{U} \left(1 + \rho_A \bullet \rho_X \right) - \sum_{i,k} J_{AB} \rho_A \rho_B . \tag{6.21}$$

From this expression, a partitioning of the total coupling constant can be figured out. The first part accounts for the metal-ligand interaction and the coupling between metal spins are addressed in the second part. In fact, the t^2/U term is related to *J* for metal-ligand interaction in the well-known Hubbard model Hamiltonian.[16] The parameters *t* and *U* in the Hubbard Hamiltonian is obtained through second quantization of the one electron and two electron operators in the many body Hamiltonian (eq 6.7) through the field operator in eq 6.8.[31] Hence the integral form of the operators can be written as

$$t_{ij} = \int dr \phi(r - r_i) \left(\frac{p^2}{2m} \right) \phi(r - r_j) \quad \text{and} \quad U = \int dr_i \int dr_j \left| \phi(r - r_i) \right|^2 \left(\frac{e^2}{r_i - r_j} \right) \left| \phi(r - r_j) \right|^2 \tag{6.22}$$

Several works are devoted for the estimation of these parameters *t* and *U*. [16, 30] However, in the present work instead of the direct estimation of *t* and *U*, eq 6.20 is used to extract the magnetic coupling constant (or t^2/U) from the second order perturbation energy for intersite charge transfer and the spin densities on the concerned sites. The second order energy corresponding to the charge transfer is computed using the natural bond orbital (NBO) analysis, which is discussed in details for particular systems in the following section. On the other hand, J_{AB} in the second part of eq 6.21 estimates direct exchange. Hence, the total coupling constant (J_{SX}) in a superexchange process can be decomposed into the coupling of metal and ligand spins (J_{ML}) and that between metallic spins (J_{MM}), which may be expressed as follows,

$$J_{SX} = \sum_{i,j} \frac{2\Delta E}{1+\rho_A \bullet \rho_X} - \sum_{i,k} \frac{E_{DX}}{\rho_A \rho_B} \equiv J_{ML} + J_{MM} \,. \qquad (6.23)$$

Such splitting of coupling constant, which is very similar to the Anderson's interpretation,[25] is exercised in several references.[21, 30, 36] The FM interaction is considered to be comparatively weaker because it operates between spatially orthogonal wave functions.[36c] However, ab initio results suggest that the sign of J_{MM} may also deviate from its usual positive sign and depends upon spin polarization of the system,[30b] which is also apparent from eq 6.23. Moreover, the kinetic exchange may not be always negative and can have a ferromagnetic nature.[36b] An explanation for this exception also may be inherent in the above expression since each interaction is governed by spin topology. In the whole mechanism, one can easily deduce the concomitant spin topology. The magnetic orbitals in *A* and *B*, i.e., set of $\sum_a n_i^a$ and $\sum_c n_k^c$ are primarily assumed to be occupied by λ spins. So far the spin density of diamagnetic *X* (ρ_X) is concerned; it is dependent on the ultimate difference of majority and minority spins during superexchange,

$$\rho_X = \sum_{j,j'} \left(\rho_{n_{j'}^b,\lambda'}(r_{j'}^b) \sim \rho_{n_j^b\lambda}(r_j^b) \right). \qquad (6.24)$$

Depending upon the "both more than half full" or "less than half full" *d*-states as described by Anderson, the nature of intersite charge transfer may vary which in its turn leads to different spin topology of the system. In case, the λ-spin orbitals in *A* and *B* are "more than half full"; the λ' spins get dispersed from the $\sum_b n_{j'}^b$ orbitals, whereas λ spins on $\sum_b n_j^b$ remain localized on *X*, and thus there occurs excess accumulation of λ spins (eq 6.24). Consequently, an identical λ spin density is expected on each of *A*, *X* and *B* atoms.

A similar treatment for "less than half full" states where few of the states (say $\sum_{\bar{a}} n_i^{\bar{a}}$ on *A*) remains completely empty, had also been proposed by Anderson.[25b] In this situation, the transfer of electron together with an additional internal exchange effect induces a third-order perturbation to the system. Let us consider that the transition is taking place from the $\sum_b n_j^b$ orbital on *X* to one of the empty states $\sum_{\bar{a}} n_i^{\bar{a}}$ on atom *A*, where other set of orbitals $\sum_a n_i^a$ is singly occupied by λ spins (Figure 1b). With this assumption the third order interaction is expressed as

$$\Delta E' = \sum_{\substack{i,j \\ a,\bar{a},b \\ \lambda,\lambda'}} \frac{t_{r_j^b, r_i^{\bar{a}}}^2 J_{n_i^a n_i^{\bar{a}}}}{U^2} f^{\dagger}_{n_i^a\lambda}(r_i^a) f^{\dagger}_{n_j^b\lambda'}(r_j^b) f_{n_i^a\lambda'}(r_i^a) f_{n_j^b\lambda}(r_j^b) \cdot \qquad (6.25)$$

Now, since the spin transfers without flipping, presence of λ spins in $\sum_a n_i^a$ set of orbitals allow the λ spins only to enter the empty $\sum_{\bar{a}} n_i^{\bar{a}}$ states obeying Hund's rule of maximum spin multiplicity. In this

condition where all the spins are λ, the above expression with application of fermion anticommutation rule (eq 6.11) and spin density operator (eq 6.13), transforms as follows

$$\Delta E' = -\sum_{\substack{i,j \\ a,\bar{a},b,\lambda}} \frac{t^2_{r_j^b r_i^{\bar{a}}} J_{n_i^a n_i^{\bar{a}}}}{U^2} \rho(r_i^a)\rho(r_j^b). \tag{6.26}$$

However, this third order correction term becomes insignificant for a large antiferromagnetic interaction between the cation and ligand.[32b] Beside λ spins, there also exists the possibility of λ' spin hopping from $\sum_b n_j^b$, on *X* to unoccupied λ' spin orbitals of atom *A* and *B* at site *i* and *k*. However, existing λ- spin moments in *A* or *B* facilitate λ- spin hopping onto its empty orbital. Therefore, more delocalization of λ spins from *X* compared to λ' spins should effect an overriding population of λ' spin on *X* (eq 6.24). Hence, the overall spin topology should display an opposite spin density on *X* to that on both of the *A* and *B* atoms.

6.3

NUMERICAL VERIFICATION

To verify the reliability of present formalism, a broad class of systems with known magnetic status, as mentioned earlier in the introduction, is selected. Magnetic characterization of such systems is performed within the framework of density functional theory. DFT is known to produce accurate spin density value which is also the key parameter in the present work.[37] Throughout this study; we stick to the B3LYP exchange-correlation functional in unrestricted framework. Geometries of simple systems such as transition metal dimers and their anionic oxides are optimized with 6-311+g (3df) basis set using *GAUSSIAN03W*.[38] The coordinates of cis azobenzene-nno and azobenzene-ver, optimized with 6-311++g(d,p) basis set are collected from the ref. 10b. Rest of the systems viz. bisoxoverdazyl, $Cu_2Cl_6^{2-}$, YAFZOU and BISDOW, are included in the open shell database and their ground state geometries are taken from various sources mentioned therein.[27, 39] Such obtained coordinates of the systems in their ground states are used in *ORCA* to perform broken symmetry calculations.[40] Though accurate wave function methods could readily be applied on simple systems, for a uniform comparison, the DFT based methods are maintained throughout this work. The broken symmetry solution is obtained from a initial guess generated by flipping the local spin density in either of the magnetic centers of the high spin solution.[40, 41] This technique, known as the spin flip DFT (SF-DFT), is employed to compute the high spin-BS energy gap. This is comparable with another approach SF-TDDFT adopted by Krylov and coworkers.[42] In this method, starting from a reference high spin state both the closed shell singlet and M_s=0 state of a triplet can be generated and used to estimate high spin-low spin energy splitting.[43] This formulation, based on noncollinear XC potential, can deal with the spin flip transition in addition to the transition treated in ordinary TDDFT. With a proper DFT formalism, this method is found efficient in correctly describing the multiplicity changing excitations.[44] Moreover, the comparison of coupling constants through this SF-TDDFT and conventional broken symmetry approach concludes that in DFT calculation the spin symmetry must be considered through the spin projected methods.[45] However, the energy difference of high spin and BS spin states, evaluated through SF-DFT method is mapped onto E_{DX} in eq 6.14 and this enables a straightforward determination of the exchange-coupling constant (J_{DX}) as follows,

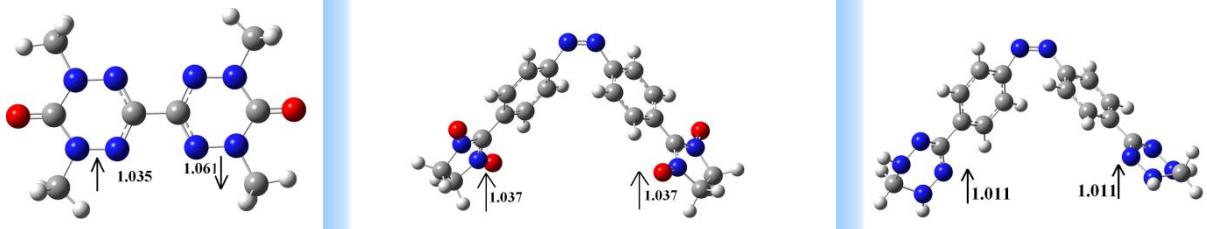
$$J_{DX} = -\frac{E_{HS} - E_{BS}}{\rho_A \rho_B} \,. \qquad (6.27)$$

The spin densities on magnetic sites (*A* and *B*) in the denominator are obtained from the Mulliken population of the high spin state which is taken as the reference state in SF-DFT approach. The exchange-coupling constants (J_{DX}) of transition metal dimers, obtained through eq 6.27, are found to be concordant with the coupling constant values (J_Y) employing the approximate spin projection technique of Yamaguchi (Table 6.1).

Table 6.1 Comparison of coupling constants (J_{DX}) obtained through eq 6.27 and approximate spin projection technique of Yamaguchi (J_Y) for Cr_2, Mn_2 and their cations. Spin densities on 1st and 2nd metals are denoted as ρ_{M1} and ρ_{M2}.

Systems	ρ_{M1}	ρ_{M2}	E_{HS} - E_{BS} (cm^{-1})	J_{DX} (cm^{-1})	J_Y (cm^{-1})
Cr_2	5	5	3408.620	–136.34	– 137.38
Cr_2^+	5.5	5.5	– 98490.635	3255.89	3181.09
Mn_2	5	5	–11489.881	459.60	441.82
Mn_2^+	5.5	5.5	–7433.394	245.73	241.08

Unlike these transition metal systems where huge spin is localized on the metal centers, in organic diradicals (Figure 6.2) spins are distributed throughout the network. Thus, to apply eq 6.27 on these systems, dispersed spins are summed up to get the overall spin density in the left and right wing of the molecules. A 6-311++g(d,p) computation on such systems produces the overall spin density in the left wing (ρ_l) and right wing (ρ_r) as follows.



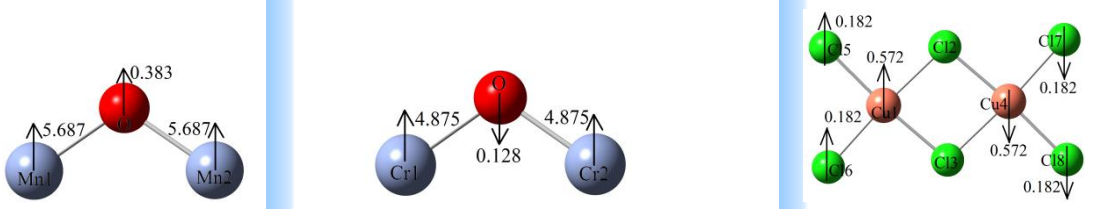
(a) (b) (c)

Figure 6.2 Ground state spin topology in (a) bisoxoverdazyl (b) azobenzene-nno and (c) azobenzene-ver (Up-arrow, down-arrow and corresponding numerical values signify up- and down-spin densities respectively; red, ash, white and blue colored atoms denote O, C, H and N).

Similar to Table 6.1, the coupling constants (J_{DX}) of the above three systems are in proximity to the J_Y (Table 6.2).

Table 6.2 Comparison of coupling constants obtained through eq 6.27 (J_{DX}), approximate spin projection technique of Yamaguchi (J_Y) and experiment (J_{expt})[27] for the systems in Figure 6.2. Spin densities on left and right wings of the diradicals are denoted as ρ_l and ρ_r .

Systems	ρ_l	ρ_r	E_{HS} - E_{BS} (cm^{-1})	J_{DX} (cm^{-1})	J_Y (cm^{-1})	J_{expt} (cm^{-1})
bisoxoverdazyl	1.035	1.061	– 666.333	– 606.64	– 650.38	– 769
azobenzene-nno	1.037	1.037	63.648	59.24	62	–
azobenzene-ver	1.011	1.011	79.010	77.28	79	–



(a) (b) (c)

Figure 6.3 Ground state spin topology in (a) Mn_2O^- (b) Cr_2O^- and (c) $Cu_2Cl_6^{2-}$ (Up-arrow, down-arrow and corresponding numerical values signify up- and down-spin densities respectively).

Now, turning to superexchange, three systems with the metals coupled via single atomic ligand are primarily selected. Among these, anionic oxide clusters of Cr and Mn have already been reported as ferromagnets in one of our previously works. [26c, 27] Another simple yet widely cultivated system $Cu_2Cl_6^{2-}$ is taken from the open shell database of Truhlar and coworkers.[16, 27, 30] The different spin topologies in these systems (Figure 6.3) is intriguing and demands evaluation in light of the present formalism. Optimization of these two clusters at UB3LYP/6-311+g(3df) level of computation produces similar spin density to the previous results. Between these two, the spin distribution in Mn_2O^- (Figure 6.3a) represents "both more than half full" occupancy status of the *d*-states to and from which the transition is taking place.[25b] In this situation, *A*, *X* and *B* are proposed to have identical spins on them which is in complete agreement with the computed spin topology of Mn_2O^- (Figure 6.3a). On the other hand, in Cr_2O^-, the spin density values (Figure 6.3b) resembles the "less than half full" case described by Anderson.[25] The spin topology (Figure 6.3b) in this case again matches with proposed alternation of spin density. Next, we put our effort to quantify the exchange interaction in these molecules executing superexchange. Since, all the elements in Mn_2O^- exhibit an identical spin density; a ferromagnetic exchange among these polarized spins is expected. Computation of exchange coupling constant through spin projection technique of Yamaguchi comes out with a positive value of J_Y and stands for spin topology based prediction. However, this coupling constant (J_Y) due to superexchange can be partitioned into the contribution from metal-metal (J_{MM}) and metal-ligand (J_{ML}) exchange as suggested in eq 6.23. In order to quantify these contributions separately, we follow a recent computational scheme of our own.[12] In this scheme, the ligand in the system is made dummy, which means that in the present case, O^{2-} remains there in the structure without any electronic contribution. This manipulation enables one to evaluate the intermetallic coupling constant ($J_{Y(Mn-Mn)}$) only. A lower positive value of $J_{Y(Mn-Mn)}$ than J_Y indicates that there exists a ferromagnetic exchange among the residual spins on metal and ligand. Now, by subtracting $J_{Y(Mn-Mn)}$

from J_Y, it becomes possible to get $2J_{Y(Mn-O)}$ which defines the exchange interaction between Mn1-O and Mn2-O pairs. Again, the interaction between a particular pair of metal and ligand (J_{Mn-O}) is quantified through eq 6.20 and the result is multiplied by two for comparison with $2J_{Y(Mn-O)}$. The second order perturbation energies (ΔE in eq 6.20) due to the charge transfer from O^{2-} to Mn1 and Mn2 are obtained from the natural bond orbital (NBO) output, carried out in the Gaussian NBO version 3.1.[46] Within a series of ΔE values corresponding to charge transfer between several donors and acceptors, we have opted for a particular donor-acceptor pair which fits best to our present model. For example, in the "both more than half full" case i.e. in Mn_2O^-, ΔE resulting from the transition of a down-spin from the lone pair of oxygen to the metal *d* orbital is used in eq 6.20. The orbital which has sp^2 character and contains lone pair of electron of oxygen is considered as the donor orbital. Whereas, the singly occupied metal orbital having significant *d*-character is considered as the recipient of the charge. Analogy between coupling constant values estimated through two different approaches is reflected in Table 6.3. A similar treatment is adopted for Cr_2O^- ("less than half full") where the ΔE corresponding to the up-spin transfer from ligand to metal is considered. In Cr_2O^-, the spin topology suggests a ferromagnetic coupling among the parallel spins on Cr atoms and antiparallel spin alignment in Cr and O leads to an antiferromagnetic interaction (Figure 6.3b). This becomes evident from the large negative value of coupling constant ($J_{Y(Cr-O)}$) obtained by spin projection technique (Table 6.3). Again, eq 6.20 is employed to find J_{Cr-O} which agrees well with the $J_{Y(Cr-O)}$ value (Table 6.3) and hence validates eq 6.20.

Table 6.3 Comparison of the metal-ligand contribution (J_{M-O}) towards the total coupling constant obtained through eq 6.20 and approximate spin projection technique of Yamaguchi ($J_{Y(M-O)}$), which in its turn is derived by subtracting the coupling constant ($J_{Y(M-M)}$) with dummy bridging atom O^{2-} from the total coupling constant (J_Y) through Yamaguchi expression. *M* implies Mn and Cr for Mn_2O^- and Cr_2O^- respectively. Spin densities on the metal and ligand are denoted as ρ_M and ρ_O.

Systems	Through Spin-projection Technique			Employing eq 6.20			
M_2O^-	J_Y (cm^{-1})	$J_{Y(M-M)}$ (cm^{-1})	$2J_{Y(M-O)}$ (cm^{-1})	ρ_M	ρ_O	ΔE (kcal/mol)	$2J_{M-O}$ (cm^{-1})
M = Mn	975.51	247.28	728.23	5.687	0.383	1.75	769
M = Cr	370.55	4619.55	– 4248.45	4.875	0.128	5.56	– 4789

In the third reference system $Cu_2Cl_6^{2-}$, along with the bridging chlorides, terminal ligands also show significant spin density which might have a role in the spin exchange. For comparison with ab initio results, all the bond lengths and angles of $Cu_2Cl_6^{2-}$ are kept same as in ref. 16. Cu-Cu distance is made equal with the experimental value of 3.44 Å.[30b] The planar configuration of this geometry is reported to have antiferromagnetic nature,[16, 30] which is also confirmed from the antiparallel spin alignment on Cu atoms (Figure 6.3c). Cu (II) has all the λ-MOs filled up and hence down-spins from the bridging chlorides (Cl2 and Cl3) and terminal chlorides (Cl5 and Cl6) may disperse into the vacant λ' orbital on Cu1. Remaining λ -spins on bridging chlorides induce λ'-spin density on Cu4 through bonding interaction. Equal dispersal of λ - and λ'-spins from bridging chlorides onto Cu4 and Cu1 respectively, should leave no excess spin on bridging chlorides according to eq 6.24. This fact is attested from zero spin density on the bridging chlorides (Figure 6.3c). Consistent to the available reports, this system

produces a small negative value of exchange coupling constant (J_Y) upon application of Yamaguchi formula (Table 6.4). With dummy bridging chlorides, a negligible AFM interaction is obtained between segregated left and right $CuCl_2$ units. Hence, the coupling constant value can be considered to originate solely from the Cu-Cl interactions. Again, the spin topology suggests that the interaction of metals and terminal chlorides ($J_{Cu\text{-}Cl}^{t}$) should differ from the coupling among metal and bridging chlorides ($J_{Cu\text{-}Cl}^{b}$). Identical spin densities on terminal ligands and allied metals indicate a positive value of $J_{Cu\text{-}Cl}^{t}$. On the other hand, a zero spin density on bridging chlorides makes it difficult to predict the nature of $J_{Cu\text{-}Cl}^{b}$. However, according to Anderson, the admixing of ligand and metal orbital leads to an antiferromagnetic interaction among metals and bridging chlorides.[25b] Now, to employ eq 6.20 on this system, second order perturbation energy (ΔE) corresponding to λ - and λ'-spin transfer from attached chlorides to Cu4 and Cu1 is taken into consideration. Ignoring small fractional values of spin density on both of the metal and ligand, the first part of eq 6.23 takes the following form.

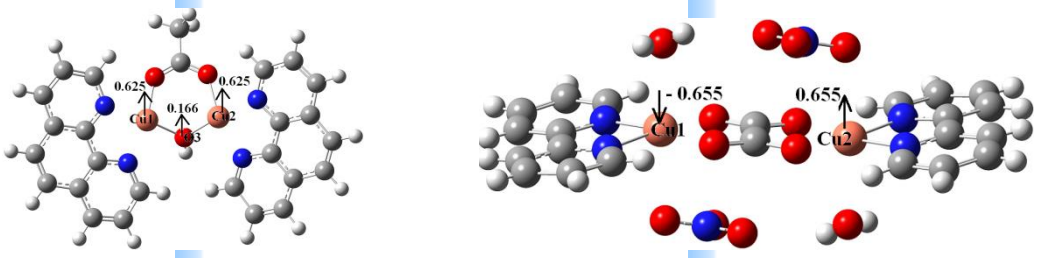
$$J_{SX} \approx 2\Delta E\,. \tag{6.28}$$

Putting appropriate values of ΔE on this expression and summing up the positive and negative contribution from $J_{Cu\text{-}Cl}^{t}$ and $J_{Cu\text{-}Cl}^{b}$ respectively, total metal-ligand interaction ($J_{Cu\text{-}Cl}$) can be quantified which is almost the same with J_Y (Table 6.4). Beside this analogy, the value of coupling constant obtained through eq 6.28 is also found to be in parity with that evaluated through CI techniques and the experimental value (J_{expt}) as well (Table 6.4).[30a,b] Again, quantification of the hopping integral t and on-site repulsion energy U through CASCI techniques yields $t^2/U = -4\ cm^{-1}$ for the system $Cu_2Cl_6^{2-}$.[30a] This t^2/U term is considered to be equivalent to the coupling constant between each pair of metal and ligand in the framework of Hubbard Hamiltonian.[16] Since, there are eight such pairs of metal and ligand in $Cu_2Cl_6^{2-}$, the total metal-ligand interaction is estimated as $-32\ cm^{-1}$, which is close to $J_{Cu\text{-}Cl}$ resulting from eq 6.28 (Table 6.4).

Table 6.4 Comparison of coupling constants ($J_{Cu\text{-}Cl}$) obtained through eq 6.28, approximate spin projection technique of Yamaguchi ($J_{Y\,(Cu\text{-}Cl)}$) and experiment (J_{expt}) [30a,b] for $Cu_2Cl_6^{2-}$.

$2\Delta E$ for $Cu\text{-}Cl^b$ pair *(kcal/mole)*	$2\Delta E$ for $Cu\text{-}Cl^t$ pair (*kcal/mole)*	$4J_{Cu\text{-}Cl}^{b}$ (*kcal/mole)*	$4J_{Cu\text{-}Cl}^{t}$ (*kcal/mole*)	$J_{Cu\text{-}Cl}$ *(cm^{-1})*	$J_{Y\,(Cu\text{-}Cl)}$ *(cm^{-1})*	J_{expt} *(cm^{-1})*
0.52	0.50	– 2.08	2.00	– 27.98	–27.89	– 40

In the next category, two Cu dinuclear systems, having extended bridging ligand between metals are taken to apply upon the formalism. Among these candidates of open shell database,[27] in the ferromagnetic YAFZOU, Cu(II) spins are coupled through the bridging hydroxo and carboxylato ligands. Whereas, in the second complex, BISDOW the exchange interaction between Cu(II) cations is mediated by an oxalato bis-chelating anion. The frozen-core LANL2DZ basis set, efficient performer particularly for metal systems,[20c] is applied on these large systems to get their ground state spin topology (Figure 6.4) and coupling constant.



(a) (b)

Figure 6.4. Ground state spin topology in (a) YAFZOU (b) BISDOW (Up-arrow, down-arrow and corresponding numerical values signify up- and down-spin densities respectively; red, ash, white, pink and blue colored atoms denote O, C, H, Cu and N).

Since, in these systems the metals are linked via extended ligands like carboxylato or oxalato; the analysis of NBO output to find out relevant charge transfers between the atoms becomes complicated. Regarding this, partitioning the molecule into fragments among which the charge transfer is taking place might be taken into consideration. Rudra et al. performed this kind of fragmentation for these systems where the spin is not localized on a single atom.[47] From the NBO output of the YAFZOU, the molecule is found to be fragmented into Cu1, Cu2, μ-OH and μ-carboxylato. Occupied up-spin orbitals in Cu(II) necessitate the migration of down-spin from the bridging ligands onto it. This fact is well supported by the presence of excess up-spin density on μ-OH following eq 6.24. Now, application of Yamaguchi expression on the whole molecule gives the total coupling constant value (J_Y), while the same method results a very weak coupling constant in YAFZOU with dummy bridging ligands. This signifies the absence of any through space interaction between metal spins making the J_{MM} term of eq 6.23 equals to zero. Thus the total coupling constant is solely due to the metal-ligand interaction (J_{ML} in eq 6.23). From the NBO output, the vacant orbitals having dominant *d* orbital contribution is regarded as the acceptor orbitals in Cu(II), whereas nearly sp^3 hybridized orbitals containing the lone pair of oxygen are recognized as the donor orbitals on μ-OH. In case of the carboxylato ligand, any such relevant pair of donor-acceptor orbitals is found missing and thus the superexchange is considered to be mediated only by μ-OH. For negligible spin density product on the participating fragments, eq 6.28 applies on this system. This equation uses second order perturbation energies [ΔE (μ-ligand→Cu1) & ΔE (μ-ligand→Cu2)] for down-spin transfer from μ-OH to Cu1 and Cu2 to give the total coupling constant (J_{SX}) which appears to be in good agreement with J_Y (Table 6.5).

Table 6.5 Comparison of Coupling constants (J_{SX}) obtained through present formalism (eq 6.28, eq 6.20 for YAFZOU, BISDOW with negligible and significant spin density product respectively), approximate spin projection technique of Yamaguchi (J_Y) and experiment (J_{expt})[27].

Systems	$2\Delta E$ (μ-ligand→Cu1) *(kcal/mole)*	$2\Delta E$ (μ-ligand→Cu2) *(kcal/mole)*	J_{SX} (cm^{-1})	J_Y (cm^{-1})	J_{expt} (cm^{-1})
YAFZOU	0.10	0.06	56	62	111
BISDOW	1.67	0.30	– 482	– 472	– 382

Unlike YAFZOU, there is no significant spin density on the bridging oxalato in BISDOW (Figure 6.4b). This fact, as also observed in $Cu_2Cl_6^{2-}$, can similarly be attributed to the equal dispersal of up-spin and down-spin from oxalato to Cu1 and Cu2. During the up-spin transfer, the molecule is partitioned into two fragments; one contains only Cu1 while Cu2 along with oxalate belongs to the

other. On the other hand, the down-spin transfers to Cu2 from the fragment holding Cu1 and oxalate together. In both the cases, concerned fragments have the significant spin density of 0.655 which are antiparallel to each other, and are considered as input in eq 6.20. To get the second order perturbation energy of this expression, nearly sp^2 orbitals of oxygen atoms in the bridging ligand are regarded as the gateways of spin transfer. Such obtained coupling constant (J_{SX}) is regarded as the total coupling constant since application of Yamaguchi expression on the system with dummy oxalato results a very weak interaction suggesting almost nil contribution from direct exchange (J_{MM} in eq 6.23). The sign and magnitude of total coupling constant through Yamaguchi technique (J_Y) agrees well with J_{SX} (Table 6.5).

6.4

CONCLUSION

In the present study, spin density emerges as an effective parameter in interpretation and quantification of magnetic interaction. This work formulates the coupling constant in direct exchange and superexchange mechanisms through which the spins are coupled in most of the magnetic systems. The exchange part of a general Hamiltonian is operated on a multi-electronic state to describe the direct exchange interaction in terms of spin density and thus the wave function concept is bridged with DFT. To deal with the superexchange process, the perturbative approach of Anderson is adopted. The total coupling constant in a superexchange mechanism is split into the contributions from metal-metal and metal-ligand interaction. The present formalism is employed on a wide spectrum of molecular systems which entail both the ferro- and antiferromagnetic compounds from organic and inorganic domain. Among these, four systems viz. bisoxoverdazyl, $Cu_2Cl_6^{2-}$, YAFZOU and BISDOW has confronted several ab initio and DFT studies.[27, 28, 16, 30a,b, 45a, 47] Comparison of reported coupling constant values in these references are found to be concordant with the *J*, resulting through present theory and hence solicits for the present theoretical construction. Moreover, the results are in good agreement with the values obtained through well-known spin projection technique of Yamaguchi. The ground state spin topologies of these systems are also in parity with the sign of coupling constant. In the systems, executing superexchange, difference of spin topology is found to stem from the occupation status of the *d*-states on the metals, to and from which the electron transfer takes place. The extent of overlap between the metal and ligand also governs the spin topology. In case of the anionic oxide of Cr with "less than half full" *d*-states, it is interesting to note an alternation of spin density in the spin topology of Cr_2O^-. The explanation given in this regard may also be useful to account for the well-observed spin density alternation in π-conjugated organic diradicals.[10a, b, c, 48]

In the estimation of exchange coupling constant, DFT has to encounter two major difficulties. In unrestricted Kohn-Sham method, $\langle S^2 \rangle$ is not well defined, particularly in the broken symmetry state.[1, 8, 45a, 47] Valero et al. concluded that this spin square term should not always be used as a reliable indicator of the success of a given calculation.[45a] Nevertheless, the present formalism offers a solution to this problem by using the spin density of the magnetic sites in estimation of *J* rather than $\langle S^2 \rangle$ value of the spin configurations. The second bottleneck in using DFT lies in the choice of the proper combination of exchange-correlation functional and basis set for accurate estimation of *J*.[7, 28, 47, 49] However; present work relates exchange-coupling constant with spin density, which can be obtained both theoretically, and experimentally.[50] Hence, one may explore the level of theory, which reproduces the experimentally obtained spin topology. Next, estimation of other parameters in eq 6.23 at the same computational level may lead to the reliable value of the coupling

constant. Thus, the present work may help in the proper selection of theoretical level for accurate estimation of *J*. Among the parameters in eq 6.23, spin density is a term, which can be realized experimentally. In case the other parameters are obtained experimentally, this work is expected to guide the estimation of coupling constant solely from experimental data. The recast of HDVV Hamiltonian in terms of spin density results in an expression similar to the well-known spin density Hamiltonian proposed by McConnell which has been the pioneer in spin-topology based prediction of magnetic behavior. However, the way it was modeled on the basis of HDVV Hamiltonian required a validation which has been provided through the present formalism.

6.5

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CHAPTER 7

Interplay among Aromaticity, Magnetism and Nonlinear Optical Response in All Metal Aromatic Systems

Abstract:

All metal aromatic molecules are the latest inclusion in the family of aromatic systems. Two different classes of all metal aromatic clusters are primarily identified; one is aromatic only in the low spin state and the other shows aromaticity even in high spin situation. This observation prompts us to investigate the effect of spin multiplicity on aromaticity, taking Al_4^{2-}, $Te_2As_2^{2-}$ and their Cu complexes as reference systems. Among these clusters, it has been found that the molecules which are aromatic only in singlet state manifest antiaromaticity in their triplet state. The aromaticity in the singlet state is characterized by the diatropic ring current circulated through the bonds, which are cleaved to generate excess spin density on the atoms in the triplet antiaromatic state. Hence, in such systems an antagonistic relationship between aromaticity and high spin situation is emerged. On the other hand, in case of triplet aromatic molecules, the magnetic orbitals and the orbitals maintaining aromaticity are different; hence aromaticity is not depleted in high spin state. The nonlinear optical (NLO) behavior of the same set of clusters in different spin states has also been addressed. We correlate the second hyperpolarizability and spin density in order to judge the effect of spin multiplicity on third-order NLO response. This correlation reveals a high degree of NLO behavior in systems with excess spin density.The variance of aromaticity and NLO response with spin multiplicity is found to stem from a single aspect, the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO); and eventually the interplay among aromaticity, magnetism and NLO response in such materials is established. Hence, the HOMO-LUMO energy gap becomes the cornerstone to tune the interplay. This correlation among the said properties is not system-specific and thus can be envisaged even beyond the periphery of all metal aromatic clusters. Such interplay is of crucial importance in tailoring novel paradigm of multifunctional materials.

7.1

INTRODUCTION

The isolation and characterization of MAl_4^{2-} (M=Na, K, Cu) by Li et al. is a breakthrough in the concept of aromatic compounds.[1a] This series of bimetallic clusters are found to have square planar Al_4^{2-}; which has been confirmed to have aromaticity through photoelectron spectroscopic investigation and electronic structure analysis by *ab initio* calculations. This finding sparked interest among the researchers to investigate the domain of all metal aromatic systems (AMAS). There are numerous reports on aromaticity in all metal clusters, whose stabilities are verified through experimental or theoretical studies.[1-13] These systems include XAl_3^- (X= Si, Ge, Sn, Pb),[2] M_4^{2-} (M=Ga, In, Tl, Sb, Bi),[3] T_5^{6-} (T=Ge, Sn, Pb),[4] M_4^{2+} (M = Se, Te),[5] M^{3-} (M= Al, Ga),[6] Al_6^{2-},[7] Hg_4,[5,8] M_5^-(M = Sb, Bi),[9] Au_5Zn^+,[10] Cu_3^{3+},[11] Cu_4^{2-},[12] $[Fe(X_5)]^+$ (X= Sb, Bi),[13] and so on. A detail explanation of the stability and reactivity of a wide range of all metal aromatic and antiaromatic systems has been given by Chattaraj and coworkers on the basis of density functional calculations.[14] Aromatic systems have usual inclination to form coordination bond with metals through their dispersed electron cloud. Mercero, Ugalde, and co-workers theoretically verified the possibility of such complexes with all metal aromatic systems and demonstrated that the all metal aromatic Al_4^{2-} deck can be used to sandwich transition-metal atoms.[15] Another possibility of such complex is explored by sandwiching transition metals between aromatic As_4^{2-} decks.[16] These works in fact invoke the synthesis of novel all metal metallocenes. Yang et al. further extended this idea of such sandwich complexes with main group metals.[17]

Origin of aromaticity in such metal clusters can be explained through Hückel $(4n+2)$ π electrons rule.[1-15] Other than this simple electron count rule, aromatic character of these metal cluster ions has also been diagnosed through their response towards magnetic field. Ability to sustain diamagnetic ring current induced by perpendicular magnetic field has been considered as the magnetic criterion of aromaticity.[18] As "diatropicity" is synonymous to "aromaticity", relying on a similar argument, it has been suggested by many authors that "paratropicity" implies "antiaromaticity".[19] The diatropic (paratropic) ring current may be maintained by circulation of either π-bonded electrons or σ-bonded electrons, and the system is termed as π-aromatic (π-antiaromatic) or σ-aromatic (σ-antiaromatic) accordingly. The AMAS exhibit somewhat different trend in magnetic properties in comparison with organic aromatic and antiaromatic compounds.[20-22] The diamagnetic ring current is found to be produced in Al_4^{2-} by the magnetic field induced σ-electron circulation as well as the π-electron circulation and this simultaneous σ-aromaticity and π-aromaticity is termed as multiple aromaticity.[1c, 15] However, Fowler and coworkers argued for only the σ-aromaticity in Al_4^{2-} through *ab initio* analysis.[20] On the other hand, π-electron circulation may induce a paramagnetic ring current out of the plane, which makes all metal clusters π-antiaromatic.[21,22] As for example, in rectangular Al_4^{4-}, paratropic ring current above the rectangular plane defines it as π-antiaromatic (as also indicated by the presence of $4n$ electrons) and a concurrent diatropic ring current in the plane of the ring makes it σ-aromatic.[1c] $Li_3Al_4^-$ is also found to have concurrent existence of σ-aromaticity and π-antiaromaticity which is termed as conflicting aromaticity.[1c, 23] Occurrence of such uncommon multiple and conflicting aromaticity in AMAS puts an impetus in investigating their magnetic criterion of aromaticity.

Nonlinear optical (NLO) properties of AMAS have also been a subject of current interest,[24-26] which has actually been triggered by the observation of exceptionally high NLO response for small clusters functionalized with various metals.[24a] Organic π-conjugated polymers show an increase in

their second and third-order nonlinear response, β and γ, with their conjugation length.[27] Again there are reports on increase in radicaloid character with increase in conjugation length of π conjugated systems.[28] Thus, it can be intuited that NLO response will increase with increasing radicaloid character. Nakano et al. pointed out that the nonlinear optical response is drastically affected by the spin multiplicity particularly in singlet systems with intermediate diradical character.[29] Singlet compounds with intermediate diradical characters are found to exhibit larger second hyperpolarizability than corresponding triplet counterparts.[29a] Also, in some other works they observed the NLO response to amplify monotonically with spin multiplicity.[29c] This observation is in agreement with the fact that systems with reduced energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have an increased NLO response.[30] In this context, it becomes significant to evoke that reduced HOMO-LUMO energy gap (ΔE_{HL}) is also the signature of antiaromaticity.[31] In contrast, aromaticity is found to be associated with large ΔE_{HL}. This relation of aromaticity and antiaromaticity with ΔE_{HL} has been the subject of several studies.[32]

The parameter ΔE_{HL}, simultaneously effecting aromaticity, magnetism and nonlinear optical response, thus bequeaths a hint of a strong connection among these properties in all metal clusters. Such interplay among a miscellany of properties may provide an innovative route to design materials with multiple properties. Simultaneous existence of various functionalities in a single entity can play a pivotal role to meet the need of fast growing technology for their potentiality to act as molecular switches with tunable properties. The bottleneck in the development of such multifunctional molecules is the lack of some common origin wherefrom all the properties may generate. For instance, NLO response is traditionally regarded within the framework of dielectrics subjected to intense electric fields and magnetism is a manifestation of interaction among spins, and that is why, rationale for linking NLO and magnetism in a single molecule is difficult to find.[33] However, from the above discussion ΔE_{HL} appears to be connected with the discussed properties and thus a link among them can be anticipated. In fact, the antiferromagnetic and ferromagnetic states exhibit different NLO effects and thus strongly hints about the connection between NLO response with the magnetic behavior of the molecule.[34] There are also reports of materials with combined properties such as conductivity and magnetism,[35] conductivity and NLO behavior, [36] or magnetism and NLO properties.[37]

The unique nature of aromaticity and the ability to produce a high value of nonlinear optical response in AMAS, as apparent from the preceding discussion, catch our interest to correlate these two aspects therein. These properties are found to vary with HOMO-LUMO energy gap, which is also a crucial parameter for controlling spin multiplicity of any system. Thence, the variance in aromaticity and NLO response with spin multiplicity emerges as the primary focus of this work. As, spin multiplicity describes the magnetic nature of any system, this study eventually offers a description of the interplay among aromaticity, magnetism and nonlinear optical response. Aromaticity of Al_4^{2-} in the singlet ground state is much cultivated. In contrast, $Te_2As_2^{2-}$, a part of the molecule $[K(18\text{-crown-}6)]_2[Te_2As_2]$, recently synthesized by Khanna and co-workers, is claimed to be the first aromatic as well as ferromagnetic compound.[38] This divergent aromaticity in the singlet ground state of Al_4^{2-} and triplet ground state of $Te_2As_2^{2-}$ urge their selection as reference systems in this work. When complexed with alkali metals, Al_4^{2-} shows an exaltation in non linearity due to the charge transfer from the alkali metals to the Al_4^{2-} ring.[24] There are many other instances where the charge transfer induce a high degree of NLO response, probably because of large charge fluctuation.[39] Moreover; if transition metals are used for the complexation, it provides an opportunity to investigate any change in the magnetic nature of the aromatic ring through interaction with unpaired electrons of transition metals. Stabilization of such clusters by the complexation with transition metals is already fortified

theoretically.[40]All these aspects prompt us also to extend this theoretical study with Cu-complexes of Al_4^{2-} and $Te_2As_2^{2-}$.

7.2

THEORETICAL DETAILS AND METHODOLOGY

7.2.1 *Aromaticity and Magnetism*

Among several indices of aromaticity, viz., bond length alteration, harmonic oscillator model of aromaticity, etc., nucleus independent chemical shift (NICS) is often considered to be the best descriptor of aromaticity.[41] The hypothesis, that magnetic shielding tensor on a test dipole at the center of a ring can be used to quantify its magnetic property was first proposed by Elser and Haddon,[42] which eventually became popular as NICS. Negative (Positive) shielding tensor values are taken to indicate the presence of a diatropic (paratropic) ring current and accordingly the system is defined as aromatic (antiaromatic).[43] Shielding tensor on any atom can be partitioned into diamagnetic and paramagnetic part.[44] Diamagnetic shielding is considered to be the effect of opposing the magnetic field by electron pair. Following the same analogy, any unpaired spin is likely to be aligned with the field and enhances the magnetic field at that particular point in space. This effect is manifested in the form of predominant paramagnetic shielding, which rather induces a deshielding effect.[45] This paramagnetic contribution to the shielding tensor is also known to be effected by the coupling of occupied and virtual orbitals.[44] Hence, a state with reduced HOMO-LUMO energy gap is expected to yield a higher contribution of paramagnetic shielding tensor. Again, as the reduced HOMO-LUMO gap is generally regarded as the archetypal of antiaromaticity,[32] an antiaromatic system can be characterized by a dominant paramagnetic contribution to the shielding tensor. In this work, shielding tensors on the dummy atom as well as on the constituent atoms are computed. In this report the isotropic shielding tensor on the dummy atom is referred to as NICS as usual,[46] and the anisotropic component of the shielding tensor on the other atoms is referred to as "σ_{II}" as this component is parallel to magnetic field and normal to the aromatic plane. While computing this σ_{II} component and NICS, the sign convention coined by Schleyer et al. is followed.[46] According to this convention the signs of the computed values are reversed and negative (positive) sign is assigned for diamagnetic (paramagnetic) shielding. The choice of the gauge for the vector potential of the magnetic field is an important factor in the computation of shielding tensors.[4] This well known gauge problem had been resolved by adopting the gauge independent atomic orbitals (GIAO) method[47] and the same method is followed in the present work to compute the shielding tensors. To find out the contribution of σ and π electrons to aromaticity, NICS has been calculated both in the center of the ring [NICS(0)],[46] and 1 Å above the plane [NICS(1)].[48] Similar to the shielding tensor, magnetic susceptibility tensor is also composed from diamagnetic and paramagnetic contributions.[49] The former is negative and the latter is known to be positive. In addition to NICS, magnetic susceptibility anisotropy has been advocated as another criterion of aromaticity.[50] We report all the three components of susceptibility tensor (χ_{xx}, χ_{yy} and χ_{zz}) to express the anisotropy. However, the susceptibility tensor normal to the ring (χ_{zz}), being much larger than the others, can alone represent the magnetic character of the molecule.[43]

7.2.2 *Nonlinear Optical Response and Magnetism*

The nonlinear optical response of an isolated molecule in an electric field F can be expressed as the coefficients of power series expansion of the total energy of the system exposed to the electric

field.[51] The following expansion is written in accordance with the "B convention", where the factorial terms in the denominator originally present in the Taylor series is absorbed, [51c]

$$E = E^0 - \sum_i \mu_i F_i - \frac{1}{2}\sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{3}\sum_{ijk} \beta_{ijk} F_i F_j F_k - \frac{1}{4}\sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l - \ldots . \quad (7.1)$$

Here E and E^0 are referred to as the energy of the perturbed state and the ground state; the tensors μ_i, α_{ij}, β_{ijk}, and γ_{ijkl} stand for dipole moment, linear polarizability, first or quadratic hyperpolarizability and second or cubic hyperpolarizability terms respectively.[51] Generally, the field is frequency dependent, as are the polarizability, hyperpolarizability terms. However, the centrosymmetric molecules do not have permanent dipole moment and thus their first hyperpolarizability becomes zero.[52] So, in the present work we have computed second hyperpolarizabilities for the centrosymmetric systems. The static (frequency=0) γ_{ijkl} is a fourth rank tensor and considered as the microscopic origin of third-order NLO response. The interaction between a molecular system and electric field is usually described in terms of time dependent perturbation theory, which becomes identical to time independent perturbation theory in the limit of a static perturbation.[53] From the eq 7.1, it is straightforward to express the third-order response as the fourth-order derivative of the total energy *E(F)* with respect to the applied field in the zero field limit[51]

$$\gamma_{ijkl} = -\frac{1}{6}\frac{\partial^4 E}{\partial F_i \partial F_j \partial F_k \partial F_l}\bigg|_{F=0} . \quad (7.2)$$

The charge density function $\rho(r, F)$ and the dipole moment μ of any system under the perturbation caused by electric field have the similar expression as eq 7.1.[51a, 54] From these power series expansions of charge density, dipole moment and the following expression,

$$\mu_i(F) = -\int \vec{r}_i \rho(r, F) \partial r^3 \quad (7.3)$$

one gets the second hyperpolarizability as,

$$\gamma_{ijkl} = -\frac{1}{6}\int \vec{r}_i \rho^{(3)}_{jkl}(r)\, \partial^3 r \quad (7.4)$$

where, $\vec{r}_i$ is the position vector with respect to the reference point on the i axis and $\rho^{(3)}_{jkl}(r) = \frac{\partial^3 \rho}{\partial F_j \partial F_k \partial F_l}\Big|_{F=0}$ is known as the second hyperpolarizability density.[55] Now, let $|S, M_s\rangle$ represents a one dimensional spin chain with n number of sites (S and M_s are the total spin angular momentum quantum number and magnetic quantum number respectively). In case, each site is occupied by one unpaired electron, then parallel and antiparallel alignment of spins on neighboring sites gives rise to two states $|n/2, n/2\rangle$ and $|n/2, 0\rangle$ respectively for even number of sites. This situation invokes the question that whether the NLO response for both the situations will be same or different. So far the eq 7.4 is concerned, both the states having same charge density, should have a

same degree of NLO response. However, following the exclusion principle, $|n/2,0\rangle$ state is likely to be more compact than $|n/2,n/2\rangle$ state, and this more diffused high spin state should give rise to a higher degree of NLO response. This conjecture is verified through the following formalism.

The longitudinal components of the integral in eq 7.4 can be approximated as a sum of contribution from individual partitioned point charges on each site.[56] For instance, the second hyperpolarizability along the direction *i* can be expressed in the static field limit as below,

$$\gamma_{iiii} \propto \sum_a \vec{r}_i \rho_a^{(3)} \delta(\vec{r}_i - r_{ia})\Big|_{F_i=0}, \tag{7.5}$$

where r_{ia} and $\rho_a^{(3)}$ are the location of site *a* and the so called γ-charge at that site respectively. The quantity $\rho_a^{(3)}$ has the similar expression to that of the hyperpolarizability density

$$\rho_a^{(3)}(r) = \frac{\partial^3 \rho_a}{\partial F_i^3}\Big|_{F_i=0}, \tag{7.6}$$

where, ρ_a is the Mulliken point charge at site *a*. Now, the number of particles at site *a* can be obtained as the expectation value of number operator ($\hat{n}_a$),[57]

$$\hat{n}_a = f_a^\dagger f_a, \tag{7.7}$$

where $f_a^\dagger$, f_a are fermion creation and annihilation operators for site *a* and can be related to the spin momentum operator $\hat{S}_a^{iz}$ at that site through following Jordon-Wigner transformation for a one-dimensional spin chain,[58]

$$\hat{S}_a^{iz} = f_a^\dagger f_a - \frac{1}{2}. \tag{7.8}$$

Using eqs 7.6,7.7, 7.8 and the following expression

$$\hat{\rho}_a^s(\vec{r}_i) = \left\langle \hat{S}^{iz} \right\rangle^{-1} \sum_a \hat{S}_a^{iz} \delta(\vec{r}_i - r_{ia}), \tag{7.9}$$

where $\hat{\rho}_a^s(\vec{r}_i)$ is the spin density operator at site *a*,[59] eq 7.5 can be written as

$$\gamma_{iiii} \propto e \sum_a \left\langle \hat{S}_a^{iz} \right\rangle \vec{r}_i \hat{\rho}_a'^s(\vec{r}_i) \tag{7.10}$$

where, *e* is the charge of an electron and the expectation value of the operator $\hat{\rho}_a'^s(\vec{r}_i)$ is the third-order derivative of Mulliken spin density with respect to the electric field at site *a*. The above expression defines that although the principal cause of the second hyperpolarizability is the charge fluctuation induced by electric field (eq 7.4); it may also vary for different spin configurations even if the charge density remains same. Eq 7.10 delineates an enhancement of second hyperpolarizability along a specific direction with the increased third-order derivative of spin density at the sites oriented along that direction. To justify eq 7.10, in the present work we focus on the determination of longitudinal components of second hyperpolarizability γ_{iiii}, using the finite field approach.[60] In this method fourth-order differentiation of energy with respect to different amplitudes of the applied external electric field is used in the following expression to determine the second hyperpolarizability: [55, 61]

$$\gamma_{iiii} = \left\{-56E_0 + 39\left[E(F_i) + E(-F_i)\right] - 12[E(2F_i) + E(-2F_i)] + [E(3F_i) + E(-3F_i)]\right\} \Big/ 36(F_i)^4 \quad (7.11)$$

where, $E(F_i)$ represents the total energy in presence of static electric field F_i, applied in *i* direction. To achieve numerical stability, several values of γ_{xxxx} are produced applying minimum field strengths in the range of 0.0001-0.01 a.u. The field strength which produces hyperpolarizability values within the precision of 10-100 a.u. are regarded as numerically stable.[29] Adopting this technique for all systems, field strength in the range of 0.001-0.009 a.u. is found to be numerically stable and has been employed in this work. The hyperpolarizability may have positive or negative value depending upon the relative spatial configuration between two hyperpolaraizability densities. The contribution of hyperpolarizability is considered positive (negative) if the direction of arrow from a spatial point with positive (negative) hyperpolarizability density to another spatial point with negative (positive) hyperpolarizability density coincides with the positive direction of coordinate system.[55, 62] The hyperpolarizability density at each spatial point in the discretized space is deduced using the following four point numerical differentiation formula, [55, 62b]

$$\rho^{(3)}_{iii}(r) = \left\{\left[\rho(r, 2F_i) - \rho(r, -2F_i)\right] - 2[\rho(r, F_i) - \rho(r, -F_i)]\right\} \Big/ 2(F_i)^3, \quad (7.12)$$

where, $\rho(r, F_i)$ represents the charge density at spatial point *r* in the presence of the field F_i. Same numerical scheme is employed on the Mulliken spin density of the system to get the third-order derivative of spin density with respect to the electric field.

7.2.3 *The Interplay*

The preceding discussions already provide a hint that HOMO-LUMO energy gap (ΔE_{HL}) is the factor which can play an important role to connect all the three properties, viz., aromaticity, magnetism and nonlinear optical response. The correlation of ΔE_{HL} with aromaticity becomes more prominent in the ipsocentric CTOCD-DZ formalism where each point in a molecule is considered as the origin of its own vector potential to tackle the gauge dependence of magnetic field induced current density.[63] In this approach, the diamagnetic contribution to the orbital current density involves translational transition moments of the form $\langle \phi_v | p_\perp | \phi_o \rangle \Big/ (\varepsilon_v - \varepsilon_o)$, where ϕ_v, ϕ_o denote the virtual

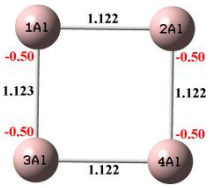
and occupied orbitals with corresponding energies ε_v and ε_o. The component of electronic linear momentum in the plane perpendicular to the applied electric field is specified by $p_\perp$. Similarly, the paramagnetic part of the current density relates the rotational transition moment of the form $\langle \phi_v | l_0 | \phi_o \rangle / (\varepsilon_v - \varepsilon_o)$ where l_0, the component of electronic angular momentum operator, is parallel to the applied magnetic field. In a state with reduced HOMO-LUMO energy gap, the paratropic current density intensifies and the diamagnetic part of the current density is subdued for the large separation between translationally accessible states. This suggests that in a high spin situation, there will be a dominant paratropic ring current in the molecule.[63c] Haddon and Fuguhata demonstrated that in annulenes, the resonance stabilization energy (RSE) ≈ $\Delta E_{HL}/24$, wherefrom a large ΔE_{HL} can be expected for resonance stabilized aromatic systems.[64] Hardness, which is the half of HOMO-LUMO energy gap, is found to show a similar variation as that of aromaticity.[32] Roy et al. confirmed this fact that increasing aromaticity causes the increase of hardness and the decrease of reactivity.[65] All these facts indicate towards a direct correspondence between aromaticity and ΔE_{HL}. The same parameter ΔE_{HL} also plays an important role in tuning the third-order nonlinear optical response. In many reports the second hyperpolarizability is found to be inversely related with the HOMO-LUMO energy gap.[66] This HOMO-LUMO energy gap can be correlated with another parameter called diradical character (Y_0) which is defined by the weight of doubly excited configuration in multi configurational self consistent field (MCSCF) theory and can also be represented by the occupation numbers of unrestricted Hartree-Fock natural orbitals.[67] It is obvious that a reduced ΔE_{HL} will effect a degenerate distribution of electrons in MOs and in case of precise equal distribution one obtains Y_0=1. Thus, any connection between the diradical character and NLO response automatically indicates the relation between ΔE_{HL} and NLO activity.[51b, 68] Although, the diradical character is applicable only for open shell singlets, ΔE_{HL} can be computed for all spin states and can be regarded as a key factor to tune the interplay among aromaticity, magnetism and NLO response.

Among the AMAS we have chosen to establish the aforesaid interplay; geometry of $Te_2As_2^{2-}$ is already available in CIF format and we take this form of the molecule as the ground state.[38] No such ground state structures are available for other systems, i.e., Al_4^{2-} and Cu complexes of Al_4^{2-} and $Te_2As_2^{2-}$; hence, we optimize their structures using unrestricted hybrid functional (UB3LYP)[69] and Los Alamos national laboratory double zeta (LANL2DZ) basis set. In this basis set, the core electrons are represented by effective core potential (ECP) and the outer electrons are represented by double-ς atomic orbitals.[70] Basically the metals are accurately described by LANL2DZ basis set for its ability to consider the relativistic effect.[70] This UB3LYP/LANL2DZ level of theory is invariably applied for each computation using GAUSSIAN03W suit of quantum chemical package.[71] To judge the adequacy of LANL2DZ results, a higher basis set 6-311+g(3df) is employed in case of Al_4^{2-}system.

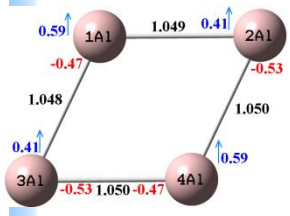
7.3

RESULTS AND DISCUSSIONS

7.3.1 *Al_4^{2-}system.*



(a) Singlet Al_4^{2-}



(b) Triplet Al_4^{2-}

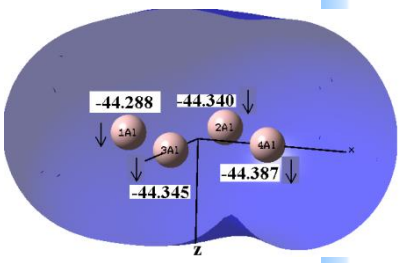
Figure 7.1 Charge density (red digits), spin density (blue digits, positive value is indicated by up-arrow) and atom-atom overlap weighted bond order (black digits).

Geometry optimization of Al_4^{2-} ascertains singlet state with D_{4h} symmetry as the ground state, while the less stable triplet state appears with D_{2h} symmetry (Figure 7.1). Accumulation of excess negative charge on Al2 and Al3, compared to Al1 and Al4 in the triplet state causes this variance in molecular structure. In a recent work, the freezing of π electrons in parallel orientation is held responsible for this distortion of geometry in the triplet state.[72] In the present case, almost equal majority spin density on each and individual Al atoms in the triplet state affirms this opinion (Figure 7.1b).

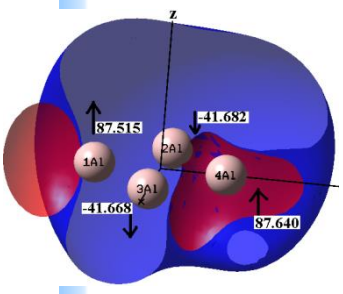
Table 7.1 NICS values (ppm) in both the spin states of Al_4^{2-}.

	Singlet	Triplet
NICS(0)	−27.357	4.238
NICS(1)	−23.345	1.071

The larger negative NICS(0) value than NICS(1) suggests that Al_4^{2-} is more σ-aromatic than π-aromatic in its singlet state (Table 7.1). On the other hand, positive values of NICS both in the plane and above the plane in triplet Al_4^{2-} speak for its antiaromatic character. We find $\sigma_{\perp}$ on each atom to have a negative value in the singlet state indicating a diamagnetic shielding in that direction (Figure 7.2). In contrast, in the triplet state, Al1 and Al4 having larger spin density than Al2 and Al3 show a deshielding effect in plane. A dominant contribution of diamagnetic susceptibility appears in the singlet state which is significantly decreased in the triplet state (Table 7.2).



(a) Singlet Al_4^{2-}



(b) Triplet Al_4^{2-}

Figure 7.2 Diamagnetic (blue) and (red) paramagnetic contributions of $\sigma_{\perp}$. Up-arrow and down-arrow denote the shielding and deshielding effects respectively.

Table 7.2 Diamagnetic and paramagnetic components of susceptibility tensors (a.u.) in both the spin states of Al_4^{2-} (magnetic field is applied along the z axis).

	Singlet			Triplet		
Components	xx	yy	zz	xx	yy	zz
χ(diamagnetic)	−49.220	−49.217	−73.892	−55. 427	−45.441	−76.433
χ(paramagnetic)	48.019	48.013	10.455	52.245	43.576	75. 580
χ (total)		−21.947			−1.967	

Molecular orbital (MO) analysis shows that p_y orbitals of Al1, Al4 and p_x orbitals of Al2, Al3 are oriented in antibonding fashion and hence the unpaired spins can be localized on Al atoms in the triplet state (Figure 7.3a). These specific orbitals are found to be in appropriate orientation for σ bonding in the singlet state as found from the scrutiny of 5th MO (Figure 7.3b). The 7th MO of singlet Al_4^{2-} is found to have a similar construction. Thus bonding electrons in the singlet state become the unpaired spins in triplet state. This statement can further be justified from the reduced atom-atom overlap weighted bond order between each Al pair in the triplet states with respect to the singlet state (Figure 7.1). So it can be concluded that the bonds, maintaining σ -aromaticity is cleaved to generate radicals and the aromaticity is lost subsequently.

Figure 7.3 (a) Magnetic orbitals in triplet Al_4^{2-} (b) σ-bonding situation in the 5th MO of singlet Al_4^{2-}.

Next, to investigate third-order nonlinear optical response, we calculate the second hyperpolarizability applying field strength of 0.003 a.u. In both the spin states *z* component of cubic hyperpolarizability is significantly less than other two components as charge fluctuate mostly in the *xy* plane (Table 7.3). A concurrent analysis of spin density clarifies that the third-order NLO response is enhanced in that directions along which the spin density grows. This observation is in accordance with direct correspondence between NLO response and third-order derivative of spin density as apparent from eq 7.10. In this point it is worth mentioning that in the unperturbed singlet spin state of Al_4^{2-} the Mulliken spin density is zero at each spatial point of the discretized space and so is its subsequent derivatives in presence of electric field (Figure 7.1a and 7.4a). Whereas, in the triplet spin state of Al_4^{2-}, non-zero spin populations are observed on the atoms in both the unperturbed and perturbed states (Figure 7.1b and 7.4b). Hence, if the increase of third-order NLO responses from singlet to triplet state is to be accounted for on the basis of spin density, their ground state spin density and its third-order derivative with respect to the field gives the same interpretation of the variant nonlinearity therein. In fact, in a number of references the variation of second hyperpolarizability is explained by the ground state charge and spin density distribution. [29a, 29c, 39b, 51b] Relying on this observation in the other systems the variation of NLO response is explained on the basis of ground state spin density distribution. Another noticeable fact is that, increase of NLO response along *y* direction is greater than that along *x* direction. This observation may be explained by eq 7.4 which suggests that more apart sites along a direction cause an increase in NLO response.[62a] Thus, the longer distance between Al2 and Al3 along *y* direction causes a higher NLO response in that direction in the triplet state of Al_4^{2-} (Figure 7.1b).

Table 7.3 Longitudinal components of second hyperpolarizability (in the unit of 10^3 a.u.) in both the spin state of Al_4^{2-}.

Spin state	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}
Singlet	− 18.352	−18.370	− 1.958
Triplet	− 22.892	−23.339	−5.898

(a) Singlet Al_4^{2-} (b) Triplet Al_4^{2-}

Figure 7.4 Third-order derivative of spin density along the *y* axis (red and blue surfaces represent the positive and negative spin density with isosurfaces 100 a.u.).

7.3.2 *$Al_4Cu_2^{2+}$ system.*

(a) Singlet $Al_4Cu_2^{2+}$ (b) Triplet $Al_4Cu_2^{2+}$

Figure 7.5 Charge density (red digits), spin density (blue digits, positive value is indicated by up-arrow) and atom-atom overlap weighted bond order (black digits).

In order to investigate the interaction between the metal and the aromatic system, geometry of this complex is partially optimized keeping the D_{4h} symmetry of aromatic Al_4^{2-} intact and sandwiching it between two Cu (II) atoms. This optimization shows negative charge density on Cu atoms and a slight excess of positive charge on Al atoms, which is in a stark contrast with the negative charge density on the Al atoms in bare Al_4^{2-} (Figure 7.1 and 7.5). This difference of charge density signifies a charge transfer from Al atoms to Cu atoms in $Al_4Cu_2^{2+}$, which is also in agreement with the observation by Datta and Pati.[24,40] This charge distribution remains more or less same in both singlet and triplet spin states (Figure 7.5). Charge acceptance by Cu (II) atoms nullifies the existence of unpaired electron in them. Consequently, feasibility of any kind of magnetic interaction between triplet Al_4^{2-} and Cu (II) is also annulled. Nevertheless, presence of excess spin density on Al centers keeps the possibility of magnetic interaction open among themselves in the triplet ground state (Figure 7.5b).

Table 7.4 NICS values (ppm) in both the spin states of $Al_4Cu_2^{2+}$.

	Singlet	Triplet
NICS(0)	−13.582	29.128
NICS(1)	−30.779	9.261

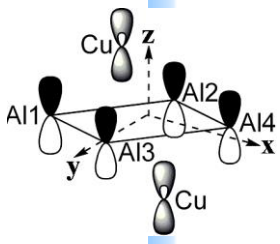


Figure 7.6 22nd α MO of singlet $Al_4Cu_2^{2+}$.

In $Al_4Cu_2^{2+}$, computed NICS values repeat the trend of its bare analogue. However, higher negative value of NICS(1) indicates predominant π-aromaticity in the singlet state of $Al_4Cu_2^{2+}$ (Table 7.4), in opposition to the dominant σ-aromaticity of bare Al_4^{2-}. This change in the nature of aromaticity with complexation arises from the increase of electron density above and below the Al_4^{2-} plane due to interaction of Al orbitals with Cu orbitals (Figure 7.6). On the other hand, positive values of NICS in the triplet state indicate antiaromaticity in this paramagnetic species. Different magnetic nature of singlet and triplet states is also observed from the nature of shielding tensors (Figure 7.7). All the atoms are shown to produce diamagnetic shielding on exposure to the external magnetic field in the singlet state, whereas the same set of atoms show paramagnetic shielding in the triplet state. This diamagnetic and paramagnetic nature of $Al_4Cu_2^{2+}$ in the singlet and triplet states respectively is further supported from their susceptibility measurement (Table 7.5).

(a) Singlet $Al_4Cu_2^{2+}$ (b) Triplet $Al_4Cu_2^{2+}$

Figure 7.7 Diamagnetic (blue) and (red) paramagnetic contributions of $\sigma_{//}$. Up-arrow and down-arrow denote the shielding and deshielding effect respectively.

Table 7.5 Diamagnetic and paramagnetic components of susceptibility tensors (a.u.) in both the spin states of $Al_4Cu_2^{2+}$ (magnetic field is applied along the z axis).

	Singlet			Triplet		
Components	xx	yy	zz	xx	yy	zz
χ(diamagnetic)	−177.569	−177.572	−52.8125	−169.396	−169.398	−53.762
χ(paramagnetic)	173.328	173.354	3.301	169.765	169.765	88.799
χ (total)		−19.324			11.926	

From MO analysis of the triplet $Al_4Cu_2^{2+}$, sp^2 hybridized orbitals (HO) of Al atoms appear as the magnetic orbitals (Figure 7.8a). The p_y and p_x components of these sp^2 HOs in triplet state form σ-bonds among Al atoms in its singlet state as can be seen from the schematic of 24th α-MO (Figure 7.8b). Lower atom-atom overlap weighted bond orders in the triplet state implies a less extent of electron circulation through the bonds compared to the singlet state (Figure 7.5). This fact and positive values of shielding tensors in the triplet state, once again complement the fact of radical generation at the expense of aromaticity.

(a) (b)

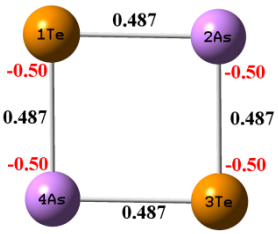
Figure 7.8 (*a*) Magnetic orbitals in triplet $Al_4Cu_2^{2+}$ (b) 24th α MO of singlet $Al_4Cu_2^{2+}$.

Nonlinear response of this molecule, produced in presence of 0.005 a.u. field strength, resembles the trend as observed for Al_4^{2-}. Here also, in the triplet state NLO response increases in the *x* and *y* directions along which the unpaired spins are oriented (Table 7.6). This observation again follows the proportionate correlation between spin density and NLO response put in eq 7.10. Here, presence of Cu along the z component causes γ_{zzzz} to attain the values not much smaller than other components as it was in their bare analogues.

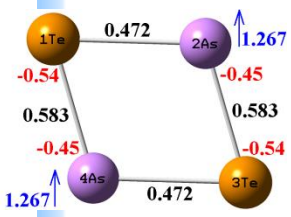
Table 7.6 Longitudinal components of second hyperpolarizability (in the unit of 10^3 a.u.) in both the spin state of $Al_4Cu_2^{2+}$.

Spin state	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}
Singlet	4.174	4.619	5.178
Triplet	6.985	6.968	5.442

7.3.3 *$Te_2As_2^{2-}$ system.*



(a) Singlet $Te_2As_2^{2-}$



(b) Triplet $Te_2As_2^{2-}$

Figure 7.9 Charge density (red digits), spin density (blue digits, positive value is indicated by up-arrow) and atom-atom overlap weighted bond order (black digits).

Ground state structure of this system has been retrieved from the crystallographic file of $[K(18\text{-crown-}6)]_2[Te_2As_2]$.[38] Triplet state of $Te_2As_2^{2-}$ has been reported by Khanna and co-workers to be of D_{2h} symmetry (Figure 7.9). However, optimization of singlet state results in a square motif of the molecule. In this molecule the relativistic effect becomes much more profound for the heavy Te. Hence, the effective core potential LANL2DZ becomes an appropriate choice for its ability to incorporate relativistic effects.[73] These geometries of singlet and triplet $Te_2As_2^{2-}$ are in striking similarity with those of Al_4^{2-} (Figure 7.1 and 7.9). Once again the explanation in ref. 72 is found to be applicable in case of the distortion of geometry in the triplet state. Slight excess distribution of charge on Te1 and Te3 atoms may also be the reason of such distortion (Figure 7.9b). Urginov et al. claim that ferromagnetism is developed in $Te_2As_2^{2-}$ due to exchange interaction between localized spins on As atoms.[38] Here, we find a support to this observation from the Mulliken spin density which shows significant spin excess on As2 and As4 atoms (Figure 7.9b).

Table 7.7 NICS values (ppm) in both the spin states of $Te_2As_2^{2-}$.

	Singlet	Triplet
NICS(0)	55.242	−14.277
NICS(1)	44.170	−8.280

The high spin state of $Te_2As_2^{2-}$is found to be aromatic as reflected through the negative NICS values and the susceptibility measurement (Table 7.7 and 7.8). At the same time a dominant paramagnetic contribution of $\sigma_{//}$ on As2 and As4 atoms in this triplet state advocates for its ferromagnetism (Figure 7.10). However, positive value of NICS in the singlet state of $Te_2As_2^{2-}$ is not in parity with the susceptibility tensor which describes diamagnetism in spite of its low negative value (Table 7.8). This fallacious value of shielding tensor may emanate from the use of small basis set like LANL2DZ. Hence, we carry out the same computation using two more different basis sets 3-21g(d,p),[74] SDDALL.[75] From the results it appears that improvement upon the value of shielding tensors can easily be performed by choosing an appropriate basis set. This basis set dependence of shielding tensor computation has been addressed in a number of earlier investigations.[48, 76] However, in this work to evaluate and compare general properties; we stick to a single basis set LANL2DZ.

(a) Singlet $Te_2As_2^{2-}$ (b) Triplet $Te_2As_2^{2-}$

Figure 7.10 Diamagnetic (blue) and (red) paramagnetic contributions of $\sigma_{//}$. Up-arrow and down-arrow denote the shielding and deshielding effect respectively.

Table 7.8 Diamagnetic and paramagnetic components of susceptibility tensors (a.u.) in both the spin states of $Te_2As_2^{2-}$ (magnetic field is applied along the z axis).

	Singlet			Triplet		
Components	xx	yy	zz	xx	yy	zz
χ(diamagnetic)	−75.430	−75.608	−117.559	−79.312	−66.831	−114.320
χ(paramagnetic)	50.864	50.203	113.674	60.284	47.203	87.664
χ (total)		−17.952			−21.771	

Coexistence of ferromagnetism and aromaticity in the triplet state of $Te_2As_2^{2-}$ indicates that the magnetic orbitals in the triplet state are excluded from the orbitals carrying diatropic ring current. This prediction is found to be correct through MO analysis of triplet $Te_2As_2^{2-}$. The 12th singly occupied α- molecular orbital (SOMO) is formed from p_z orbitals of Te1, As2, Te3 and As4 (Figure 7.11a). Different phase signs on Te-p_z and As-p_z orbitals hinder them to form π bond and the electrons in As-p_z orbitals stay unpaired. Whereas, the analysis of the 13th SOMO locates the unpaired spins on As atoms in sp^2 HOs. Two lobes among the three of these HOs on each As atom find sp^2 orbitals of both the Te atoms to form σ bonds and the remaining lobe of sp^2 HOs become the magnetic orbitals primarily located in As atoms (Figure 7.11b). From α spin density matrix, it is clear that density is much higher in As-p_z orbitals relative to sp^2 HOs (Supporting Information); hence, the spin exchange between the electrons on p_z orbital is more profound than that between the spins on As-sp^2 HOs. Thus, it can be concluded that any change in the bonding orbitals in *xy* plane would not affect the magnetic p_z orbital. However, Te1-As4 and As2-Te3 pairs surprisingly show a significant decrease in bond order in the singlet state (Figure 7.9). To explain this anomaly, Figure 7.11b is recalled. This 13th MO of triplet state shows a strong overlap between Te1-As4 and As2-Te3 pairs, whereas this particular bonding situation is found missing between the same pairs among all the MOs of singlet state. This absence of overlap between neighboring atomic orbitals in fact causes a cessation in the flow of electrons and consequently the singlet state tends towards antiaromaticity. This fact of reducing aromaticity from triplet to singlet state is prominent from the comparison of susceptibilities therein (Table 7.8).

Figure 7.11 (a) 12th SOMO and (b) 13th SOMO in the triplet state of $Te_2As_2^{2-}$.

The second hyperpolarizability is computed applying a finite field of 0.0015 a.u. During this computation the coordinate axes are set through the middle of the bond between Te and As (Figure 7.12) and hence we can not relate the growing spin density on the atoms and NLO response as before. Nevertheless, it follows from the table 7.9 that the increase in NLO response in *y* direction is one order of magnitude higher than that along *x* direction. This can be explained by eq 7.4 which predicts an increase in NLO behavior with increased second hyperpolarizability density. From Figure 7.9, it is evident that atom-atom weighted bond order between Te1-As4 and As2-Te3 pairs increases in the triplet state compared to the singlet state owing to the formation of σ bonds. The σ bonding causes more accumulation of electron density in between the atoms and this amplified charge density gives rise to the significant enhancement in cubic hyperpolarizability in the *y* direction (Table 7.9). The hyperpolarizability density plot along the *y* direction also supports the fact (Figure 7.12) and hence it can be concluded that the unperturbed charge density and second hyperpolarizability density leads to the similar interpretation of NLO response.

(a) Singlet $Te_2As_2^{2-}$ (b) Triplet $Te_2As_2^{2-}$

Figure 7.12 Hyperpolarizability density ($\rho_{yyy}^{(3)}(r)$) distribution (red and blue surfaces represent the positive and negative γ- density with isosurfaces 30 a.u.).

Table 7.9 Longitudinal components of second hyperpolarizability (in the unit of 10^3 a.u.) in both the spin states of $Te_2As_2^{2-}$.

Spin state	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}
Singlet	− 4.489	− 4.480	0.210
Triplet	− 9.265	− 28.178	3.742

7.3.4 *$Te_2As_2Cu_2^{2+}$ system.*

(a) Singlet $Te_2As_2Cu_2^{2+}$ (b) Triplet $Te_2As_2Cu_2^{2+}$

Figure 7.13 Charge density (red digits), spin density (blue digits, positive value is indicated by up-arrow) and atom-atom overlap weighted bond order (black digits).

The geometry of this molecule is partially optimized keeping the aromaticity of triplet $Te_2As_2^{2-}$ intact and sandwiching it between two Cu (II) atoms. In the triplet state, Cu5 and Cu6 atoms are found to form strong bonds with Te3 and Te1 atoms respectively, whereas in the singlet state Cu atoms remain equidistant from all the atoms in $Te_2As_2^{2-}$ plane (Figure 7.13). With this variation in the structure the triplet state appears to be the ground state.

Table 7.10 NICS values (ppm) in both the spin states of $Te_2As_2Cu_2^{2+}$.

	Singlet	Triplet
NICS(0)	−6.754	−5.104
NICS(1)	−24.614	−1.878

Larger negative NICS(1) value signifies a prevailing π-aromaticity in the singlet state of $Te_2As_2Cu_2^{2+}$ (Table 7.10) which may be attributed to the interaction of orbitals belonging to Te and As with that of Cu (Figure 7.14a). This NICS(1) value is significantly decreased in the triplet state (Table 7.10) owing to the bonding of Cu atoms with Te atoms only (Figure 7.13b). Due to this bonding pattern, the charge density above and below the plane loses its symmetry, leading to loss of diatropic ring current through π bond and subsequent π-aromaticity. This decrease in π-electron circulation finds its evidence in the decrease in atom-atom weighted bond order while going from the singlet to triplet state (Figure 7.13). However, in spite of a considerable decrease in π-aromaticity, the σ-aromaticity remains almost unaltered with change in spin multiplicity due to the possibility of σ-bonding interaction in both the spin states. The orbital orientation, as visible from 16th MO, creates the required zone for itinerancy of electrons to induce σ-aromaticity in both the spin states (Figure 7.14b). Moreover, the σ-aromaticity in *xy* plane does not disturb the magnetic orbitals on As atoms oriented along *z* direction (Figure 7.14c).

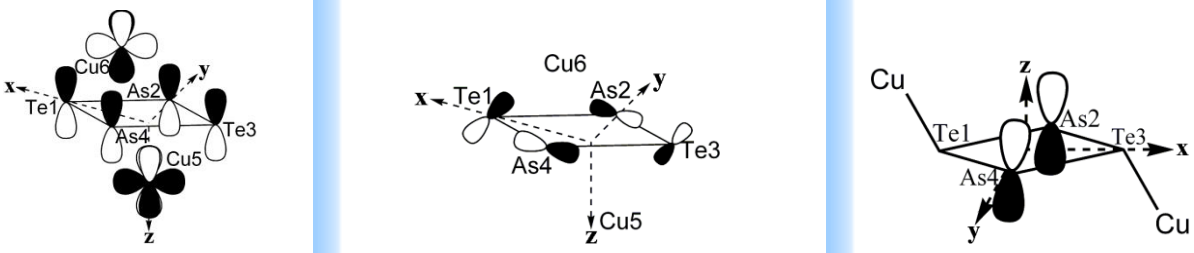


Figure 7.14 (a) 13th α MO of singlet $Te_2As_2Cu_2^{2+}$ (b) 16th α MO in $Te_2As_2Cu_2^{2+}$ (c) Magnetic orbital in triplet $Te_2As_2Cu_2^{2+}$.

The bonding of Cu atoms with Te atoms only causes the accumulation of excess spin on As2 and As4 atoms as can be seen from the HOMO of the triplet state (Figure 7.14c). The growing radical character of As atoms in the triplet state is well reflected through dominant paramagnetic contribution of $\sigma_{//}$ value. Different nature of shielding tensors in low and high spin states is distinct from Figure 7.15. However, the sign of total susceptibility and NICS remain negative in both the spin states, indicating the retention of aromatic character (Table 7.10 and Table 7.11).

a. Singlet $Te_2As_2Cu_2^{2+}$ b. Triplet $Te_2As_2Cu_2^{2+}$

Figure 7.15 Diamagnetic (blue) and (red) paramagnetic contributions of $\sigma_{//}$. Up-arrow and down-arrow denote the shielding and deshielding effect respectively.

Table 7.11 Diamagnetic and paramagnetic components of susceptibility tensors (a.u.) in both the spin states of $Te_2As_2Cu_2^{2+}$ (magnetic field is applied along z direction).

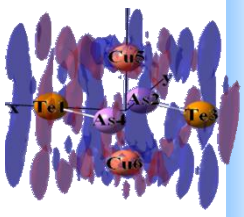
	Singlet			Triplet		
Components	xx	yy	zz	xx	yy	zz
χ(diamagnetic)	−193.149	−188.246	−100.815	−342.479	−368.498	−500.822
χ(paramagnetic)	177.943	180.592	71.867	320.957	349.125	480.112
χ (total)		−17.270			−20.535	

The hyperpolarizabilities are calculated in the numerically stable field of strength 0.002 a.u. The hyperpolarizability exaltation along *z* direction in the Cu complex in comparison with $Te_2As_2^{2-}$ can be attributed to the presence of Cu in that direction (Table 7.12). Following the previous trends, cubic hyperpolarizability along *y* direction is increased with increased spin density on As atoms in the triplet state. The intense increase in γ_{xxxx} in the triplet state can be explained by eq 7.4, according to which increased second hyperpolarizability density should bring about the increase in third-order non linearity. In the triplet state the *x* axis is slightly distorted from its position in singlet state and pass

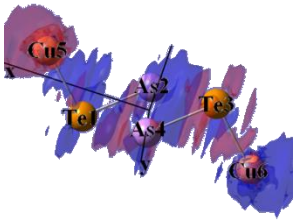
through the newly formed bonds between Te and As atoms (Figure 7.16). Consequently more electron density is available along that direction in the triplet state than in singlet state, which causes this noticeable increase in hyperpolarizability density in that direction (Figure 7.16).

Table 7.12 Longitudinal components of second hyperpolarizability (in the unit of 10^3 a.u.) in both the spin states of $Te_2As_2Cu_2^{2+}$.

Spin state	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}
Singlet	1.802	1.524	5.960
Triplet	58.493	4.248	8.974



(a) Singlet $Te_2As_2Cu_2^{2+}$



(b) Triplet $Te_2As_2Cu_2^{2+}$

Figure 7.16 Hyperpolarizability density ($\rho_{xxx}^{(3)}(r)$) distribution (red and blue surfaces represent the positive and negative γ- density with isosurfaces 100 a.u.).

7.4

CONCLUSIONS

The AMAS investigated in this work are found to have multiple aromaticity irrespective of the spin states. On the basis of their change in aromaticity with spin state, they can be categorized in two distinct classes. At one end, Al_4^{2-} and $Al_4Cu_2^{2+}$, which are aromatic in the singlet state, behave as antiaromatic in their triplet state. This swap of aromaticity is found to be associated with the weakening of σ-bonds while going from the singlet to the triplet state. A similar type of alternation in aromaticity pattern vis-a-vis bond-stretch isomerism was noticed in X_3^{2-} (X= Be, Mg, and Ca) and their Na complexes, where in few cases swapping of frontier MOs been observed.[77] Thus it can be surmised that the orbitals used to maintain the diatropic ring current in the singlet state turn into the magnetic orbitals in the triplet state; and this in turn establishes an antagonistic relationship between aromaticity and spin excess in the first type of AMAS. On the contrary, in $Te_2As_2^{2-}$ and $Te_2As_2Cu_2^{2+}$, one can trace the simultaneous existence of aromaticity and high spin state. This situation arises because the magnetic orbitals, containing the spin excess and the orbitals required for diatropic ring current leading to aromaticity are not the same. However, in the singlet state they show a tendency towards antiaromaticity, which becomes apparent from the decrease in the negative value of susceptibility. This propensity towards antiaromaticity in the singlet state can be explained by the simple electron count rule. For all the systems under investigation, the atoms with excess spin density are found to be associated with an enhanced paramagnetic contribution of the shielding tensor. Moreover, this overriding paramagnetic contribution of $\sigma_{//}$ is found in the states which are predominantly antiaromatic. Both of this dominant paramagnetic $\sigma_{//}$ and antiaromaticity is observed in the higher spin states. This can be well explained from the relative lowering of the HOMO-LUMO

energy gap in these states (Table 7.13). This reduced ΔE_{HL} facilitates the mixing of HOMO and LUMO which in turn gives rise to the antiaromaticity and exaltation of paramagnetic shielding tensor.

Table 7.13 HOMO-LUMO energy gap (ΔE_{HL}) of all the compounds under investigation.

System	Spin multiplicity	ΔE_{HL} (a.u)
Al_4^{2-}	1	0.086
	3	0.006
$Al_4Cu_2^{2+}$	1	0.040
	3	0.018
$Te_2As_2^{2-}$	1	0.033
	3	0.005
$Te_2As_2Cu_2^{2+}$	1	0.070
	3	0.019

A significant number of works highlight the variance of NLO response with the change in spin multiplicity.[29, 78] A detailed study of the nonlinear optical behavior in open shell systems also displays the dependence of NLO response on the nature of spin.[79] We rationalize these observations by correlating NLO response with the spin density of any system. In a recent work it has been shown that the inherent magnetism of any material is dependent on the spin density at the magnetic sites.[80] Hence, the correlation between spin density and NLO response enables one to relate the magnetism with NLO behavior. From the computation of second hyperpolarizability, increase in NLO response is observed in the systems with excess spin density in them as expected from eq 7.10. In the Cu complexes of Al_4^{2-} and $Te_2As_2^{2-}$, presence of Cu along *z* direction causes an increase of charge density and subsequent exaltation in γ_{zzzz} in that direction. However, as the NLO response is related with the third-order derivative of the electron density with respect to the electric field (eq 7.4), it becomes important to check the variation of hyperpolarizability density. From Figures 7.12 and 7.16, it has been already found that the ground state charge density distribution explains the variation of NLO response in the same way as does the hyperpolarizability density. This trend is also found to be true for the γ_{zzzz} components. The increase of hyperpolarizability density along the *z* direction of $Al_4Cu_2^{2+}$ compared to Al_4^{2-} is similar to their ground state charge distribution and hence the ground state charge density becomes equally meaningful as second hyperpolarizability density in explaining the increase in γ_{zzzz} component. Interestingly, the γ components are also changed in sign upon introduction of Cu (II) atoms into planar Al_4^{2-} and $Te_2As_2^{2-}$ structures. This fact can be explained by comparing corresponding hyperpolarizability density plots. It is distinct from Figure 7.17 that the relative spatial orientation of hyperpolarizability densities is changed along *z* direction causing the inversion of sign in the γ_{zzzz} component from Al_4^{2-} to $Al_4Cu_2^{2+}$ (Table 7.3 and 7.6). Similar hyperpolarizability density plots are observed in all other cases where such inversion of sign in the γ

component occurs. This spatial inversion of the positive and negative γ-density may be attributed to the charge transfer between Cu and metal ring.[24, 40]

(a) Singlet Al_4^{2-} (b) Singlet $Al_4Cu_2^{2+}$

Figure 7.17 Hyperpolarizability density ($\rho_{zzz}^{(3)}(r)$) distribution (red and blue surfaces represent the positive and negative γ- density with isosurfaces with 100 a.u.).

To summarize, in the investigated all metal aromatic clusters, the properties viz., aromaticity, magnetism and nonlinear optical response are found to be correlated. The reason of such interplay among the properties underlies basically in the tuning of the HOMO-LUMO energy gap. As parameter ΔE_{HL} also affects the hardness and hence reactivity of any system, higher reactivity of any system can be associated with antiaromaticity[81] as well as high NLO response. Nevertheless, from the analysis that how different parameters like charge density, spin density or HOMO-LUMO energy gap can control the interplay, it becomes obvious that this interplay is system independent and should have subsistence beyond the domain of all metal aromatic clusters. Simultaneous existence of different important properties in AMAS certainly provides a boost in the quest of multifunctional materials. The increase in NLO response with spin density may stimulate the idea of a new class of "spin-enhanced NLO systems".[29c, 36b] Such systems with large NLO response can be cast as the building block of optoelectronic devices for telecommunication and information storage, optical switches for signal processing, sensors for biological or chemical process and so on.[82]

7.5

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CHAPTER 8

Towards magnetic control of bond dissociation

Abstract:

In every aspect, bond dissociation is imperative in chemistry. Since, singlet pairing of electrons gives rise to a covalent bond; the parallel alignment of electron spins is an antithesis to bonding. The spin- parallel situation can be facilitated by magnetic field and thus the covalent bond dissociation can be catalysed with external magnetic field. This possibility is explored theoretically in this work taking simple dimer molecules as references. In general, the excited high spin state is far away from the corresponding singlet ground state in the reference molecules. However, at the upper vibronic levels, where the bond length is significantly longer than the equilibrium value, the high spin - low spin energy splitting is too low to be compensated by moderate magnetic field. As for example, a magnetic field of 50 Tesla is found to increase the rate of bond dissociation almost four times in Cr_2.

8.1

INTRODUCTION

As defined by Lewis, a chemical bond is an outcome of singlet pairing of electron spins.[1] Hence, a bond can be viewed as an extreme case of antiferromagnetic (AFM) coupling,[2] whereas the ferromagnetic (FM) coupling is an antithesis to bonding.[3] This fact can also be understood from the Pauli exclusion principle which keeps two electrons with identical spins apart from each other, nullifying the probability of bond formation.[4] The wave function, describing a bond, has symmetric space part and hence corresponding spin part of the wave function must be antisymmetric leading to an AFM situation. On the other hand, in the antibonding situation, the space part of the wave function is already antisymmetric, and corresponding spin function must be symmetrized, causing the appearance of the triplet state.[5] Thus, singlet and triplet states being the obvious choice in a bonding and antibonding situation, the singlet-triplet energy splitting can be an important parameter to measure the strength of a bond.[6-8] March defined the ground state energy as a function of force constant.[9,10] Hence, non-degenerate high spin and low spin states must have different force constants as well. In fact, Siegbahn et al. correlated the dissociation of weak hextuple bond in the Cr dimer in terms of exchange coupling constant.[11] In another work, absorption spectra is correlated with spin state in ferriheme proteins where the high spin state exhibits maxima at about 1000 - 1100 nm, and a peak of 1450 - 1750 nm is observed for the low spin state.[12] This difference between the stretching frequencies stems from the different bond lengths at high spin and low spin states. During dissociation, a closed-shell two electron bond generates singlet diradicals. The diradical character (y_i) takes the value of zero and one in closed-shell and pure diradical states respectively. Thus, the "diradical character" can be described as the fingerprint of instability of a chemical bond.[13-16] The diradical character is defined by the weight of the doubly excited configuration in multi-configurational self consistent field (MCSCF) theory and formally expressed by the overlap (T_i) between localized natural orbitals [highest occupied molecular orbital (HOMO) – i and lowest unoccupied molecular orbital (LUMO) + i],[13-16] i being the number of molecular orbital

$$y_i = 1 - \frac{2T_i}{1+T_i^2}. \tag{8.1}$$

The parameter T_i can be estimated from the occupation number n_i of the unrestricted Hartree Fock (UHF) natural orbitals (UNOs),

$$T_i = \frac{n_{HOMO-i} - n_{LUMO+i}}{2}. \tag{8.2}$$

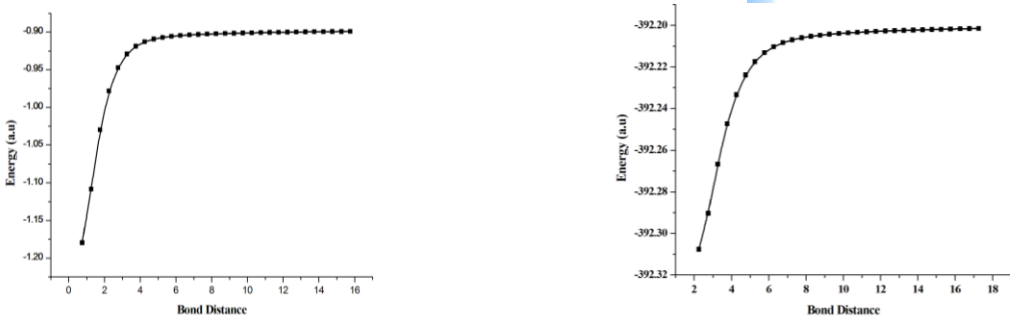
In general, the UHF MO method offers a qualitatively correct orbital correlation diagram for covalent bond dissociation.[17,18] All these facts connect the stability of a bond with its spin characteristics and necessitate explanation of such correlation.

In case different spin states are optimized to their minimum energy structures, almost invariably one can find different bond lengths for different spin multiplets. This spin-dependency of bond length and hence bond strength is also evident from ref 12, where at high and low spin states different stretching frequencies are reported. Now the question arises, "if the internuclear separation is same between two sites, does the force constant vary at high spin and low spin states of the dimer"? If so, then what may be the quantum chemical origin of such phenomenon? Seeking the answers of

these questions turns essential to meet the primary objective of this work. By considering the same internuclear distance, the effect of bond length on the bond strength or force constant can be avoided and thus spin configuration of the dimer is the only possible parameter which could affect the value of the force constant. At the ground state geometry of any molecule without unpaired spin, the high spin state is a remote possibility. For example, in the ground state, a two electron two radical system necessarily exists in the singlet state and the triplet state belongs to highly excited level. However, with the increase in bond distance this rigid preference for singlet spin state can be relaxed. To investigate this issue, in this work, energies and force constants of a dimer in its high spin and low spin states are compared with increasing internuclear separation, starting from ground state bond distance. This comparison is continued up to near-dissociation zone of the dimer. For a two electron two radical system, if the bonding orbitals are beyond the range of any kind of interaction, the unrestricted formalism produces an equal mixture of singlet state (S=0) and triplet state (S=1).[19] Thus the spin square value can be a good signature of the bond strength. Thus, the spin square value of the molecules is assessed with increasing bond distance. The diradical character is also evaluated to check the validity of the spin-dependence on force constant of a particular bond. In case, the dimers produce different force constants at high spin and low spin situations, the phenomenon can be promising as far as the magnetic control of bond dissociation is concerned. In fact, magnetic field can have dramatic effect on certain chemical reactions which involve the intermediacy of transient radicals. Such effects are interpreted using the radical pair mechanism (RPM) and central to the field known as "spin chemistry".[20] A number of studies has already shown that chemical reactions are controlled either by static field or by oscillating magnetic fields.[21] However to our knowledge, the use of magnetic field to break a covalent bond is not known till date. Hence, among the traditional techniques[22] viz. photolysis, thermolysis, electrolysis, chemical reaction and mechanical strain to break a bond; the magneto-catalysis of bond dissociation can be an alternate and novel route.

8.2
RESULTS AND DISCUSSIONS

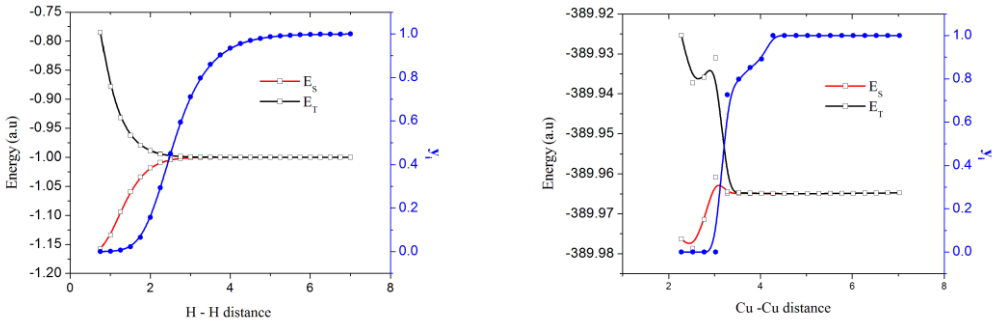
To comply with the above mentioned proposal, two simple diatomic molecules H_2 and Cu_2 are chosen as reference systems and their geometries are optimized at UB3LYP/6-311++g(d,p) and UB3LYP/LANL2DZ level of theories respectively. Next, starting from the equilibrium bond distance, which are 0.744 Å and 3.161 Å for H_2 and Cu_2 respectively, their potential energies are scanned (Figure 1) at the corresponding level of theories. From the inflection point in the plot (Figure 8.1), near-dissociation zone of the dimers can be characterized.[22] Particular values of bond distance, ranging from the equilibrium value up to the proximity of the inflection points, are chosen for further investigations.



(a) H_2 (b) Cu_2

Figure 8.1 Potential energy scan in (a) H_2 and (b) Cu_2 with respect to the internuclear bond distance (Å)

In both the systems, number of electrons participating in the bond formation is two, one from each atom. The parallel and antiparallel alignment of these two active electrons lead to singlet and triplet spin states respectively. However, at the equilibrium bond distance the systems are in closed-shell singlet state and the triplet state is a highly excited state in this geometry. Hence, to identify the bond distance where contribution from triplet state is significant, the diradical character and spin square value are estimated with varying the internuclear separation starting from ground state bond distance. Evaluation of diradical characters of singlet dimers is carried out through complete active space self consistent field (CASSCF) method with active space of (2, 6) and the basis sets 6-311++g(d,p) and lanl2dz for H_2 and Cu_2 respectively (Figure 8.2). The energies of singlet (E_S) and triplet (E_T) states of the dimers obtained through CAS method are also plotted to point out the critical bond distance wherefrom the weight of triplet state begins to increase (Figure 8.2). With the increase of internuclear separation, the variation of diradical character (obtained through ab initio method), the alteration in spin density and spin square value (obtained through DFT) are given in the Table 8.1. From the ab initio calculation the diradical character is found to approach unity with increase in bond distance. Following the sane trend, DFT result shows that the $\langle \hat{S}^2 \rangle$ gradually attains the value of one (Table 8.1). Though, in the ab initio level the spin square values of the singlet and triplet states are zero and one throughout the potential energy curve, the variation of diradical character supports the spin expectation value obtained in DFT framework. Thus, both the methods indicate about the gradual accumulation of spin on the atoms with increase in internuclear separation, which is also noticed in other works.[23] From the Table 8.1, it appears that at 2.251 Å in H_2 and 4.260 Å in Cu_2; the radical character starts to grow in the molecules and hence onward those distances the triplet state becomes more probable.



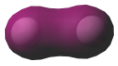
(a) H_2 (b) Cu_2

Figure 8.2 Plot of energy at singlet state (E_S), triplet state (E_T), and diradical character (y_i) against increasing bond length (Å).

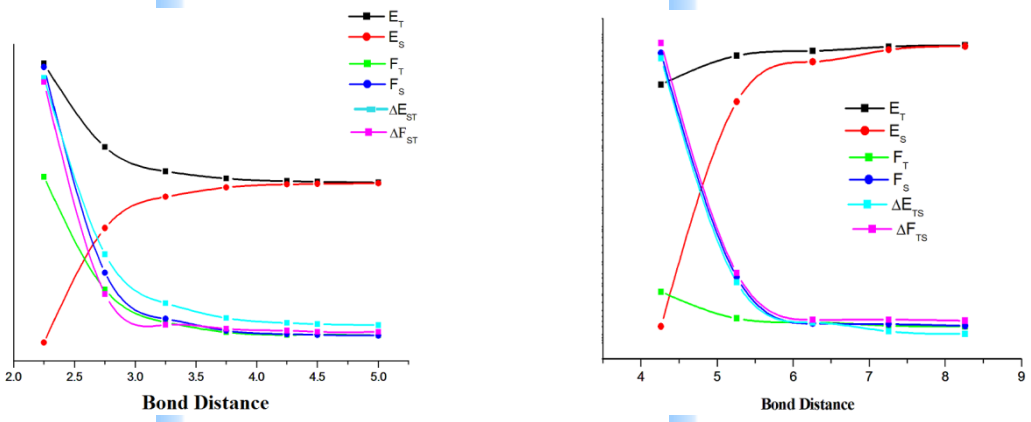
At a bond distance, significantly larger than the ground state value, the $\langle \hat{S}^2 \rangle$ gradually attains the value of one, an average of spin multiplicities two and zero at triplet and singlet states respectively. This fact is well in accordance with ref. 19, which says that at an internuclear separation where orbitals are beyond the range of any kind of interaction, there the spin state is a weighted average of high spin and low spin states. Noodleman et al. described such a spin state to be a broken symmetry (BS) state which is obtained by polarizing spins with antiparallel alignment at different magnetic sites within unrestricted formalism.[24, 25] However, here we see that near the dissociation point of a bond, the dimeric molecule spontaneously reaches the BS state which is characterized by

spin square value of one and the up-spin and down-spin polarization on the atoms (Table 1). Hence, spin square value of a singlet molecule can also characterize the near dissociation zone of a singlet molecule where occurs an automatic onset of the broken symmetry situation.

Table 8.1 Variation of diradical character (y_i) and $\langle \hat{S}^2 \rangle$ varying bond distance (r) in H_2 and Cu_2; different colors indicate up-spin and down-spin density.

Systems	r (Å)	y_i	$\langle \hat{S}^2 \rangle$	Total Density	Spin Density
H_2	0.751	0.000	0.000		NIL
Cu_2	2.260	0.000	0.000		
H_2	1.251	0.006	0.000		NIL
Cu_2	3.260	0.000	0.000		
H_2	2.251	0.294	0.856		
Cu_2	4.260	0.726	0.778		
H_2	3.251	0.797	0.992	No further change	No further change
Cu_2	5.260	1.000	0.972		
H_2	4.251	0.955	0.999	No further change	No further change
Cu_2	6.260	1.000	0.997		

After the DFT is found to be equally efficient as ab initio method in correctly describing the change in spin characteristics of the molecules with increasing internuclear separation; the performance of DFT in predicting the variation of singlet and triplet state is also tested. The variation in energies (E_S and E_T) of the singlet and triplet states (Figure 8.3) again shows a similar trend as observed in Figure 8.2. Thus the suitability of the adopted DFT framework is validated and applied for following calculations. Now to understand the spin dependence of the bond strength, the force constant (F_S) at singlet state is compared to that (F_T) at the triplet state in H_2 and Cu_2 keeping the same internuclear separation and this test is continued varying the interatomic distances as shown in Figure 8.3 . The plots in Figure 8.2 and Figure 8.3 reveal that the singlet-triplet energy splitting ($\Delta E_{ST} = E_T - E_S$) gradually vanishes to zero with increase in bond distance. Hence, DFT as well as ab-initio results suggest that with increase in internuclear separation, the preference for singlet state is relaxed and both the singlet and triplet states become equally favored. This observation is consistent with the fact that near the dissociation limit, the correlation energy is dominated not by short-range; i.e., dynamical correlation, rather by non-dynamical correlation, which comes from the near degeneracy of electronic configurations.[26] It is further interesting to discern different values of force constant are associated with singlet and triplet states of both the systems, though the internuclear separation is same at both the spin states (Figure 8.3). Irrespective of the system, F_T is found to be lower than F_S implying spin-dependency of bond strength. The ΔE_{ST} and the difference of force constants ($\Delta F_{ST} = F_S - F_T$) at singlet and triplet states are also plotted against the internuclear separation. With increase in bond-distance, the variation of ΔF_{ST} shows a similar trend to that of ΔE_{ST}. This resemblance in the nature of ΔF_{ST} and ΔE_{ST} (Figure 8.3) supports the argument that the singlet-triplet energy splitting can also be regarded as the measure of bond strength.



(a) H_2 (b) Cu_2

Figure 8.3 Plot of energy at singlet state (E_S), triplet state (E_T), frequency at singlet state (F_S), triplet state (F_T), singlet-triplet energy splitting (ΔE_{ST}), difference of force constants (ΔF_{ST}) against increasing bond length (Å).

In spite of so many important facts, which take place with increase in bond length, the variance of force constant at high spin and low spin states demands special attention to correspond with the major objective of the present work; i.e., magnetic control of bond dissociation. Hence in the following section, the quantum chemical origin of such spin-dependence of force constant is explored.

A Force constant F_{ij} is defined as the second order derivative of the molecular energy E, with respect to the internal coordinate R in the equilibrium configuration, [27 - 29]

$$F_{ij} = \frac{\partial^2 E}{\partial R^2} \tag{8.3}$$

and hence,

$$E = \iint F_{ij} \partial R^2 \,. \tag{8.4}$$

This simple expression actually turns into the key to explain the difference of force constant in different spin states as obvious from the preceding discussions. From the data in Table 8.1, it is evident that at and onwards a particular bond distance (2.251 Å in H_2 and 4.260 Å in Cu_2), the singlet state acquires the nature of broken-symmetry wave function which is characterized by the spin square values and spin-polarized character of dimers (Table 8.1). The wave function corresponding to the BS state in a dimer A – B can be represented as,[24,25,30 - 32]

$$\psi_{BS} = \left|\phi_A \bar{\phi}_B\right| \quad \text{or} \quad \left|\phi_A \bar{\phi}_B\right| \tag{8.5}$$

where ϕ_A and ϕ_B are the orbitals localized on atoms A and B. The singlet state can be well approximated as the single-determinant BS state in density functional theory formalism.[33,34] Similarly, the $M_S = 0$ component of the triplet state can be constructed by the combination of BS wave functions as,

$$\psi_T = \frac{\left(\left|\phi_A\bar{\phi}_B\right| + \left|\bar{\phi}_A\phi_B\right|\right)}{\sqrt{2 + 2\left\langle\phi_A\bar{\phi}_B \mid \bar{\phi}_A\phi_B\right\rangle}}. \tag{8.6}$$

The overlap between BS wave functions can be approximated as the overlap between magnetic orbitals localized on A and B.[30] However, here the atoms are too apart to have any kind of overlap between such orbitals and hence the overlap can be regarded as zero. Using eqs (8.4), (8.5) and (8.6), the energies of these states can be equated with the force constant as,

$$\left\langle\psi_{BS}\left|\hat{H}\right|\psi_{BS}\right\rangle = \iint F_{BS}\partial R^2$$

and,

$$\left\langle\psi_T\left|\hat{H}\right|\psi_T\right\rangle = \iint F_T\partial R^2 \tag{8.7}$$

where, F_{BS} and F_T are the force constants in the BS and triplet states. Now, in case the energies of BS and the triplet states are different, the values of force constants should also be different as evident from Figure 8.3.

8.3

APPLICATION

Johnston showed that the bond order, as defined by Pauling,[35] is proportional to the force constant.[36] As apparent from the results and subsequent discussions, owing to the spin parallel situation and consequent lower value of force constant, the triplet state is more susceptible towards bond cleavage. Hence, stabilization of triplet state by magnetic field can be an interesting way for easy bond cleavage of the molecule. The triplet state in present benchmark systems can be stabilized over singlet state by only an amount of 93 cm^{-1} even with magnetic field as high as 100 Tesla following eq (8.8). Hence, this Zeeman stabilization of energy (E_Z) by magnetic field may not be sufficient to make up the singlet – triplet energy gap in the equilibrium geometry of present systems,

$$E_Z = gM_S H\mu_B. \tag{8.8}$$

Here, g = 2; M_S = expectation value of spin angular momentum operator along z axis; H = applied magnetic field; μ_B = Bohr Magneton. Though magnetic field strength as high as 700 – 800 Tesla is now-a-days available through the use of pulsed magnetic field,[37] requirement of such huge field to get the sufficient Zeeman stabilization energy for spin crossover delimits the execution of the process. Alternatively, the Zeeman stabilization energy can be accentuated by applying a moderately strong field on a metal dimer with large number of unpaired electrons. Hence, Cr_2 can be ideal in this regard which is singlet in its ground state and in case of weak bonding interaction 13-tuplet state is energetically closer to the singlet state compared to other possible spin multiplets.[38 – 40] This fact is also apparent from the energy comparison of different spin multiplets with increase in internuclear separation. The plot of potential energy against internuclear separation in Cr_2 resembles those of H_2 and Cu_2 (Figure 8.1). The bond dissociation energy (ΔE_1 = 8362 cm^{-1}) of Cr_2 can be calculated from the difference of energy at equilibrium bond distance (r_{eq}) of 2.399 Å and at the inflection point of the

curve corresponding to dissociation limit (Figure 8.4). However, the high spin – low spin energy difference in Cr_2 is small enough (244 cm^{-1}) to be compensated by a magnetic field of 50 Tesla at a internuclear separation of 5.662 Å. This distance is much larger than the equilibrium bond distance (2.399 Å), yet much smaller than the internuclear separation at dissociation limit (10.856 Å), at which the system reaches its highest potential energy. Hence, the bond in Cr_2 can now be broken by imposition of magnetic field at the vibronic level corresponding to this distance of 5.662 Å which is only 8084 cm^{-1} (ΔE_2) away from the ground state. The rate of Cr_2 bond dissociation occurring normally through the dissociation limit (K_1) and the rate constant (K_2) for magnetic field induced bond dissociation occurring at r = 5.662 Å (Figure 8.4) can be compared through Arrhenius equation as follows,

$$K_2 = K_1 \exp\left(\frac{\Delta E}{KT}\right) \tag{8.9}$$

where, ($\Delta E = \Delta E_1 - \Delta E_2$); K = Boltzman Constant and T = 298 Kelvin. With computational value of ΔE at UB3LYP/LANL2DZ level, equation (8.9) yields

$$K_2 \cong 4K_1. \tag{8.10}$$

Hence, much before the dissociation limit is reached, the molecule can have a magnetic field stabilized triplet state. This state being susceptible towards bond cleavage (Figure 8.4), the rate constant of the bond dissociation can be increased nearly four times in Cr_2.

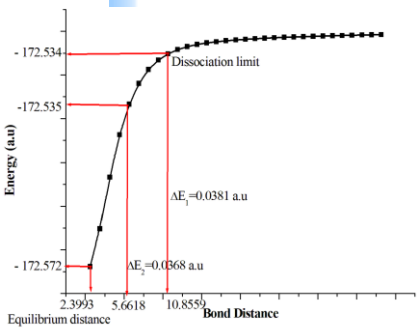


Figure 8.4 Potential energy curve at different internuclear bond distances (Å) in Cr_2.

All the computational results are obtained through GAUSSIAN suite of quantum chemical package.[41]

8.4

CONCLUSION

The response of a molecule to a magnetic field depends on the spin state of the system. Thus, while exploring the feasibility of magnetic catalysis of bond cleavage, first we look into the effect of spin state on the strength of a bond. The high spin state is found to have lower value of force constant than the low spin state, which is attributed to the different construct of wave function in these spin states. The lower force constant and a spin parallel situation in the high spin state alludes easy bond cleavage. The high spin state can be induced by application of magnetic field. However, spin-pairing

of the bonding electrons stabilizes the singlet state and huge magnetic field is thus required to achieve the lowest lying high spin state. This makes the scheme of magnetic catalysis difficult and unrealistic, which can be avoided if the higher vibronic levels are considered. Though small, these vibronic levels are supposed to have population even at room temperature. Since, at these vibronic levels the molecule is far from its minima, the Hessian in equation (3) is not necessarily positive,[42] giving rise to imaginary frequency. However, even with the imaginary frequency, the molecule does not reach its dissociation limit as inferred from the transition state calculation. This is similar to the presence of normal mode vibrations with imaginary frequency in solid which is considered to be the measure of anharmonicity in the potential energy surface and do not correspond to the barrier heights of the diffusive process.[42] The molecules at upper vibronic layers have larger internuclear separation than in the ground state, which brings about the breaking of symmetry in the dimer molecules. Similar observation is made for bimetallic systems M_2Cl_9 [M = Cr(III), Mo(III), W(III), Re(IV)], where authors report localization of metal-based electrons causing weak antiferromagnetic interaction between two centers.[43] The broken symmetry state is defined as an open shell singlet which is different from the singlet ground state with $S = 0$, and can be expressed as the weighted average of different spin multiplets. Thus the transition state in the process of bond dissociation can be characterized by the $\langle \hat{S}^2 \rangle$ value corresponding to the BS state. However, in the present context, the fact what is important is the weighted participation of all the spin states to construct the BS state at this larger separation of atoms. The small high spin – low spin energy splitting at this BS state makes it easier to stabilize the high spin state with moderate magnetic field. Thus achieved high spin state prepared has low force constant and is susceptible for bond cleavage. This conjecture is tested for Cr_2 which bears as much as twelve unpaired electrons in its lowest lying excited state and is singlet in the ground state. Here, it has been shown that the application of 50 Tesla magnetic field can accelerate the rate of bond dissociation nearly four times. Hence, imposition of magnetic field can also be instrumental to facilitate the bond dissociation along with other traditional techniques. Since the Zeeman stabilization is proportional to the spin density, the bond between atoms with large number of unpaired spins will be more responsive towards the magnetic field compared to the bond between atoms with less spin density. Thus, this technique can even be more important for regio-selective bond dissociation which is the basis of bond-selective chemistry.[44 - 46]

8.5

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CHAPTER 9

Conclusion

Abstract:

The purpose of this chapter is to recapitulate the keynotes of the preceding chapters and to analyse the significance of the present investigation. The discussions in this chapter are arranged in the perspective of objectives suggested at the very beginning of this report.

This chapter contains the summary of the vast span of critical issues on the magnetism of metal-based systems, which has been ploughed through. The discussion starts with different types of building blocks of magnetic materials with their major applications in the first chapter. This classification of molecular magnets helps to conceive the notion of different mechanisms responsible for setting a magnetic ordering in the systems. To quantify the magnetic interaction, the best mathematical tool has been the HDVV Hamiltonian (eq 2.1). The exchange coupling constant *J*, a parameter in this Hamiltonian turns out to be the best descriptor of the nature and degree of magnetic interaction. Thus, it becomes crucial to find out the value of *J*. The sign of *J* becomes even more important to predict the magnetic status, as because the positive and negative values of *J* represent the inherent ferro- and antiferro-magnetism. Almost all the techniques equate the difference between the energies of the high spin and low spin states with the coupling constant *J*. However, the exchange energy being minor to the molecular energy, a rigorous theoretical treatment is needed to ensure the desired accuracy for *J*. In particular, the construction of the low spin state is intricate. A single determinant is not sufficient to express the low spin state and thus it requires multi-reference configuration interaction to define the state properly. However, the ab initio approaches, too have limitations which restrict their wide applicability. To overcome this hurdle, the best computational framework has been found to be the broken symmetry approach implemented in the platform of the Density Functional Theory. The single determinantal BS state within DFT framework is trusted to be an ideal representative of the low spin, particularly a singlet state. Since the BS state is constructed by polarizing the up- and down-spins at different magnetic sites, any overlap between these magnetic sites plays a vital role in the estimation of *J*. To take this issue into account, many theoretical formalisms have been framed (eqs 2.24, 2.25, 2.26, 2.30, 2.37, 2.38, 2.39, 2.40, 2.41), of which the spin projection technique of Yamaguchi (2.40) is found to work properly for a wide range of weak to strong coupling limit. The BS-DFT method of Yamaguchi is successfully applied to estimate *J* in a large number of systems which basically include the organic radicals with fewer references of metal-based systems. The difficulty to employ the BS-DFT method on the metallic systems is related to the presence of large number of unpaired electrons in the metal magnetic sites. The BS state is defined as the weighted average of the all possible pure spin multiplets (eq 2.22). Hence, the presence of more than one unpaired electrons in each magnetic site necessitates the determination of the weight of all possible spin states in terms of the Clebsch-Gordon coefficient and in turn intricates the determination of the BS state. All these factors along with a brief overview of the experimental techniques adopted to estimate *J* is central to the second chapter.

In response to the problem defined at chapter two, the transition metal clusters such as $Cr_2O_n^-$(n = 1, 2, 3), Mn_2 , Mn_2^+ and Mn_2O^- are subjected to extensive theoretical investigation in the following chapters three and four and the results are verified against their already reported magnetic nature. To overcome the problem of accurate assignment of the BS state in a system with more than one electron per magnetic site, the prescription of Dai and Whangbo (eq 3.5) is found to be very much effective. In a seminal work, they suggest that a particular spin multiplicity can be assigned to the BS state of a diradical system with *M* and *N* spins on two different magnetic sites, according to the expression in eq 3.5. With the help of this equation it becomes easy to trace out the BS state and use its energy to estimate *J* through the spin projection technique of Yamaguchi. In addition to a straightforward estimation of *J*, other important observations are also apparent from these two chapters three and four. In case of $Cr_2O_n^-$(n = 1, 2, 3), the value of coupling constant shows a monotonic decrease with increase in the oxygen content. This observation is explained by the dispersal of unpaired spins, centred on Cr through legation or due to the consumption of spin by covalent interaction with oxygen atom. On the other hand, in manganese-based clusters, the variation

in the value of coupling constant with increase in the distance between magnetic sites is studied, which reveals the ferromagnetism at its zenith near the equilibrium bond distance.

Last decade has witnessed an emerging interest in the fabrication of single molecular magnets of which the ideal examples are organic polyradicals and polynuclear transition metal complexes. In such systems with multiple magnetic centers (SMMS), which have the possibility of simultaneous and conflicting magnetic interactions in different directions, the estimation of exchange coupling constant becomes much more complicated. To circumvent this problem, usually the energies of $n+1$ spin states of a system with n number of magnetic sites are first evaluated. Then from the energy difference, which is correlated to the diagonal terms of the Hamiltonian matrix, n different coupling constants are estimated. Nonetheless, this process becomes progressively complex with increasing size of the system because a system with n paramagnetic sites, each with spin S, requires diagonalization of a $(2S+1)^n \times (2S+1)^n$ matrix. In the fifth chapter, we put our endeavour to frame a computational strategy to ease up the estimation of J. In this scheme, we perform spin mapping on the ground state of the SMMS. With this spin distribution, exchange coupling constants for a specific pair of magnetic sites in polynuclear magnetic systems are calculated, while keeping the other paramagnetic sites inert. However, magnetic effects of disregarded atoms on concerned paramagnetic pair are not ignored as they are primarily taken into account in the use of the ground state values of spins and charges in course of estimation of J. This is rationalized by writing the HDVV Hamiltonian in terms of spin density (eq 5.7). Application of this computational strategy on the benchmark systems, viz., Mn_3^+, 1,3,5-benzenetriyltris (N-tert-butyl nitroxide), and $Mn_5\{N(SiMe_3)_2\}\{\mu_4\text{-}PSi\textit{i}Pr_3\}_2\{\mu\text{-}P(H)\text{-}Si\textit{i}Pr_3\}_5$ reproduced the known nature of magnetic interactions between the spin pairs in all the three systems. The proposed technique significantly reduces the computational rigor as the computation of energy differences among all possible spin states is skipped and electronic environment of disregarded atoms is nullified by assigning them as dummies. Although, estimated values of magnetic exchange coupling constants in some of the cases seem to be overestimated, the sign of J between magnetic sites is concordant with the spin density distribution and are in agreement with reported nature of magnetic interactions. Thus, independent estimation of each coupling constant by considering only two paramagnetic centres seems to be an economical and rational approach, irrespective of systems and nature of magnetic interactions.

In the estimation of exchange coupling constant through the most practiced broken symmetry approach within unrestricted density functional theory, one has to encounter two major difficulties. The first problem is the adoption of the right combination of the exchange-correlation functional and the basis set for getting a trustworthy value of coupling constant. The other bottleneck is that the expectation value $\langle S^2 \rangle$ is not always well defined, particularly in the BS state. Also, in case of the remote magnetic sites, the computation of BS state becomes increasingly difficult. In an effort to sort out the remedy, we find the spin density to be an excellent parameter, which can be obtained both theoretically and experimentally. Hence, in the sixth chapter, the coupling constant in direct exchange and superexchange mechanisms are correlated to the spin density. The coupling constant in a direct exchange process is equated with the spin density of the magnetic sites (eq 6.14) by second quantization of the exchange part of a general many body Hamiltonian. On the other hand, to deal with the superexchange process, the perturbative approach of Anderson is adopted (eq 6.15). Starting from the Anderson's formalism, the coupling constant in a superexchange process is expressed in terms of the second order perturbation energy for intersite charge transfer and the spin densities on the concerned sites (eq 6.20). Through the use of spin density in obtaining the coupling constant, the use

of $\langle S^2 \rangle$ can be avoided. Moreover, the spin density, being an experimentally achievable parameter, can be verified against the computed value and thus the proper theoretical framework befitting the experimental result can be figured out. The present formalism is employed on a wide spectrum of molecular systems which entail both the ferro- and antiferro-magnetic compounds from organic and inorganic domain. The value of coupling constant in these systems are found to agree with the reported values as well as the values obtained through well-known spin projection technique of Yamaguchi (eq 2.40). The simultaneous use of this new theoretical approach and the computational scheme discussed in the fifth chapter where some part of the molecule is made dummy is found instrumental in obtaining the separate contribution of metal – metal and metal – ligand interaction towards the total coupling constant *J*. The ground state spin topologies of the systems under investigation are found to be in parity with the sign of coupling constant. In the systems, executing superexchange, difference of spin topology is found to stem from the occupation status of the *d*-states on the metals, to and from which the electron transfer takes place. The extent of overlap between the metal and ligand also governs the spin topology. In case of the anionic oxide of Cr with "less than half full" *d*-states, it is interesting to note an alternation of spin density in the spin topology of Cr_2O^-. The explanation given in this regard may also be useful to account for the well-observed spin density alternation in π-conjugated organic diradicals. The present exercise of the recast of HDVV Hamiltonian in terms of spin density results in an expression similar to the well-known spin density Hamiltonian proposed by McConnell (eq 6.3) which has been the pioneer in spin-topology based prediction of magnetic behaviour. However, the way it was modelled on the basis of HDVV Hamiltonian required a validation which is also inherent in the present formalism.

Next, in the chapter seven and chapter eight, a connection between the magnetism and other electronic properties in a molecule is sought for. In the first step of this effort, a correlation between magnetism and aromaticity is explored in the seventh chapter. The all metal aromatic systems (AMAS) are set as the target materials for this task since metals can be a good source of unpaired electrons, a necessary requirement for having magnetic moment. On the basis of their change in aromaticity with spin state, the AMAS can be categorized in two distinct classes. At one end, Al_4^{2-} and $Al_4Cu_2^{2+}$, which are aromatic in the singlet state, behave as antiaromatic in their triplet state. This swap of aromaticity is found to be associated with the weakening of σ-bonds while going from the singlet to the triplet state. Thus it can be surmised that the orbitals used to maintain the diatropic ring current in the singlet state turn into the magnetic orbitals in the triplet state; and this in turn establishes an antagonistic relationship between aromaticity and spin density in the first type of AMAS. On the contrary, in $Te_2As_2^{2-}$ and $Te_2As_2Cu_2^{2+}$, one can trace the simultaneous existence of aromaticity and high spin state. This situation arises because the magnetic orbitals, containing the spin excess and the orbitals required for diatropic ring current leading to aromaticity are not the same. After finding this distinct relationship between magnetism and aromaticity, we are attracted to another interesting property, the non linear optical (NLO) response, which is a characteristic feature of the AMAS. A significant number of works underline the variance of NLO response with the change in spin multiplicity. Though, this observation indicates a plausible connection between magnetism and NLO response, no such study to clarify the link these two properties are found in the literature. Hence, we take up the task to correlate NLO response with magnetism taking the same group of molecules, the AMAS as references. The NLO response is measured in terms of second (third order) hyperpolarizability (γ_{iiii}). This parameter is the third order derivative of the charge density with respect to the static electric field. Starting from this definition, the second hyperpolarizability is shown to be related with the third order derivative of the spin density in the similar way (eq 7.10). This new equation suggests that although the principal cause of the second hyperpolarizability is the

charge fluctuation induced by electric field; it may also vary for different spin configurations even if the charge density remains same. In compliance with this expression in eq 7.10, an increase in NLO response is observed in the systems with excess spin density in the systems under investigation. Now, since, magnetism is correlated with aromaticity and NLO response, interplay between these three can be intuited. From the analysis of relative energy ordering of the molecular orbitals associated with the change in spin density, NLO response or aromaticity, the HOMO – LUMO gap turns out to be the ultimate key, which alone can control all the properties. Hence, the HOMO – LUMO energy gap becomes the cornerstone to tune the interplay among magnetism, aromaticiy and NLO response as summarized in the following Figure 9.1. Nevertheless, from the course of the discussion, it becomes obvious that this interplay is system independent and should have subsistence beyond the domain of all metal aromatic clusters. Simultaneous existence of different important properties in AMAS certainly provides a boost in the quest of multifunctional materials.

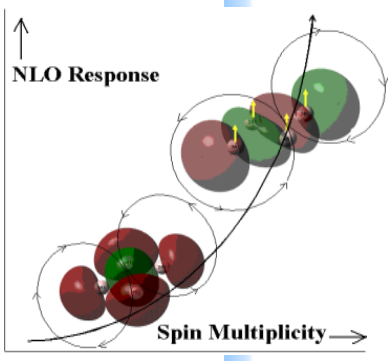

Figure 9.1 The interplay among aromaticity, magnetism and non linear optical response in AMAS. Anticlockwise and clockwise arrows imply diatropic and paratropic ring current in aromatic and antiaromatic systems respectively. Yellow arrows indicate the accumulation of excess spin density in the antiaromatic high spin state with exalted NLO response.

The obvious connection of aromaticity and NLO response with spin characteristics spurs the interest to look for other electronic properties which could have some bearing on interaction of spins and the consequent magnetism. So, a correlation between the spin character and bond strength is investigated in the eighth chapter. In fact, the high spin and low spin states of a molecule in its optimized geometry will obviously show a difference in the bond strength, simply because the states differ in their optimized bond length. Now, the question arises that whether the bond strength varies in case the bond distance remains unaltered in the high spin and low spin situations in a simple dimer molecule, where the spin characteristics is due to the bonding electrons. To investigate this issue, the force constant which is a direct measure of the bond strength is computed at the high and low spin states of the simple dimer molecules keeping the internuclear distance same. In consequence, the high spin state is found to have lower value of force constant than the low spin state (Figures 8.2 and 8.3). Since the force constant is the second order derivative of molecular energy (eq 8.3), different construct of the wave function for the high and low spin state can easily explain the observation of spin dependent force constant. The lower force constant and a spin parallel situation in the high spin state alludes easy bond cleavage. So, the bond dissociation can be accelerated through inducing the spin parallel situation in the bonding electrons by the application of magnetic field. However, in the singlet ground states, it requires an abnormally high magnetic field to create the spin parallel situation in the spin-paired bonding electrons. This makes the scheme of magnetic catalysis of bond dissociation difficult and unrealistic, which can be avoided if the higher vibronic levels are

considered. Though small, these vibronic levels are supposed to have population even at room temperature. The molecules at upper vibronic layers have larger internuclear separation than in the ground state, which brings about the breaking of symmetry in the dimer molecules. The broken symmetry state is defined as an open shell singlet which is different from the singlet ground state with $S = 0$, and can be expressed as the weighted average of different spin multiplets. Thus the transition state in the process of bond dissociation can be characterized by the $\left\langle \hat{S}^2 \right\rangle$ value corresponding to the BS state. However, in the present context, the fact what is important is the weighted participation of all the spin states to construct the BS state at this larger separation of atoms. The small high spin – low spin energy splitting at this BS state makes it easier to stabilize the high spin state with moderate magnetic field. The high spin state prepared in this way has low force constant and susceptible for easy bond cleavage. This conjecture is tested for Cr_2 which bears as much as twelve unpaired electrons in its lowest lying excited state and is singlet in the ground state. The rate of bond dissociation in this molecule is found to increase nearly four times (eq 8.9) with the application of 50 Tesla magnetic field. Hence, imposition of magnetic field can also be instrumental to facilitate the bond dissociation along with other traditional techniques.

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CHAPTER 1

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