Chapter 9

Summary and Outlook

This thesis is devoted to the investigation of microscopic origin of many exciting and intriguing physical properties of different complex and novel materials, employing primarily first principles technique. In chapters 3-8, we have considered three different category of compounds, namely i) perovskite structured transition metal oxides, (Sr,Ca)RuO$_3$ and BiCoO$_3$, ii) low dimensional quantum spin systems Sr$_2$BB'O$_6$ (B=Ni/Cu, B'=Pt/Ir), and Zn$_2$VO(PO$_4$)$_2$ in pristine and Ti substituted form, and iii) metalorganic compounds, Mn-succinate and Fe-Nb coordination polymer. In the present chapter we summarize the central findings that emerge out of our study and discuss the future directions.

9.1 Summary

Chapter 3:
In this chapter we have studied the different aspects of perovskite ruthenate compounds SrRuO$_3$ and CaRuO$_3$. Objective of our study was two fold. Firstly, we wanted to understand the contrasting magnetic behavior of isovalent and isostructural compounds SrRuO$_3$ and CaRuO$_3$. Secondly, to explore the effect of correlation on the electronic properties of SrRuO$_3$ and CaRuO$_3$. The major findings of this study are as follows:

(i) Our study revealed an unusual evolution of the local structural parameters involving Sr atoms upon switching on magnetism. This is counter intuitive given the common belief that A-site cation
plays the role of a "spectator". This finding indicates that in these ruthenates compounds the magnetostructural coupling is mediated by the A-site cation. Our theoretical results are supported by experimental measurements.

(ii) Our DFT calculations combined with DMFT show both SrRuO$_3$ and CaRuO$_3$ to be correlated metals with reasonably high mass enhancements. The coherence temperature for CaRuO$_3$ is found to be substantially lower than that for SrRuO$_3$, providing a possible explanation for the observed non-Fermi liquid like behavior in CaRuO$_3$ and its absence in SrRuO$_3$.

Chapter 4:
In this chapter, we investigated the issue related to the changes in the electronic structure of BiCoO$_3$ between the ambient pressure (AP) phase and high pressure (HP) phase. There is an apparent controversy on the HP phase crystal symmetry and physical properties between different theoretical studies. We settle down the physical properties and crystal symmetry of BiCoO$_3$ in both ambient pressure and high pressure phase. The major findings of this study are as follows:

(i) In AP phase Co$^{4+}$ is in high spin state ($S=2$) with a large gap at the Fermi level. In HP phase Co$^{4+}$ is in low spin state ($S=0$) with a small but finite gap in the Fermi level. The opening of the gap is driven by the octahedral distortion. Calculated energy gap values in the two phases are consistent with the experimental resistivity measurements.

(ii) BiCoO$_3$ exists in a polar tetragonal structure and distorted orthorhombic structure in AP phase and HP phase respectively. The obtained crystal symmetry and electronic behavior are found to be guided by the the covalent mixing between O-$p$ states with Bi lone pair $s$ and $p$ states.

Chapter 5:
Using first principle density functional theory, in this chapter we investigated the electronic structure of
a class of low dimensional quantum spin chain compounds of general formula $A_3B B'O_6$. B and $B'$ sites can host a wide verity of magnetic or non-magnetic cations giving rise to intra-chain and inter-chain coupling of variable sign and magnitude. In our study, we focused on three compounds, $Sr_3NiPtO_6$, $Sr_3CuPtO_6$, $Sr_3NiIrO_6$ formed from choice of $3d$ and $5d$ elements in B and $B'$ sites. In the first two cases i.e $Sr_3NiPtO_6$ and $Sr_3CuPtO_6$, Ni and Cu are magnetic but Pt is nonmagnetic whereas for the case of $Sr_3NiIrO_6$ both Ni and Ir are magnetic. The major findings of this study are as follows:

(i) In all the three cases the intra-chain interaction is substantially large compared to the other inter-chain interactions. The strength of inter-chain interactions in the case of $Sr_3CuPtO_6$ is found larger compared to the inter-chain interactions of the other compounds.

(ii) Calculating magnetic exchanges from total energy calculation of different magnetic configurations we found that for $Sr_3NiPtO_6$ intra-chain interaction is antiferromagnetic in nature and inter-chain interaction is of ferromagnetic nature. For $Sr_3CuPtO_6$ compound both intra-chain and inter-chain interactions are antiferromagnetic type while in the case of $Sr_3NiIrO_6$ the intra-chain and inter-chain interactions are found to be ferromagnetic and antiferromagnetic type, respectively.

(iii) Calculations of magneto-crystalline anisotropy energy show easy axis anisotropy in the case of $Sr_3NiPtO_6$ and $Sr_3CuPtO_6$ compound and easy plan anisotropy for $Sr_3NiIrO_6$ compound.

Chapter 6:
In this chapter, we studied another low dimensional quantum spin system of chemical formula $Zn_2VO(PO_4)_2$. Our aim was to settle down the apparent controversy that whether this system can be represented by 1D chain or 2D square lattice system. The other important motivation was how to destabilize the long range magnetic ordering found in the pristine system by external perturbation. The major findings of this study are as follows:

(i) From our calculated magnetic exchange interaction we found that in-plane exchange interactions
of square geometry are much stronger than the out of plane interactions of 1-D geometry. Our calculations, therefore, confirm that Zn$_2$VO(PO$_4$)$_2$ should be considered as a 2D antiferromagnetic square lattice spin $\frac{1}{2}$ system instead of previous prediction of 1D spin chain system.

(ii) We substituted $\frac{1}{4}$ of vanadium site by isovalent Ti atom. Ti substitution is found to destabilize long range antiferromagnetic ordering in 2D square lattice of the parent compound giving rise to spin gapped ground state. The underlying spin model is that of a weakly interacting 1-D spin chain. Our predictions may be verified in terms of future experimental measurements comparing with our computed thermodynamic properties.

Chapter 7:
In this chapter, we studied the electronic and magnetic structure of the organic-inorganic hybrid framework compound, Mn-succinate [Mn(C$_4$H$_4$O$_4$)]. This compound contains extended connectivity of Mn layers which are separated by succinate ligands. Experimentally it was found that this system undergoes two step magnetic ordering of Mn spins. This type of multiple transition of the same element (i.e Mn) is rare among the conventional inorganic system. The major findings of our study on this hybrid material are as follows:

(i) Our calculations showed that the magnetic interactions within the Mn layer formed by edge sharing of MnO$_6$ octahedra, to be stronger than that within the Mn layer formed by corner shared MnO$_6$ octahedra, with almost no interaction between the two layers. These leads to two step magnetic ordering, with edge shared octahedral Mn spins ordering first, followed by the ordering of corner shared octahedral Mn spins. These is in accordance with experimental observations. The microscopic origin of this behavior, turn out to be driven by the differential strength of covalency between Mn-$d$ and $p$ states of surrounding oxygen and carbon atoms in the edge shared and corner shared layers.

(ii) We found from our calculation the the ratio of mean field transition temperatures for two magnetic ordering is 0.6, while agrees with the experimental estimates, 6 K and 10 K for the two magnetic.
9.2 Scope for future work:

transitions.

Chapter 8:

In the last chapter we studied another hybrid organic-inorganic system, coordination polymer compound Fe₂[Nb(CN)₆]₆(4-pyridinealdoxime)₆.2H₂O. This system is known for its spin cross over phenomena upon application of light. In this study our aim was to explore other possible route of the spin state transition in this system as well as tuning of the magnetic ground state. Our major findings are as follows:

(i) This system undergoes two step spin state transition from high spin state (S=2) to low spin state (S=0) transition by the application of hydrostatic pressure. During the transition the system travel through a new intermediate spin state (S=1), which was previously not known. Both the transitions are found to be accompanied by the hysteresis effect.

(ii) The system also show spin state transition upon application of temperature.

(iii) One can tune the magnetic ordering from ferrimagnetic to ferromagnetic alignment between Fe and Nb spins by the combined route of application of temperature and pressure.

(iv) We studied the Mn variant of this system and found that it shows one step spin state transition from high spin state (S=5/2) to low spin (S=1/2) state.

9.2 Scope for future work:

(i) Study of BaRuO₃: Perovskite ruthenates are interesting, due to the possible interplay between the structural aspect and electron-electron correlation aspect. In literature there exists a large number of reported ruthenate materials which are not properly understood at microscopic level. As an extension
of our work on ruthenates we would wish to explore the compound BaRuO₃. Though BaRuO₃ is isovalent and has same electronic configuration as that of the previously studied two ruthenates, SrRuO₃ and CaRuO₃, it shows very different properties compared to other two. Due to the larger ionic radius of Ba²⁺ compared to Sr²⁺ and Ca²⁺ the crystal structure of BaRuO₃ is very different than the others. In the case of BaRuO₃ the tolerance factor is $t = \frac{\text{Ba}-\text{O}}{\sqrt{\text{Ru}-\text{O}}} > 1$, which favors hexagonal poly-type structures as opposed to SrRuO₃ and CaRuO₃, for which $t < 1$ favoring orthorhombic structure with cubic stacking. BaRuO₃ form in a different crystal structures depending on the synthesis pressure, from 9R [ambient pressure] to 4H [3 GPa] to 6H [5 GPa], all based on hexagonal symmetry [1]. Only recently, cubic phase of BaRuO₃ has been synthesized under very high pressure condition [2]. The hexagonal close stacking versus cubic close stacking of BaO₂ layers corresponds to the face sharing versus corner sharing connections between the two neighboring RuO₆ octahedra. The four poly-types of BaRuO₃ 9R, 4H, 6H and 3C exhibit varying properties. The study of BaRuO₃, therefore, provide an unique opportunity to study the influence structural changes within the same compound.

(ii) Surface Electronic Structure of BiCoO₃: In the next step in our study on BiCoO₃, we wish to extend our investigation to surface electronic structure of BiCoO₃. In particular, we wish to focus on strong spin-orbit interaction of Bi lone pair, how it modifies the surface electronic structure of BiCoO₃.

(iii) Study of Cooperativity in Metalorganics: The cooperative effect in extended metalorganic systems is very important. This cooperative effect arises in extended systems and not observed in isolated molecular magnetic systems. Generally this cooperative effect is manifested in terms of memory effect via commonly used temperature driven path. To simulate the temperature driven hysteresis effect in the case of large extended system containing 300-400 atoms per unit cell is a major challenge from computational perspective. For this purpose, one needs to carry out ab-initio molecular dynamics at each temperature step once in forward cycle (heating) and another is backward cycle (cooling). Our next aim is to carry out such a detailed ab-initio molecular dynamic simulation and reproduce the temperate driven hysteresis effect, pinpointing the influencing factors.
Bibliography
