

ABSTRACT

The first chapter provides a brief account of the history and significant advances in the fields of aromaticity and magnetism. In this chapter a concise history of the origin and advancement of research in aromaticity is given which correlates the chronological development of the subjects with the evolution of new materials. The current status of the research in aromaticity, with special emphasis on the metal based aromatic molecules, is provided. Magnetism is also discussed according to the chronology of the advancement of the theory and explored materials. The effect of dimension in the magnetic properties is also discussed here. The emergence of new molecules for nanomagnets and the role of the theoretical advancement in designing such materials also discussed in this chapter.

The second chapter presents a concise report of the basic theoretical background related to aromaticity, magnetic exchange coupling constant and magnetic anisotropy. The significance of the quantification of aromaticity has been discussed with special emphasis on the fundamental categories based on which the assessment of aromaticity is performed. A short description of the available methods for quantification of aromaticity, which are of subsequent use in this work, is also presented. A brief background for the estimation of magnetic exchange coupling constant has been provided. Two different methods of determination of the magnetic exchange coupling constant (J) is given, namely, the broken symmetry approach and the spin-flip DFT approach. The theoretical approach behind these two methods are discussed elaborately. A short account of the basic theory behind the quantification of magnetic anisotropy is also provided here. There are two popular methods for the quantification of magnetic anisotropy. The Pederson-Khanna (PK) approach and the Neese method for quantification of zero-field splitting (ZFS) parameter D , in connection to the magnetic anisotropy are discussed with proper emphasis on the estimation of the spin-orbit coupling in spin-systems.

Gradual migration of Na^+ from Mg_3^{2-} brings about fascinating change in aromatic and magnetic behavior of inorganic Mg_3Na_2 cluster, which is addressed at the B3LYP and QCISD levels is discussed in the third chapter. During this process, Na^+ takes away the electron density from Mg_3^{2-} causing a net decrease in aromaticity. A tug-of-war between the Pauli repulsion and the aromaticity is shown to be responsible for the observed stability and aromaticity trends in singlet and triplet states. Implications of a spin crossover vis-à-vis a possible superexchange are also explored.

The fourth chapter is on the magnetism in metallocene based donor-acceptor complexes, which stems from the donor to acceptor charge transfer. Thus, to correlate the exchange coupling constant J and the charge transfer integral, a formalism is developed which enables one to obtain the coupling constant from the value of the charge transfer integral and the spin topology of the system. The variance in the magnetic interaction between donor and acceptor is also investigated along two perpendicular directions in the three dimensional crystal structure of the reference system, decamethylchromocenium ethyl tricyanoethylenecarboxylate $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$. These donor-acceptor pairs (V-pair and H-pair), oriented along vertical and horizontal directions respectively, are found to have different extents of J , which is attributed to the difference in exchange coupling mechanisms, viz., direct exchange and super exchange. Next, V-pair and H-pair are taken together to treat both the intra chain and inter chain magnetic interactions, since this competition is necessary to decipher the overall magnetic ordering in the bulk phase. In fact, this truncated model produces a small positive value of J supporting the weak ferromagnetic nature of the

complex. Lastly, a periodic condition is imposed on the system to comprehend the nature of magnetism in the extended system. Interestingly, the ferromagnetism, prevailing in the aperiodic system, turns into weak antiferromagnetism in the periodic environment. This is explained through the comparison of density of states (DOS) plots in aperiodic and periodic systems. This DOS analysis reveals proximity of the donor and acceptor orbitals, facilitating their mixing in periodic conditions. This mixing causes the antiferromagnetic interaction to prevail over the ferromagnetic one, and imparts an overall antiferromagnetic nature in periodic conditions. This change over in magnetic nature with the imposition of periodicity may be useful to understand the dependence of magnetic behavior with dimensionality in extended systems.

Magnetic anisotropy of a set of octahedral Cr(III) complexes is the key deliberation of chapter five. The magnetic anisotropy is quantified in terms of zero-field splitting (ZFS) parameter D , which appeared sensitive toward ligand substitution. The increased π -donation capacity of the ligand enhances the magnetic anisotropy of the complexes. The axial π -donor ligand of a complex is found to produce an easy-plane type ($D > 0$) magnetic anisotropy, while the replacement of the axial ligands with π -acceptors entails the inversion of magnetic anisotropy into the easy-axis type ($D < 0$). This observation enables one to fabricate a single molecule magnet for which easy-axis type magnetic anisotropy is an indispensable criterion. The equatorial ligands are also found to play a role in tuning the magnetic anisotropy. The magnetic anisotropy property is also correlated with the nonlinear optical (NLO) response. The value of the first hyperpolarizability varies proportionately with the magnitude of the ZFS parameter. Finally, it has also been shown that a rational design of simple octahedral complexes with desired anisotropy characteristics is possible through the proper ligand selection.

In chapter six, the effect of an external electric field on the magnetic anisotropy of a single-molecule magnet has been investigated, with the help of DFT. The magnetic anisotropy of a pseudo-octahedral Co(II) complex namely, $[\text{Co}^{\text{II}}(\text{dmphen})_2(\text{NCS})_2]$, has been investigated in connection to the tunability of the magnetic anisotropy through external electric field. The application of an electric field can alter the magnetic anisotropy from “easy-plane” ($D > 0$) to “easy-axis” ($D < 0$) type. The alteration in the magnetic anisotropy is found due to the change in the Rashba spin-orbit coupling by the external electric field. This variation in the Rashba spin-orbit coupling is further confirmed by the generation of the spin dependent force in the molecule which is later found to manifest separation of α - and β - spins in opposite ends of the molecule. The excitation analysis performed through time-dependent DFT also predicts that the external electric field facilitates metal to π -acceptor ligand charge transfer, leading to uniaxial magnetic anisotropy and concomitant spin Hall effect in a single molecule.

Finally chapter seven presents a general and comprehensive conclusion of all the chapters.