

CHAPTER 4

Effect of charge transfer and periodicity on the magnetism of [Cr(Cp)₂][ETCE]*

Abstract

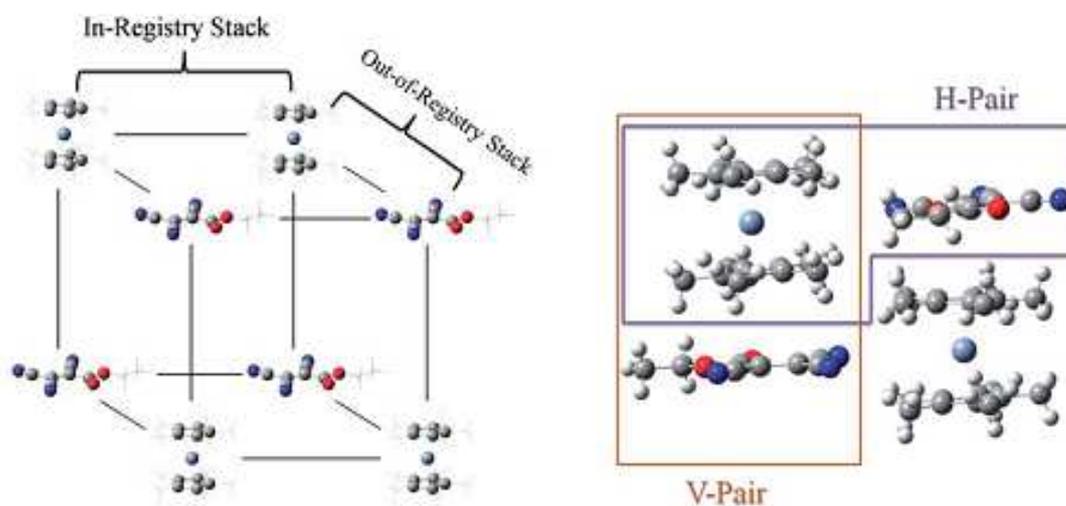
Magnetism in metallocene based donor–acceptor complexes stems from the donor to acceptor charge transfer. Thus, to correlate the exchange coupling constant J and the charge transfer integral, a formalism is developed which enables one to obtain the coupling constant from the value of the charge transfer 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 [Cr(Cp*)₂][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 superexchange. Next, V-pair and H-pair are taken together to treat both the intrachain and interchain 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.

4.1. Introduction

The synthesis and characterization of charge transfer (CT) ferromagnetic compound $[\text{Fe}(\text{Cp}^*)_2][\text{TCNE}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ and $\text{TCNE} = \text{tetracyanoethylene}$) by Miller *et al.* in 1985 was a breakthrough in the field of metallocene-based magnets.¹ This was the first reported complex where the unpaired electron of a p -orbital also participates in the exchange interaction along with metal d -electrons. Nanoscale charge transfer is also known to have widespread application in sensors, photonics, electrocatalysis, solar photoconversion, molecular electronics and soon.² The occurrence of charge transfer in organoligand–metal fragments is found to induce a high dielectric polarization and concomitant intense nonlinear optical (NLO) response.³ Long spin coherence time in such materials renders them as potential candidates for high-density information storage and also for quantum computing.⁴ Their applicability can further be proliferated by simply tuning their magnetic interaction through simple adjustment of organic fragments therein. All these facts tantalize the scientific community to explore a plethora of such metallocene based charge transfer complexes (MBCTCs).^{5–7} In these compounds such as $[\text{M}(\text{Cp}^*)_2][\text{TCNE}]$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe); $[\text{M}(\text{Cp}^*)_2]$ fragment donates one electron from the magnetic orbital of the metal to the initially diamagnetic $[\text{TCNE}]$ part. This leads to ferromagnetic interaction among the localized spins on the donor part (D^+) and the acceptor part (A^-).⁷ Divergent mechanisms have been proposed for the spin exchange in these CT salts. One such proposition is the McConnell-II mechanism where the stability of a particular spin state is attributed to the interaction of ground spin state and lowest excited state of same spin multiplicity.⁸ Miller *et al.* supported this mechanism assuming a forward charge transfer from the donor to the acceptor leading to the triplet excited state.^{7b} In $[\text{Fe}(\text{Cp}^*)_2]^+[\text{TCNE}]^-$, the triplet ground state becomes stabilized through its interaction with the lowest lying triplet excited state.^{8c} However, in case of $[\text{Mn}(\text{Cp}^*)_2]^+[\text{TCNE}]^-$ and $[\text{Cr}(\text{Cp}^*)_2]^+[\text{TCNE}]^-$, the interaction between the ground and excited states leads to the stabilization of the antiferromagnetic situation which is in opposition to the experimentally reported high spin state of the molecules. Hence, the McConnell-II mechanism based explanation appears insufficient to justify this observation.^{7b,c,9} To explain this anomaly, Kollmar and Kahn coined a new mechanism of back charge transfer from A^- to D^+ , which is justified by the presence of positive spin density on Cp^* ring.^{9b} Another proposition is McConnell-I mechanism,¹⁰ where a large positive spin density on the transition metal induces a negative spin density on Cp^* ring, which again induces a positive spin density on the acceptor. These conflicting mechanisms about the origin of magnetic nature in MBCTCs urge for the development of a complete theoretical model.^{7b}

To investigate the charge transfer induced magnetic interaction in the MBCTCs, the compound *decamethylchromocenium ethyl tricyanoethylenecarboxylate* $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ is taken as the representative system in the present work. This complex is recently synthesized by Wang *et al.* and found to have a ferrimagnetic ordering.¹¹ This ferrimagnetism may arise from the competition of ferro- and antiferro-magnetic interactions in three different lattice dimensions as interestingly probed by Datta and Misra.¹² The $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ is known to crystallize in orthorhombic geometry with parallel arrangement of vertical one dimensional

D^+A^- chains. These one dimensional chains in a crystal can have two possible parallel orientations. In one type, the D^+ segments are oriented side by side and termed as in registry chains (Figure 4.1a). On the other hand, in the out of registry chains, D^+ finds A^- in the neighboring chain in its nearest position (Figure 4.1).^{11,13} The D^+A^- pair of a vertical chain is defined as the V-pair in this work (Figure 4.1b). As the nearest neighbor spin interaction is known to govern the magnetic nature of any system,¹³ a nearest D^+A^- pair from the horizontally stacked out of registry chains is selected for this investigation. This D^+A^- pair, where the D^+ and A^- belong to two different vertical columns arranged in an out of registry manner which is termed as H-pair in this work (Figure 4.1b). Although, the origin of ferromagnetism in the V-pair has been well explained by McConnell-I mechanism,¹⁰ the weak ferromagnetic ordering of H-pair is not yet addressed properly.¹¹



(a) Three dimensional motif of $[Cr(Cp^*)_2][ETCE]$ (b) Out of registry D^+A^- pairs

Figure 4.1. (a) Representation of the in registry and out of registry chains (b) blue and brown rectangles in the out of registry chains designate the H-pair and V-pair respectively.

This study makes an attempt to address the charge transfer induced magnetism in a particular MBCTC, $[Cr(Cp^*)_2][ETCE]$, keeping three different goals in its focus. Primarily, the charge transfer in between donor and acceptor is explored and the donor–acceptor magnetic coupling is quantified in terms of this charge transfer energy. Secondly, the architecture of this complex hints towards a different degree of magnetic interaction between the donor and the acceptor in V-pair and H-pair. In the V-pair, the d -electrons on Cr can be transferred to the acceptor via Cp* bridge;¹⁴ whereas, absence of any such mediator in case of H-pair obstacles the CT process. The difference in horizontal and vertical direction definitely has an important role in governing the overall magnetic nature of this crystal. This stimulates us to investigate the nature of magnetic interaction in the V-pair and H-pair individually and

in presence of each other. Lastly, we cultivate the role of periodicity in governing charge transfer and concomitant magnetic interaction. Dealing with such extended system also enables one to explore the effect of dimension on magnetic characteristics. The systems in reduced dimension are found to depart from their usual bulk behavior which inspires the study of electronic properties in nano scale.¹⁵ Intensified magnetism in the reduced dimension has recently been the subject of several theoretical and experimental investigations.¹⁶ This fact has already been realized in cases of Au-nanoparticle, alkali metal clusters, Mn nanosheet and many other systems.^{16e,h,17} All these facts spur the study of the effect of periodicity on the magnetic behavior of $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$.

4.2. Theoretical Framework

The magnetic sites in a system are characterized by a non-vanishing spin angular momentum quantum number, S_i . Interaction among these localized spin moments govern the overall magnetic nature of the system. The magnetic interaction, often termed as exchange coupling is described by the well-known phenomenological Heisenberg–Dirac–van Vleck (HDvV) Hamiltonian, which describes the isotropic interaction between localized magnetic moments S_i and S_j as

$$\hat{H} = -\sum_{i<j} J_{ij} S_i S_j \quad (4.1)$$

where, J_{ij} is the exchange coupling constant between the localized spin moments, and the i, j symbols indicate that the sum extends to the nearest neighbor interactions only. According to the spin Hamiltonian in eqn (4.1), a positive (negative) value of J_{ij} corresponds to a ferromagnetic (antiferromagnetic) interaction, thus favoring a situation with parallel (antiparallel) spins. 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.¹⁸ Therefore, the removal of all symmetry elements connecting the magnetic centers is necessary to account for weak coupling limit. Noodleman and co-workers worked out a “broken-symmetry” (BS) approach, where the space and spin symmetry can be removed by polarizing the up-spin and down-spin onto different magnetic centers.¹⁹ Later on, Bencini and Ruiz modified this expression for the limit of strongly interacting magnetic sites.²⁰ On the other hand, Yamaguchi's expression encompasses the appropriate limit, depending on the interaction strength and thus fulfils the criterion of general applicability,²¹

$$J_{ij} = \frac{E^{HS} - E^{BS}}{\langle \hat{S}^2 \rangle^{BS} - \langle \hat{S}^2 \rangle^{HS}}. \quad (4.2)$$

The general applicability of the eqn (4.2) can be understood through the following dependence of $\langle \hat{S}^2 \rangle$ on the overlap of magnetic orbitals²²

$$\langle \hat{S}^2 \rangle = M_S(M_S + 1) + N_\beta - \sum_{i,j}^{N_\alpha, N_\beta} (O_{ij}^{\alpha\beta})^2. \quad (4.3)$$

Here, $O_{ij}^{\alpha\beta}$ is an integral describing the overlap between the spatial parts of α and β spin orbitals.^{22,23} In the strong coupling limit, all pairs of α and β orbitals overlap and the double sum in eqn (4.3) is reduced to N_β . Therefore, the total spin expectation value indicates a pure spin state with $\langle \hat{S}^2 \rangle_{BS} = 0$ for a diradical with equal number of α and β electrons. Hence, the denominator in eqn (4.2) transforms to $S_{HS}(S_{HS} + 1)$ which resembles the Noodleman–Bencini–Ruiz formula.²⁰ On the other hand, if magnetic orbitals do not overlap (BS determinant), the sum in eqn (4.3) becomes $N_\beta - 2S_A$, where S_A is the sum of α and β magnetic orbitals. In this weakly coupled limit, $\langle \hat{S}^2 \rangle_{BS} = 2S_A = S_{HS}$ and resembles Noodleman's original expression.²³ The BS state is usually constructed by mixing two magnetic orbitals which usually belongs to different irreducible representations.^{19,20b} So, the magnetic orbitals should be close enough in order to interact with each other. Hence, for the remote magnetic sites, the construction of BS state becomes difficult. However, the BS state is usually achieved by performing HF or DFT in spin-unrestricted formalism where up-spin and down-spin densities are allowed to localize on different centers.^{20b} Though an open shell singlet state can best be represented through multi-configuration techniques;²⁴ DFT uses a single Slater determinant to describe the BS state and thus becomes more advantageous than post-HF methods in handling larger systems.^{20b}

As discussed in the introduction, the donor–acceptor magnetic coupling is induced by electron transfer from donor to acceptor. Among the various models of charge transfer in electronic systems, a perturbative treatment has widely been adopted to account for the electron tunnelling process.²⁵ Anderson in his pioneering work, derived the second order perturbation energy (DE) for such an intersite charge transfer and correlated this energy with magnetic interaction as,²⁶

$$\Delta E = \frac{t_{ij}^2}{U} \left(\frac{1}{2} + 2\hat{S}_i \hat{S}_j \right). \quad (4.4)$$

Here, t_{ij} is the hopping integral which carries an electron from site i to site j and U is the single ion repulsion energy. However, this t^2/U term is well-known in the Hubbard model and related to the exchange coupling constant (J).²⁷ In their seminal works Calzado et al. Applied ab initio CI techniques to compute these individual contributions to the magnetic coupling constant using effective Hamiltonian theory.²⁸ However, in a recent formalism, instead of direct estimation of this t^2/U term; the above expression is modified to estimate the coupling constant (J_{SX}) in a superexchange process in terms of the second order perturbation energy (ΔE) for charge transfer between sites and spin population on those centers (ρ_i and ρ_j),²⁹

$$J_{SX} = \frac{2\Delta E}{1 + \rho_i \rho_j}. \quad (4.5)$$

The charge transfer matrix element between the donor and acceptor can be expressed as^{30–33}

$$H_{DA} = \frac{E_D - E_A}{2}. \quad (4.6)$$

where, H_{DA} is a pure one electron matrix element, coupling the effective donor and acceptor orbitals as

$$H_{DA} = \langle \phi_D | \hat{H} | \phi_A \rangle. \quad (4.7)$$

and, E_D and E_A are the energies of the LUMO in cationic donor and neutral acceptor. Again, the second order perturbation energy (ΔE) for the charge transfer process is related to the transfer matrix element H_{DA} for the donor–acceptor pair in the following manner,³⁴

$$\Delta E = \frac{|H_{DA}|^2}{E_D - E_A}. \quad (4.8)$$

Now, substituting $2\Delta E$ term in eqn (4.5), using eqn (4.8) and (4.6), the following modified form is obtained,

$$J_T = \frac{H_{DA}}{1 + \rho_D \rho_A}. \quad (4.9)$$

This can be conveniently used to calculate the exchange coupling constant value (J_T) in electron transfer systems.

4.3. Computational Details

In the present work, the effective exchange integral J is estimated in two approaches, one of which is the state-of-the-art spin projection technique of Yamaguchi (eqn (4.2)). In the second approach, the electron transfer matrix element for charge transfer from donor to acceptor and the spin populations on the donor and acceptor sites are used to estimate J through presently derived eqn (4.9). The eqn (4.2) is generally implemented through an unrestricted or spin polarized formalism, where the up-spin and down-spin densities are allowed to localize on magnetic sites.^{21,22} Thus, in the present work unrestricted DFT (U-DFT) is applied to compute the coupling constant. The same U-DFT method is adopted to derive the parameters in eqn (4.9). The U-DFT method is reported to produce a reliable estimate of such transfer integrals, at least in cases of metal-based systems.³⁵ To evaluate J through eqn (4.9), standard DFT calculation on the isolated donor and acceptor molecules is first carried out to extract the energies of the LUMO of the cationic fragment $[\text{Cr}(\text{Cp}^*)_2]^+$ and that of the neutral acceptor [ETCE]. These energy values along with the spin populations on the donor and acceptor in the ground state of dimer $[\text{Cr}(\text{Cp}^*)_2]^+[\text{ETCE}]^-$ are utilized to compute the J_T in eqn (4.9).

To understand the magnetic effect of V-pair on H-pair and vice versa in the crystal motif of $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$, it becomes necessary to estimate the exchange-coupling constant between every D^+A^- pair in vertical and horizontal directions in presence of each other. A recently adopted technique to determine J in a system with multiple magnetic sites becomes useful in this regard.³¹ In this particular strategy, which is mentioned as the “dummy approach” in the present work; first the effect of all the magnetic sites on each other is realized in the form of ground state spin population. Then the exchange coupling constant between any two magnetic sites is calculated on the basis of their ground state spin population while regarding other magnetic sites inert. However, in the present context the computational scheme of ref. 31 is applied on a 2D crystal motif displayed in Figure 4.1b so as to consider both the direct exchange and superexchange in the H-pair and V-pair respectively. The spin density distribution of this system is first obtained. Next, the exchange coupling for one V-pair is computed while its neighboring V-pair is made dummy. Although, other than a specific magnetic pair all other magnetic sites are made dummy, their effect is imposed on the specific pair in terms of pre-calculated spin population which can be understood from the spin density parameterization of the Heisenberg Hamiltonian.³¹

In order to investigate the effect of periodicity on the magnetic interaction, the periodic boundary condition is imposed on the system. To deal with the extended solid, different level of theoretical platforms are used which ranges from the simple tight-binding model to the ab initio periodic Hartree–Fock and modern DFT based methods.³³ The eigenstates of such periodic system can be labelled by the reciprocal lattice vectors, \mathbf{k} , in the first Brillouin zone (BZ).³³ Since the system is infinite, the quantum numbers \mathbf{k} are continuous. Calculation of the total energy requires a self-consistent calculation of the eigenvalues, which are performed at a finite number of points in the Brillouin zone.³⁴ A recent work expresses the charge transfer integral as the function of \mathbf{k} point³⁶ and thus

stimulates us to investigate the influence of increasing k point (within the first BZ) on the charge transfer induced magnetism.

The structure of the complex is available in crystallographic file format,¹¹ this geometry of the complex is taken as its ground state structure. While doing the periodic boundary calculation with different k points, the Perdew–Burke–Ernzerhof exchange and correlation functional (PBE) is employed.³⁷ This exchange correlation functional is found to produce superior accuracy for a broad variety of systems under periodic boundary conditions.³⁸ This advanced GGA functional includes some electron correlation effects at larger distances. The LANL2DZ basis set is chosen selectively for Cr atoms and 6-311++g(d,p) for all other atoms and this has been maintained throughout for DFT calculations. The success of exchange correlation functionals in accurate estimation of J is believed to be intrinsically linked to the introduction of an amount of Hartree–Fock (HF) exchange.³⁹ In this regard, the B(X)LYP functional is prescribed as the optimum performer, where X is related to the percentage of Fock exchange.⁴⁰ However, Martin and Illas have shown that the coupling constant vary with X and the result becomes satisfactory with X=50.⁴¹ Hence, in this work we use BHandHLYP functional with X=50, which has already been found efficient to reproduce the experimental value of coupling constant.⁴² This particular functional is characterized to be a 1 : 1 mixture of DFT and exact exchange energies which can be represented as $E_{XC}=0.5E_{HF}^X + 0.5E_{LSDA}^X + 0.5\Delta E_{Becke88}^X + E_{LYP}^C$.⁴³ This is also supported by Caballolet *al.*⁴⁴ who have concluded that functionals assuming fully delocalized open shell magnetic orbitals, such as B3LYP, produce a poor description of local moments.⁴¹ Particularly, the B3LYP functional is reported to produce inaccurate structural and thermochemical parameters in the extended systems due to its failure to attain homogeneous electron gas limit.⁴⁵ On the contrary, another school of thought advocate the use of B3LYP with less amount of HF exchange to get a reliable estimate of J .⁴⁶ Nevertheless, the hybrid functionals are questioned for their tendency to overstabilize the higher spin multiplet, whereas the GGA functionals overestimate the stability of the ground state.⁴⁷ On the other hand, the hybrid meta GGA functional TPSSh with 10% HF exchange shows a minimum deviation (10–15%) in the J value compared to experiment.⁴⁸ Thus, among several other functionals, the TPSSh functional is chosen by several groups for evaluating the exchange coupling constant.⁴⁹ In order to get a self-consistent result, here also a set of exchange correlational functionals is applied to compute the exchange coupling constant. The results obtained with DFT are also validated with the multireference Complete Active Space Self-Consistent Field (CASSCF) technique, based on the active electron approximation. This technique incorporates several important physical effects in both direct exchange and superexchange cases for the calculation of magnetic interaction.⁵⁰ However, the CAS method disregards important physical mechanisms like ligand-spin polarization, dynamic spin polarization, double spin polarization etc. and underestimates the coupling constant in effect.⁵¹ These effects can be included through the second order perturbation theory based upon the UHF wave function. The complete active space second-order perturbation theory (CASPT2) is a method which imposes second order correction to the CAS wave functions, and found useful in producing J close to experimental values.⁵² This method can further be refined by considering “external correlation” through multireference configuration interaction

(MRCI) tools,⁵³ among which the difference dedicated CI(DDCI) approach by Miralles et al. has been particularly successful to produce the desired degree of accuracy.⁵⁴ However, to avoid computational rigor associated with such sophisticated methods, in the present work the CASSCF is used with a large active space which includes different configurations connected to charge transfer excitation,⁵⁵ and thus partially overrule the limitations of CASSCF. An active space often electrons in nine orbitals [CASSCF (10, 9)] is used to calculate the exchange coupling constant of the V-pair in this work. All calculations are performed using Gaussian 09W suite of quantum chemical package.⁵⁶ The density of states (DOS) plots are generated with GaussSum 2.2.⁵⁷

4.4. Results and Discussion

Before dealing with the present dimeric system $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$, first the ground states of monomers (D and A) are taken for pursuit. Since, there exists a probability for the neutral $[\text{Cr}^{\text{II}}(\text{Cp}^*)_2]$ to remain in the low-spin triplet or high-spin quintet state, it requires a theoretical confirmation. The ground state of the monomers is thus checked with different DFT functional. These results are also compared with multireference CASSCF to verify the reliability of DFT methods in properly describing the ground state of the monomers. Everywhere, the ground state is recognized as the low-spin triplet (Table B.S1 in Appendix B), which is also reported experimentally.⁴² Concerning to an orbitally degenerate ground state of $[\text{Cr}^{\text{II}}(\text{Cp}^*)_2]$, Cr^{2+} ion is supposed to experience a quenching of the orbital angular momentum due to static Jahn–Teller (JT) effect.⁵⁸ Moreover, the Cr ion in the D^+A^- species is also reported to be reluctant to magnetic hysteresis and exhibit no magnetic anisotropy.¹¹ The neutral acceptor unit, which initially exists in singlet ground state, turns into an anionic doublet after accepting an electron from neutral donor, leaving the donor in cationic quartet state. The overall quintet spin state in $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ dimer, with three d -electrons on the Cr atom and one in the acceptor unit finds validation in its spin density plot and references of similar systems.^{11,9b} From the molecular orbital (MO) analysis of V-pair and H-pair, 131 to 134 MOs appear as singly occupied molecular orbitals (SOMO), of which 133 α MO is found to be composed of the acceptor orbitals solely in both the pairs (Figure 4.2). Since, the computations are performed at U-DFT level, all the occupied orbitals are in fact possessed by single electrons. Thus, here the SOMOs are referred to as the α -occupied MOs which do not have any β -counterpart of comparable energy.

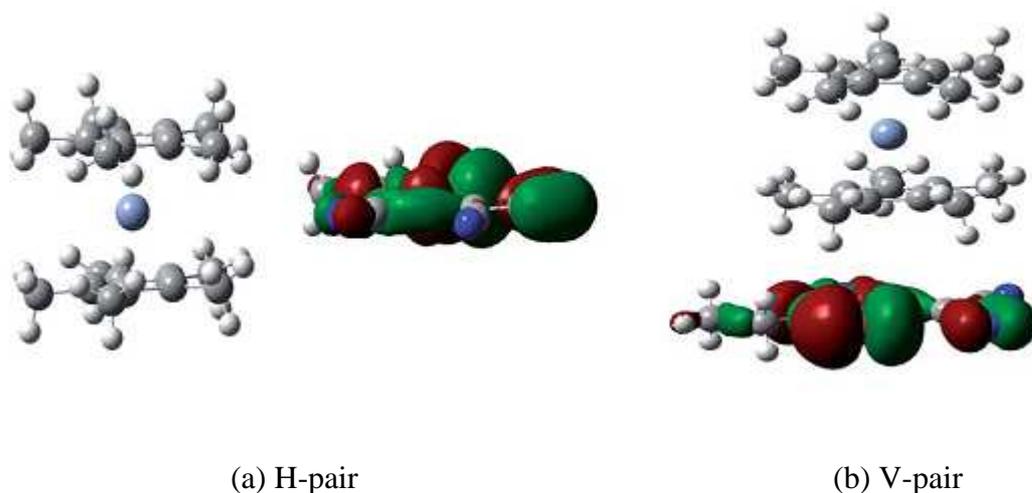


Figure 4.2. The 133rd α -SOMO in (a) H-pair, and (b) V-pair, solely centered on the acceptor.

Existence of this MO advocates for the single electron transfer to the acceptor moiety. Rest of the SOMOs shows an equitable contribution of Cp* and ETCE orbitals. Although in such complexes metal d -orbitals are reported as magnetic orbitals,¹³ in the present case any contribution from Cr d -orbitals is found surprisingly missing in the construction of the highest occupied α -MOs. This contradiction probably stems from the non-Aufbau kind of behavior, where the singly occupied metal orbitals are buried below doubly occupied orbitals.⁴⁴ The density of states (DOS) plot which shows the highest occupied β -spin orbitals at higher energy levels than the highest occupied α -MOs (Figure 4.3) also supports this observation. This problem is often encountered in systems having bonds with prevalently ionic character. Due to this rearrangement of the electrons in shuffled MOs, the contribution of d -orbitals is found in 126, 127 and 128 α -MOs which are below the so called SOMOs. However, applying spin projection technique (eqn (4.2)), the coupling is found to be very weak ($J = 0.004 \text{ cm}^{-1}$) in the H-pair, compared to V-pair ($J = 511 \text{ cm}^{-1}$). Though weakly coupled, the H-pair takes a decisive role in setting up the gross magnetic behavior in such crystals.^{6b}

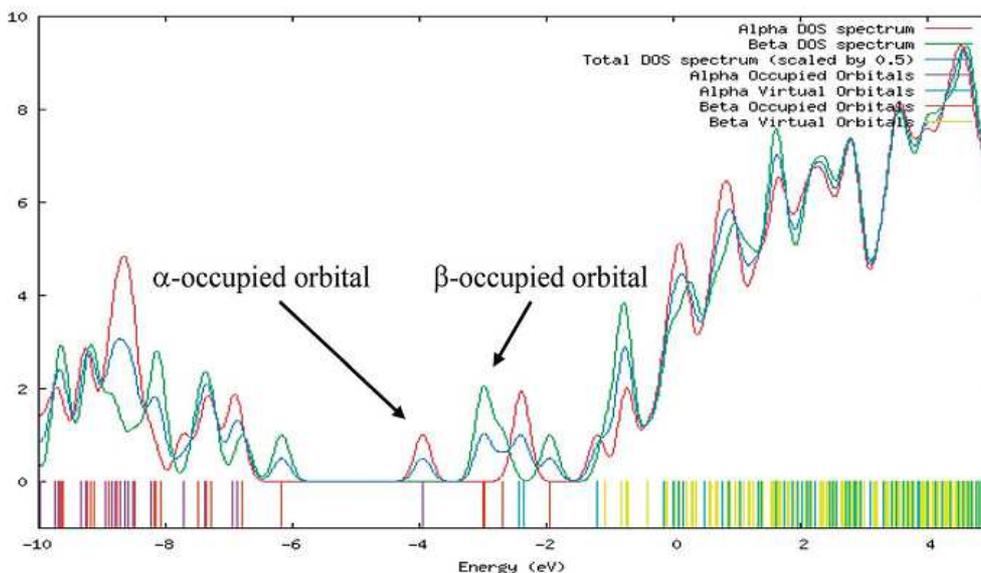


Figure 4.3. The DOS plot of the V-pair.

Now, to understand the charge transfer phenomenon, the electronic configuration of D^+ and A^- in the V-pair is compared with its neutral analogues (D^0 and A^0). From the comparison of the molecular orbitals of the individual D^0 and A^0 units, it appears that the electron transits from the 86th β -orbital of D^0 to the 46th α -MO of A^0 . In the receptor part, the antibonding nature of the olefinic C–C orbitals further clarifies that this is the π^* MO (Figure 4.4). This analysis, performed in the background of monomer approach, also provides necessary information for the appropriate selection of donor and acceptor orbitals, participating in the charge transfer process. To trace the charge transfer process, the system is analyzed at the transition state, when one electron is being transferred from the donor β -orbital to the π^* MO of the acceptor. It has been shown previously that the superexchange electronic charge resonance energy, which we have denoted here as $2\Delta E$ in eqn (4.5), can be substituted by the charge transfer integral (H_{DA}) or the direct vacuum electronic coupling term.⁵⁹ The initial and final states of electron transfer has been crucial in the determination of the two-state approximation. In determining the initial and final states of the electron transfer, the β -LUMO of the isolated donor D^+ is taken as the donor orbital since the electron was initially localized on that particular orbital. Whereas, in the acceptor part A, the α -LUMO is taken as the recipient orbital since the hopping electron is going to be localized on that orbital.⁴⁶ Using the energies of the concerned orbitals, the magnetic exchange coupling constant is estimated as 514 cm^{-1} through eqn (4.9) (at UBH and HLYP/6-311++g(d,p) with LANL2DZ extrabasis on Cr) which is in reasonable agreement with the J , estimated at same level of theory through the famous spin projection technique (eqn (4.2)) of Yamaguchi (Table 4.1). To compare these values obtained through DFT, a more accurate CASSCF technique is adopted as well, which is capable to describe the multireference character of involved radicals. The CASSCF wave function is constructed allowing all possible combination of ten electrons in nine orbitals resulting in a CASSCF (10,9) active space. The active space includes SOMOs, i.e., Cr d_z^2 , $d_{x^2-y^2}$ and d_{xy} -orbitals on the donor fragment and also the singly occupied π^* -orbital on the acceptor fragment. The orbitals, which on a test calculation using a

larger active space (namely a 14 electrons and 11 orbitals space), shows an occupancy of 1.99 electrons, are moved to core orbitals. The chosen active orbitals are shown in Figure 4.5. From Table 1, the chosen functional BHandHLYP and CASSCF are found to produce similar value of exchange coupling constant. Moreover, in all the methodologies, same kind of spin density alternation (up–down–up) in Cr–Cp*–ETCE is observed, which is indicative of the superexchange mechanism (see Table B.S2 in Appendix B).

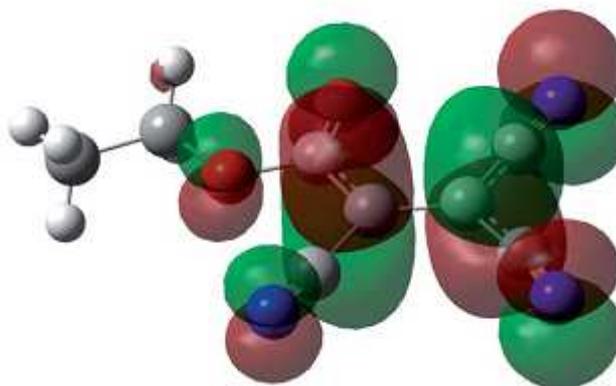


Figure 4.4. The 46th α -MO of acceptor unit in both of the V-pair and H-pair.

Table 4.1. Comparison of coupling constant values (J) for the V-pair, obtained through different methodology.

Level of theory	J in cm^{-1}
BHandHLYP/6-311++g(d,p) with LANL2DZ extrabasis on Cr	511
CASSCF(10,9)/LANL2DZ	439

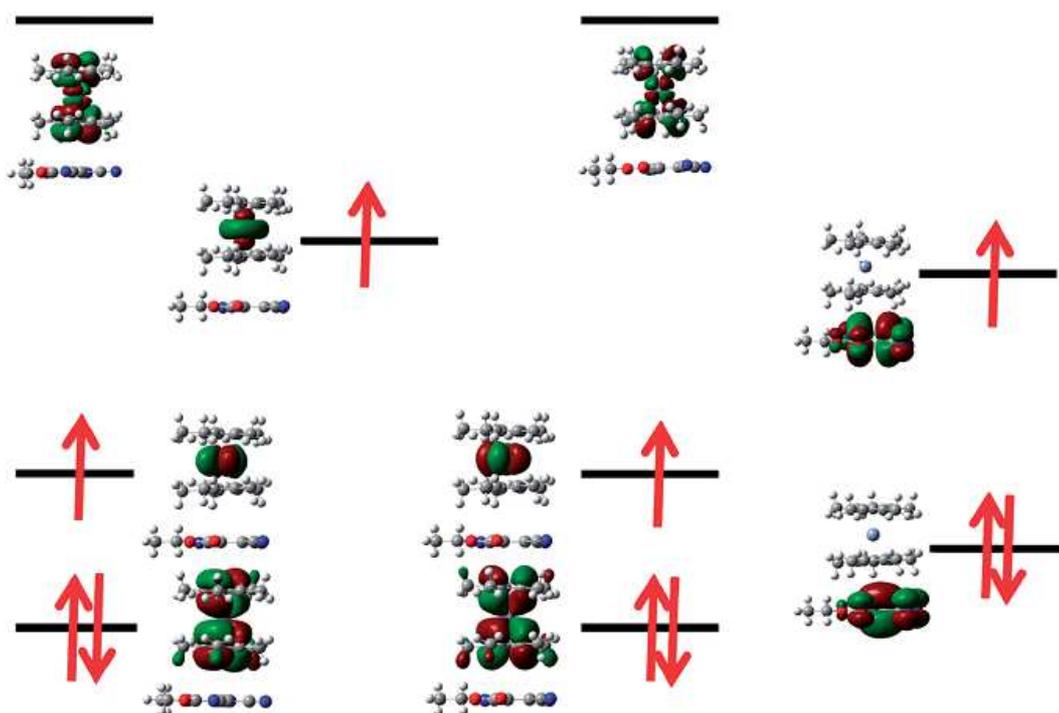


Figure 4.5. A qualitative MO diagram of the chosen active space for the CASSCF calculation, containing 10 electrons in 9 orbitals.

4.4.1. Competition between exchange mechanisms

So far the spin topology of the V-pair is concerned, it is interesting to note significant spin density on Cp* moiety which intervenes the magnetic sites Cr and the acceptor ETCE. This observation suggests that bridging Cp* ligand is playing a role to couple the spins on Cr and ETCE through superexchange process. The spin density alternation further affirms the possibility of superexchange.⁴⁷ The spin density alternation in the V-pair also justifies the McConnell-I mechanism, according to which, the majority spin on the metal atom induces a negative spin density on the Cp* motif, which in its turn spawns positive spin density on the acceptor part. On the other hand, absence of any such bridging ligand in between the magnetic sites of H-pair makes direct exchange the only mechanism for the interaction of spins. Earlier studies pointed out two such contributions to the magnetic coupling;

$$\begin{aligned}
 J &\equiv J_F \left(\text{for FM interaction} \right) + J_{AF} \left(\text{for AFM interaction} \right) \\
 &= 2K_{ij} - 4 \frac{t_{ij}^2}{U}
 \end{aligned}
 \tag{4.10}$$

where K_{ij} describes direct exchange between magnetic orbitals and generally considered as ferromagnetic contribution.⁴⁸ The second part, including the hopping integral t_{ij}^2 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.⁴⁹ In a model proposed by Heitler and London, J is similarly split into ferro- and antiferro-magnetic parts

$$J = K + 2\beta S . \quad (4.11)$$

The first part, being the two-electron exchange integral is necessarily positive; whereas the second part contains resonance integral (β) and an overlap integral (S), which are of opposite sign and thus their product becomes negative. Hence, the value of overlap integral plays a crucial role in controlling the overall nature of magnetic interaction.^{9b} However, the value of direct exchange coupling constant, estimated through spin projection technique, in case of H-pair is found to be very weak (0.004 cm^{-1}) compared to that (511 cm^{-1}) in case of V-pair, where the superexchange is operative. This observation is in agreement with Anderson's explanation where the superexchange is argued to be more intense than direct exchange on the basis of metal–ligand overlap.^{48b} The direct exchange interaction is considered to be comparatively weaker because it operates between spatially orthogonal wave functions.⁵⁰ Further, the degree of exchange is found to be largely affected from the distance between the magnetic sites.⁵¹ Hence, the large distance of 7.248\AA between the donor and acceptor in H-pair is another reason for the weaker direct exchange compared to superexchange. This observation is in agreement with the result of theoretical and experimental works, executed on similar systems,⁵⁷ where the intrachain (V-pair) magnetic interaction is found to be much stronger than interchain (H-pair) interaction.

Though weak, the interchain coupling takes a significant role in deciding the overall magnetic ordering of the system.^{6b,11,57} Hence, both of these V-pair superexchange and H-pair direct exchange are to be simultaneously taken into account to explain the bulk magnetic behavior. As a replica of the bulk system, a two-dimensional (2D) motif of the crystal (Figure 4.1b) is scooped out where both H-pair and V-pair are present. Next, following the computational strategy stated in ref. 31, the second vertical column is made dummy in order to compute the coupling constant in the 1st V-pair. The exchange interaction between the donor–acceptor pair in horizontal direction is quantified through similar approach. A comparable approach requires embedding the central unit in a field of point charges.⁶⁰ Inclusion of neighboring units is found to be a good approximation to the bulk property.⁶¹ The value of coupling constant (J_D), obtained in this way for the V-pair considerably decreased to 13 cm^{-1} compared to the earlier computed J value of 511 cm^{-1} (Table 4.1). On the other hand, in the H-pair there is a slight increase (0.007 cm^{-1}). This indicates some kind of antagonism between direct exchange and superexchange. Since this truncated model reproduces the bulk-behavior, the coupling constant of this system is ideal to compare with that obtained from experimental data.

The value of J drastically decreases in a two-dimensional system, compared to that in the single V-pair. A close comparison of the parameters, required to get coupling constant from eqn (4.2), reveals that except the energy of BS state all other factors are nearly same in single pair and 2D model. This clearly indicates that in the 2D model the BS state gets more stability compared to single D^+A^- pair, which can be attributed to the interchain interaction.

In the extended model, one single D^+A^- pair finds another such A^-D^+ pair in its neighbor, which causes a distortion in its equilibrium configuration.⁵⁷ Following the second order perturbation it can be shown that there is an orbital interaction between neighboring chains, which eventually stabilizes the broken-symmetry state.⁶² Moreover, the difference of spin density in these two situations, also contributes to such steep change in the value of coupling constant (see Figure B.S1 in Appendix B). A decrease of spin density is noticed in the two dimensional array due to dispersion of spin densities from magnetic sites, which affect the coupling constants. This fact finds its support from the recent works which advocate for an intimate relationship between the spin population and coupling constant.^{29,31}

4.4.2. Effect of periodicity

For a proper understanding of the magnetic interaction in the extended system, one must concentrate on studying the magnetic interaction as a periodic function. To gain an insight to the magnetic property in the periodic lattice system, periodic boundary condition is imposed on the system with the translational vectors 10.796 Å in the vertical direction and 16.161 Å in the horizontal direction. An attempt to compute the J value in the periodic boundary is failed in case of the horizontal pair because of the non-convergence of BS solution. This can be attributed to the large distance between donor and acceptor which does not allow mixing of the orbitals on magnetic centers and the BS state cannot be constructed in consequence. This fact is also ensured from a very weak value of coupling constant for H-pair. The electron tunnelling rate is also found to decay exponentially with distance.^{59,63} For this, the vertical pair is only chosen to investigate the effect of periodicity on its magnetism.

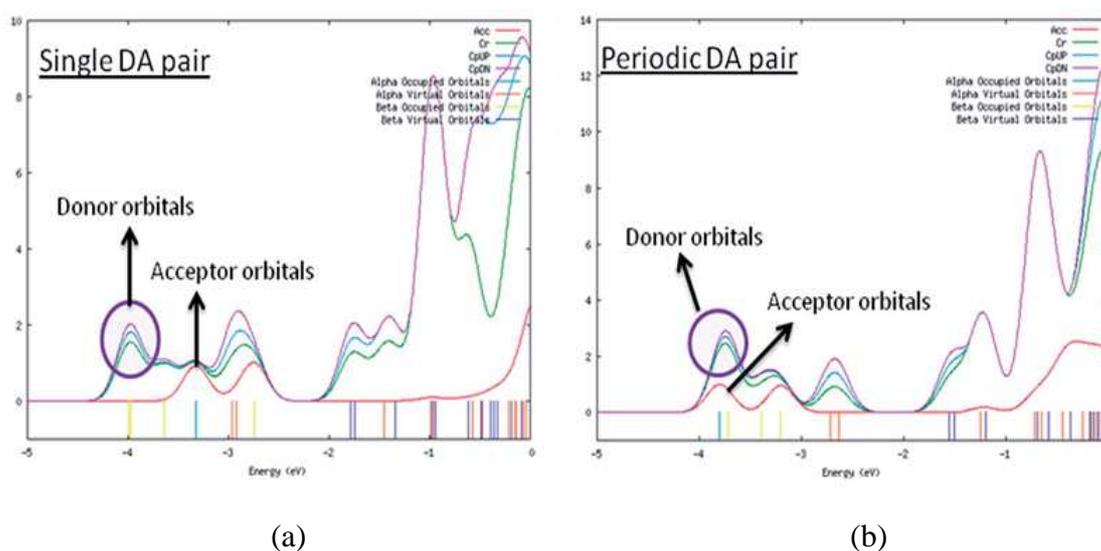


Figure 4.6. The density of states plots of the V-pair in (a) gas phase and (b) under periodic boundary condition.

It has been previously anticipated that the prediction of a local property, e.g., spin density for a system in cluster or in PBC are similar for a particular functional.⁶⁴ The comparison of spin density in PBE functional can be found in Tables B.S2 and B.S3 of Appendix B. A close inspection of Tables B.S2 and B.S3 reveals a change in the spin density

under PBC (see Table B.S3 in Appendix B). This is expected to bring about the variation in magnetic interaction. However, a variation in the choice of the k -point grid shows that after the 3rd k -point, the change in spin density becomes insignificant which implies the attainment of the bulk limit. Computation of magnetic exchange coupling constant with the constraint of periodic boundary reveals an antiferromagnetic (AFM) interaction in vertical direction. The AFM interaction in the V-pair under periodic boundary condition (PBC) is in the stark contrast to the positive value of coupling constant in absence of PBC. The change over from FM to AFM exchange within the periodic boundary condition may be argued to be arising out of this difference in functionals. To verify this, in absence of PBC the exchange coupling constant for the V-pair is also estimated using PBE functional in unrestricted framework which results in the J value of 133 cm⁻¹. This result shows that from the methodological point of concern, though the functional may alter the extent of coupling,⁶⁵ it cannot overturn the magnetic nature at least in the present case. Thus imposition of periodicity only can be attributed to such change in the magnetic behavior. This spin crossover can be understood in terms of charge transfer integral t_{ij} in eqn (4.4).⁶⁶ In this extended model, a particular donor (D⁺) finds two acceptor units (A⁻) below and above it unlike in the single V-pair. This increases the possibility of charge transfer, leading to the stabilization of AFM state. The exchange coupling constant under PBC is also calculated in the hybrid PBE0 functional for convenience,⁶⁷ which also predicts antiferromagnetic exchange in the periodic lattice. The results are given in Table B.S4 of Appendix B. The larger estimate of J produced by the hybrid PBE0 functional, in comparison to the pure PBE functional, can be explained due to the presence of a fraction of exact exchange which has a much larger extent than the DFT exchange considered in the pure functional. The AFM exchange coupling within the periodic boundary approach can further be envisaged as the effect induced by increasing the degrees of freedom of an electron. Thus the system gains stabilization in presence of PBC which can be confirmed from the energy comparison of V-pair, computed at same theoretical level [UPBEPBE/6-311++g(d,p) level with LANL2DZ as extrabasis on Cr atom]. The energy of the system without periodic boundary is -2445.135 a.u. and with the periodic boundary the energy is -2445.142 a.u. The periodic electron density can thus be assumed to be more delocalized which in turn induces a decreasing shift in Hubbard U parameter.⁶⁸ Now, there is a report of the lowering of energy of the d -states with increase in U parameter.⁶⁹ So, a decreasing shift in U should uplift the energy levels of d -states, which is apparent from the DOS plots in aperiodic and periodic conditions (Figure 4.6). Hence, a small value of U is expected in a periodic boundary formulation.⁶⁸ From the comparison of DOS plots in aperiodic and periodic systems, not only the upliftment of Cr d -states, but also the destabilization of Cp* ligands can be noticed. In addition, the up-spin orbital of acceptor lowers down in energy in the periodic condition. This situation brings the down-spin orbital of lower Cp* ring and the up-spin orbital of acceptor unit within the same energy range and thus facilitate their overlap in the periodic condition of the system. Hence, a small value of U together with non-zero value of S result in a stronger AFM interaction, which eventually supersedes the FM interaction and turns the system into a weak antiferromagnet in the periodic condition. However, the overall ferromagnetism in the bulk is manifested through an ensemble of different mechanisms.^{6b,66,70,71}

4.5. Conclusion

The phenomenon of charge transfer (CT) is of paramount impact in guiding the courses of several biological and chemical processes. In the present study, the charge transfer process is also found effective in governing the magnetic behavior of metallocene based charge transfer complexes. A recently synthesized system, $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ is taken as the representative MBCTC to explore the influence of charge transfer on the magnetic behavior of such donor–acceptor complexes. Anderson in his pioneering work ascribed charge transfer as the origin of kinetic exchange and correlated this exchange with the second order perturbation energy for such charge transfer. In a recent work, using this approach of Anderson, the coupling constant is parameterized with spin population (eqn (4.5)). However, eqn (4.5) is employed to account for through bond charge transfer in a superexchange process. On the contrary, NBO analysis for the present system clarifies a zero overlap status in between the donor and acceptor, which necessitates the tunnelling of electron in its journey from the donor to the acceptor. Hence, in the present work, eqn (4.5) is modified to take the electron tunnelling matrix element (H_{DA}) into account to determine the coupling constant. This integral, is evaluated from the zeroth order eigenvalues of pure donor and acceptor at the transition state of the electron transfer process. The exchange coupling constant (J_{T}), obtained in this way (eqn (4.9)) is well in agreement with J , the coupling constant derived through well-known spin projection technique of Yamaguchi (eqn (4.2)). The charge transfer interaction happens to be the central in such type of complexes where the magnetic interaction begins after the charge dislocates from the donor to the acceptor creating one magnetic site at the acceptor.

The topological difference of V-pair and H-pair leads to the possibility of concurrent and competitive exchange interactions at different directions. In V-pair, the intervening Cp^* ring assists the transfer of electron from metal to acceptor unit and hence there operates the superexchange process in this direction. In the other direction, the donor and acceptor are far separated and there is no such aid for the spins to be transferred from the donor to the acceptor. Hence the direct exchange process becomes only viable in H-pair. From the comparison of the coupling constant values, the superexchange interaction is found dominant in between two exchange processes in $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$. Since, the weak interaction in the horizontal direction takes a decisive role to render overall magnetic ordering; the V- and H-pairs are simultaneously taken into account. This situation opens up the possibility of several exchange interactions among multiple magnetic sites, which is estimated through one of our earlier developed computational scheme, referred to as dummy approach within the text. The coupling constant value for the V-pair, obtained through this approach is found to be very low compared to the previous value, where only the V-pair is considered. The drastic decrease in the J value through dummy approach is attributed to the interchain interaction. The coexistence of competitive superexchange and direct exchange in this truncated model replicates the bulk behavior. The small positive value of J supports the weak ferromagnetic nature of this MBCTC by Wang *et al.*¹¹

It has been of optimal challenge to investigate the nature of magnetism in a crystal system. The best way to mimic the real network of spins of a cluster demands the application

of periodic boundary condition. The PBC can treat systems in bulk condition with much less computational effort without taking the finite size-effect and border-effect. Our calculation clearly shows that the magnetic interaction in one dimensional periodic lattice of such kind of system in the vertical direction is antiferromagnetic and the extent of magnetism is too low. Moreover, it is interesting to note that the FM system turns into an AFM one with imposition of periodic boundary condition. This change over in the magnetic status of the system is explained with the rearrangement of the density of states in $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$. In this condition, there occurs a simultaneous higher and lower energy shifts in the donor and acceptor orbitals respectively and the donor–acceptor overlap integral gains a non-zero value, which is otherwise zero in the system. This lift in energy of the d -states is also supported from the easy dispersion of alpha spin to the Cp^* ligand orbital. Hence, this situation facilitates electron delocalization and results a lower Hubbard U value. As a consequence of all these facts the $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ which exhibits ferromagnetic coupling in the single D^+A^- pair, turns into a antiferromagnetic system in the periodic condition along vertical direction. However, the convolution of different exchanges pervading the crystal makes it a weak ferromagnet. An extended review on MBCTC divulges that there is a delicate balance in the sign of coupling constant in horizontal direction.⁶⁵ This weak, still competing magnetic interaction is regarded as the principle criterion for metamagnetism.⁷² However, this work suggests a delicate poise of magnetic interaction in the vertical direction as well.

4.6. References

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