
Chapter 7

Conclusions

Comprehensive conclusions of all the chapters are given in this chapter.

Conclusions

This chapter contains the summary of preceding chapters with the emphasis on the importance of obtained results. In chapter one, we have discussed the general introduction about the magnetic and transport behavior of molecules and radicals. The different types of magnetic molecules based on organic radicals and charge-transfer complexes have been discussed. The stability of organic radicals and their magnetic nature has also been elaborated. The different types of mechanisms in charge transfer complexes have been discussed in detail. The electrical transport properties of single molecule, radical have been discussed along with their possible applications.

Chapter two deals with the theoretical platform, where stands the computational results and their physical interpretation exercised in this thesis. Various methodologies about the evaluation of magnetic exchange coupling constant have been discussed. The DFT based spin projected BS methodology given by Yamaguchi has been used to evaluate the magnetic exchange coupling constant of the molecules. The transport property of molecules has been estimated through Green's function based technique coupled with DFT.

In chapter three, we theoretically design and investigate the photomagnetic property of azobenzene based diradical systems, where trans isomers convert into corresponding cis forms upon irradiation with light of appropriate wavelength. In all three systems investigated, antiferromagnetic trans isomers turn into ferromagnetic cis forms when exposed to light. Analysis of density of states shows intense spin polarization in ferromagnetic cis isomers, which supports the usefulness of such systems for spintronic applications. In ferromagnetic cis form, the difference in DOS of up and down spins at Fermi level is found to be directly proportional to J values. Therefore, a system with higher value of exchange coupling constant would be more useful as spintronic material.

We study the effect of aromaticity of linear and their corresponding angular polyacenes on the magnetic exchange of polyacene coupled diradicals in chapter four. It has been found that the linear polyacenes are less aromatic compared to the angular one. The variation of aromaticity of the polyacenes cannot be addressed by NICS, rather by the HOMA values. HOMA being a geometry based index, it can describe the aromaticity due to change in geometry in a better way.

The low HOMO-LUMO gap in the linear aromatic coupler turns appropriate for getting high value of coupling constant of designed diradicals. To illustrate the mechanism of itinerant exchange and to investigate the role of LUMO, we plot the spatial distribution of MOs. We find that the position of LUMO in the diradical plays an important role in the extent and mechanism of magnetic interaction. If the SOMOs and LUMO cover the whole molecule and have the same spatial position in the molecule, magnetic exchange is facilitated through LUMO. The occupation number of LUMO also indicates towards the possibility of LUMO – mediated magnetic exchange interaction in the diradicals.

In chapter five, we have studied mixed stack charge transfer complexes to elucidate the origin of the ferromagnetic interaction through DFT calculations. The parallel spin alignment in the ground state of both the complexes stems from the transfer of a spin from β -HOMO of neutral donor (D) to the β -LUMO of neutral acceptor (A). These parallel spins undergo through-space direct exchange to set in ferromagnetism in both the complexes. The through-space nature of exchange is ensured from the zero value of overlap between magnetic orbitals. Next, the geometry of the complexes is altered by changing the rotational angle between the layers. The plot of J against different rotational angle divulges maximum degree of ferromagnetic interaction in their minimum energy state for which the crystallographic file format is available.

In chapter six, we study the effect of external electric field on biphenyl, methylene substituted biphenyl mono- and di-radicals. We apply electric field parallel to the molecule (E_{\parallel}) and perpendicular to the molecular plane (E_{\perp}). It has been observed that one can reversibly tune the molecular conformation by external electric field. This result provides an alternative way to change the molecular conformation without any chemical substitution; i.e, tuning of molecular conformation by external means. The energy and spatial distribution of molecular orbital are found to be the function of external electric field. The low HL gap has been achieved in case of diradical by application of external electric field. This low HL gap has wide applicability in the field of molecular electronics. The spin density distribution of the monoradical and diradical are dependent on the strength and direction of the external electric field. It has been found that E_{\parallel} has more effect on spin density than E_{\perp} . With increasing field strength the spin density on radical centre decreases and increases on the coupler. The lower dihedral angle facilitates the higher conjugation between the spins in diradical resulting the increase in magnetic exchange coupling

constant. Therefore, one can tune the strength of magnetic exchange coupling constant by external electric field. With increase in the magnetic exchange coupling constant, conduction within the diradical also increases. There is appreciable difference of up spin and down spin transmission spectra at lower dihedral angle. This observation confirms the spin filtering ability of the diradical at lower dihedral angle. It is seen that at ground state geometry of the diradical, the up and down spins conduct comparable current. While, with decreasing dihedral angle the up spin conduction decreases, on the other hand down spin conduction increases. That is, at lower dihedral angle the diradical acts as an efficient spin filter. Therefore, a single molecule can be used for different application like unimolecular rectifier, spin filter and molecular conductor varying the strength of the external electric field.