Chapter 4

Transition Metal Doped Smaller Fullerenes ($C_n$ for $n \leq 50$)

4.1 Introduction

Carbon is one of the most exciting group-IV element which offers many novel electronic, structural and magnetic applications. Carbon (C) in its ground state has an electronic configuration of $1s^2$, $2s^2$, $2p^2$ and because of a very small energy difference between $2s$ and $2p$ orbitals, C atoms are able to form a number of $s$ $p$-hybridized atomic orbitals. This enables carbon forming a wide variety of bonding configurations and allotropes. Before 1985, carbon was best known in the forms of amorphous carbon (soot and coal), diamond (hardest known natural mineral) and graphite (one of the softest substances). However in 1985, a new form of carbon named "Fullerene" was discovered by H. Kroto, R. Curl Jr. and R. Smalley along with J. R. Heath and S. C. O'Brien [1]. Fullerenes have shown completely different properties from earlier forms of carbon and hence drew considerable attention of scientific community. Functionalization of fullerenes can modify its properties, particularly the charge distributions, electronic structures, and energy gaps between HOMO and LUMO as it has strong influence on the molecular, as well as bulk, properties [2,3].

Recent experimental results on magnetism in carbon based materials have renewed interest in carbon systems as possible new magnetic materials due to their technological advantages over conventional magnetic materials [4], though the origin of the magnetic ordering in these systems is still debated. The quest for carbon based ferromagnetism has occupied theoreticians for many years and its origin has
been proposed due to the dislocations, vacancies and impurity atoms [5]. Till date the focus has been to understand the magnetic properties of metallofullerenes larger than \( C_{60} \) [6-8] due to their stability and larger volume available for encapsulation. Lopez et al. [9] have studied magnetic properties of carbon clusters, clusters inside fullerenes and graphitic nanoribbons. The entrapped atoms bring with them an array of useful physical properties with possible applications in electronic devices [10], organic solar cells [11], spin-based quantum computing [12, 13], medicine [14], specifically contrast agents for magnetic resonance imaging (MRI) as well as for radio-pharmaceutical candidates [15].

The recent work on successful synthesis of many endohedral derivations of smaller fullerenes \( (C_n; n<60) \) have acquired special significance. The smaller fullerenes violate the isolated pentagon rule and the fused pentagon structures in this class of fullerenes have strong effect on their stability and electronic properties. Surprisingly, small endohedral metallofullerenes remains to be explored and their magnetic properties have not been investigated inspite of the successful production of many small fullerenes [16-19]. \( U^{\infty}C_{28} \) films were synthesized in cationic form by laser vaporization of \( UO_2/\text{graphite} \) mixture [20]. Besides \( U^{\infty}C_{28} \), the signals of \( U^{\infty}C_{36}, U^{\infty}C_{44} \) and \( U^{\infty}C_{58} \) were also observed in the mass spectrum with lower intensities. Thus the internal Uranium atom has apparently stabilized the fullerene cage and made \( U^{\infty}C_{28} \) the end point of laser shrinking. The presence of Zr, Hf, Ti and Sc inside \( C_{28} \) cage has also been confirmed in the mass spectrum obtained from laser vaporization of graphite/metal-oxide composite discs [20]. Following these experiments, many theoretical groups have performed a systematic investigation of series of \( M@C_{28} \) (\( M = \text{Mg, Al, Ca, Sc, Ti, Ge, Zr and Sn} \) [21] and found that only \( \text{Sc@C}_{28} \) and \( \text{Zn@C}_{28} \) are thermodynamically stable in consequence of their large binding energies. Sun et al. [22] studied the encapsulation of thirteen atoms from group IA to group VA (i.e. H, Li, Na, K, Be, Mg, Ca, B, Al, C, Si, N, P) and nine cations from group IA to group IIIA (i.e. \( H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, B^{3+} \) and \( Al^{3+} \)) inside \( C_{32} \) cage. Recently, Chen et al. [23] investigated the stabilities and molecular structures of noble gas atoms (i.e. He, Ne, Ar, and Kr) inside \( C_{32} \) cage. Subsequently, inspired by the finding of \( U^{\infty}C_{36} \), Kang [24] gave a detailed calculation of the possible encapsulation of alkali metals (i.e. Li, Na, K) inside \( C_{36} \). However, so far there has been no study reported on trapping of transition metals (TM) inside small fullerene cage structures.

In this chapter, we present a systematic investigation of the electronic and mag-
netic properties of $TM@C_n$, $n \leq 50$ where $TM = Ti, V, Cr, Mn, Fe, Co, Ni$ and Cu using spin polarized density functional theory. Our results show that magnetic properties of $TM@C_n$ apart from dependence on 3d configuration and charge transfer from TM atom to carbon cage also depend on the specific geometric structure of the cage as well as location of the TM atom. The investigations highlight the possibility of designing magnetic devices if high spin configurations of 3d TMs can be preserved as the ground state or different spin manipulation.

4.2 Computational details

We have used the spin polarized density functional theory to study the magnetic properties of $TM@C_n$ complexes as implemented in the Spanish Initiative for Electronic Simulation with thousands of atoms (SIESTA) computational code [25]. The electron exchange interactions were considered using generalized gradient approximation (GGA) that implements Perdew, Burke and Ernzerhof (PBE) exchange-correlation [26]. The core electrons are replaced by non-local, norm-conserving pseudo potentials factorized in the Kleinman-Bylander form [27], whereas valence electrons are described using linear combination of numerical pseudo atomic orbitals of the Sankey-Niklewski type [28] but generalized for multiple-ζ and polarization functions. In this work, we have used a split valence double-ζ polarized (DZP) basis set. We considered 3d$^2$4s$^2$, 3d$^3$4s$^2$, 3d$^4$4s$^1$, 3d$^5$4s$^2$, 3d$^6$4s$^2$, 3d$^7$4s$^2$, 3d$^8$4s$^2$ and 3d$^{10}$4s$^1$ electronic configurations for Ti, V, Cr, Mn, Fe, Co, Ni and Cu respectively. The structures are obtained by minimization of the total energy using Hellmann-Feynman forces, including Pulay like corrections. Structural optimizations were performed using conjugate gradient algorithm until the residual forces in the optimization are smaller than 0.001 eV/A. We have studied $C_{60}$ based heterofullerenes [29,30] and endohedral complexes [31] with similar methodology and parameters as described above. This validates the applicability and accuracy of our calculations to investigate smaller carbon fullerenes based systems.

4.3 Test Calculations

The test calculations are performed on $C_{60}$ molecule, which is optimized to ground state configuration till the atomic forces on each atom were reduced to 0.001 eV/A.
The optimized structure of C\textsubscript{60} along with numbering of atoms is shown in Figure 4.1.

**Figure 4.1:** Optimized geometry of C\textsubscript{60} with numbering of the C atoms. The calculated C\textendash C and C\textendash C bond distances and bond angles are expressed in Angstroms and degrees respectively.

The C\textendash C and C=C bond lengths are found to be 1.40 Å and 1.46 Å, which are in excellent agreement with experimental values 1.40 Å and 1.46 Å respectively [32]. The observed mean diameter of C\textsubscript{60} is 7.14 Å as compared to the experimental value of 7.12 Å [33]. The calculated binding energy is 7.72 eV/atom in agreement with the reported value [34] but higher than reported in the literature using DFT with B3LYP hybrid functional [35]. The ionization potential and electron affinity (6.9 eV and 2.70 eV) agrees well with the experimental values of 7.5 ± 0.01 [36] and 2.689 ± 0.008 [37] respectively. The test calculations are also performed on TM dimers and the calculated magnetic moments (MM) and bond lengths of all the clusters are tabulated in Table 4.1. Our results are in good agreement with the existing experimental and theoretical results [38–40].
Table 4.1: Magnetic moments (MM) of single TM atoms and TM-TM bond length with ferromagnetic (FM) and antiferromagnetic (AFM) interactions (in Å).

<table>
<thead>
<tr>
<th>Atom</th>
<th>MM in μ$_B$ TM</th>
<th>FM $R_{TM-TM}$</th>
<th>AFM $R_{TM-TM}$</th>
<th>Interactions</th>
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4.4 Results and Discussion

4.4.1 Structures and stabilities of $TM@C_{20}$ complexes

The $C_{20}$ cage with $I_h$ symmetry (Figure 4.2) is considered as the starting cage configuration to investigate the effect of 3d TMs. The average diameter and bond length of $C_{20}$ is found to be 4.11 Å and 1.47 Å which are in agreement with E. Malolepsza et al. [41]. The binding energy is 8.32 eV per atom for $I_h$ symmetry which possesses a MM of 2 μ$_B$ in agreement with [42]. However, there is a considerable disagreement among theoreticians regarding symmetry and magnetic state of $C_{20}$. This may be due to the importance of accurate treatment of electron correlation [43] in smaller fullerenes. Galli et al. [44] used LDA and GGA to predict $C_{20}$ cage with $D_{3d}$ symmetry as the most stable Jahn Teller distorted cage structure. Wang et al. [45] using hybrid DFT predicted $C_{2h}$ symmetry as the most stable structure. X. Lu et al. [46] using tight binding model found that $C_{20}$ undergoes a magnetic to nonmagnetic behavior and nonmagnetic to magnetic transition for $I_h$ and $D_{3d}$ symmetries respectively.

The TMs prefer to stabilize at central position in $C_{20}$ and with their encapsulation, the variation in the C-C and C=C bond lengths of all the fullerene cages are tabulated in Table 4.2. The average C-C bond length in $C_{20}$ is 1.47 Å and it increases to 1.48-1.54 Å in TM encapsulated complexes. The diameter of $TM@C_{20}$ complexes increase from 4.21 to 4.27 Å from Ti to Cu. The binding energy per atom shows maximum value of 8.2 eV for Ti@C$_{20}$ which decreases with increasing
Figure 4.2: Optimized geometries of pure fullerenes along with their symmetries.

atomic number of 3d TMs to 7.66 eV in Cu@C\textsubscript{20}. Further, the interaction between fullerene cage and TMs along with the stabilities of TM@C\textsubscript{n} complexes is described by evaluating their cohesive energies. We define the cohesive energy of TM@C\textsubscript{n} complexes as follows:

\[
\Delta E = E_{\text{Total}}(TM@C_n) - E(C_n) - E(TM) \tag{4.1}
\]

where \(E_{\text{Total}}\), \((TM@C_n)\), \(E(C_n)\) and \(E(TM)\) are the total energies of endohedral complex, isolated fullerene and TM atoms respectively. The cohesive energies "\(\Delta E\)" calculated using equation (4.1) are tabulated in Table 4.3. The positive value of \(\Delta E\) indicate the greater stability of TMs inside fullerene cage and are likely to be formed experimentally. The negative value of \(\Delta E\) indicate that corresponding TM encapsulated inside fullerene cage is unstable or less stable.

From Table 4.3, it is clear that only Ti and V possess positive values for C\textsubscript{20} cage thereby suggesting the stabilities of these are likely to form complexes with C\textsubscript{20}.

C\textsubscript{28} fullerene with \(T_d\) symmetry and zero MM is found to be the most stable geometry than the other isomers considered. The TMs have a tendency to occupy off-center positions inside C\textsubscript{28} and larger fullerenes as shown in Figure 4.3. The average diameter of C\textsubscript{28} comes out to be 4.88 Å with 8.67 eV as binding energy per
Table 4.2: Average C-C and C=C bond lengths (in Å) for all fullerene cages when encapsulated with 3d-TM.

| TM | $C_{20}$ C-C | | $C_{28}$ C-C | | $C_{32}$ C=C | | $C_{36}$ C=C |
|----|--------------|---|--------------|---|--------------|---|
| Ti | 1.48-1.51    | | 1.46-1.51    | | 1.43  | | 1.48-1.49    | | 1.43  | | 1.46-1.49    | | 1.44  |
| V  | 1.51-1.53    | | 1.49-1.52    | | 1.42-1.44 | | 1.46-1.50    | | 1.42-1.43 | | 1.44-1.49    | | 1.44  |
| Cr | 1.47-1.51    | | 1.50-1.54    | | 1.44  | | 1.46-1.49    | | 1.42  | | 1.47-1.49    | | 1.46  |
| Mn | 1.51-1.54    | | 1.49-1.54    | | 1.44  | | 1.46-1.50    | | 1.45  | | 1.46-1.49    | | 1.44-1.46|
| Fe | 1.52-1.54    | | 1.47-1.53    | | 1.43  | | 1.46-1.49    | | 1.42-1.44 | | 1.46-1.49    | | 1.44-1.46|
| Co | 1.51-1.53    | | 1.46-1.53    | | 1.44  | | 1.47-1.48    | | 1.42-1.45 | | 1.45-1.49    | | 1.44-1.45|
| Ni | 1.51-1.54    | | 1.47-1.53    | | 1.43-1.44 | | 1.46-1.51    | | 1.42-1.44 | | 1.46-1.50    | | 1.45  |
| Cu | 1.50-1.54    | | 1.47-1.52    | | 1.44  | | 1.46-1.50    | | 1.42-1.44 | | 1.46-1.50    | | 1.43-1.45|

Table 4.3: The cohesive energy ($\Delta E$) of TM encapsulated inside small fullerene cages. The negative value of $\Delta E$ corresponds to unstable TM encapsulated inside the cage.

| TM | $TM@C_{20}$ | | $TM@C_{28}$ | | $TM@C_{32}$ | | $TM@C_{36}$ |
|----|-------------|---|-------------|---|-------------|---|
| Ti | 3.80        | | 2.88        | | 2.69        | | 3.05        |
| V  | 1.93        | | 2.18        | | 2.11        | | 2.12        |
| Cr | -3.23       | | -0.60       | | -0.05       | | 0.52        |
| Mn | -6.31       | | 0.41        | | 0.37        | | 0.85        |
| Fe | -3.47       | | 1.35        | | 0.73        | | 0.99        |
| Co | -4.19       | | 0.27        | | -0.54       | | -0.26       |
| Ni | -4.75       | | 0.54        | | 0.25        | | 0.55        |
| Cu | -7.52       | | -0.59       | | -0.08       | | 0.21        |
atom.The average C-C and C=C bond lengths of $C_{28}$ are 1.45-1.47 Å and 1.42 Å whereas $TM@C_{28}$ complexes show an increase in them to 1.49-1.54 Å and 1.44 Å respectively. The average diameter shows a maximum value of 4.98 Å in $Cr@C_{28}$. The binding energy per atom is highest for $Ti@C_{28}$ and $V@C_{28}$, again predicting their larger stability than their counterparts. $\Delta E$ for all TMs, except Cr and Cu, show positive values which indicates their stability inside $C_{28}$.

![Figure 4.3: Optimized geometries of fullerenes doped with transition metals.](image)

$C_{32}$ with $D_3$ symmetry forms the stable cage with zero MM. $C_{32}$ has an average diameter of 5.08 Å and the binding energy per atom is 8.83 eV with the average C-C and C=C bond lengths 1.47-1.49 Å and 1.44 Å respectively. As a result of TM substitution inside $C_{32}$ cage, the average diameter shows a slight increase with a maximum value of 5.16 Å for $Co@C_{32}$. The average C-C and C=C bond lengths of $TM@C_{32}$ complexes lie in the range 1.46-1.51 Å and 1.42-1.45 Å respectively (Table 4.2). The binding energies show similar pattern as shown by $C_{20}$ and $C_{28}$ i.e. higher values of 8.65 eV and 8.63 eV for Ti and V respectively and decreasing value for other TMs. The cohesive energies tabulated in Table 4.3 show, very small negative cohesive energies for Cr, Co, and Cu which suggests their less stability and it is may not be feasible to encapsulate them inside $C_{32}$. All the other TMs show positive cohesive energies leading to fact that they all form stable complexes with $C_{32}$.

$C_{36}$ with $D_{6h}$ symmetry is found to be the most stable geometry with an average diameter of 5.30 Å and 8.89 eV binding energy per atom. The average C-C and C=C
bond lengths lies in the range 1.45-1.50 Å and 1.43-1.45 Å respectively. The TM substitution does not change the diameter to a large extent rather it remains nearly constant between 5.30-5.33 Å and the average bond lengths are same for C-C but C=C changes to 1.44-1.46 Å. The binding energy show the same trend as shown by other smaller fullerenes. The cohesive energies tabulated in Table 4.3 shows positive value for all TMs except for Co which shows negative value of -0.26 eV. Further we can conclude that C_{36} is the smallest fullerene to encapsulate Cr and Cu.

From the above structural analysis, we find that all the TMs prefer to place themselves at central position for n = 20 and nearly off-center positions for n ≥ 28 within cage by distorting the cage symmetry. The distortion in fullerene cages due to TM encapsulation is maximum for n = 20 and minimum for n = 36. The binding energy of TM@C_{n} decreases with increasing atomic number from Ti to Cu in all the fullerenes considered although the rate of decrease falls with increasing diameter. The average bond lengths and diameters also show an increase due to TM encapsulation. The positive or negative ΔE values indicate the feasibility of formation of these endohedral complexes. Ti and V are the only two TMs which show positive values for all the fullerene cages which suggest a strong possibility of their formation experimentally. Only Cr and Cu show negative values for C_{28} and all the other TMs form stable complexes with C_{28}. Similarly, in C_{32}, Cr and Cu show small negative values which suggests that these complexes can be formed but with somewhat less stability. However, Co shows comparatively higher negative value which indicates its unstable nature inside C_{32} cage. Further, in C_{36}, except Co, the cohesive energies show positive values which suggest the stability of all TMs inside this cage.

4.4.2 Electronic and Magnetic properties of TM@C_{n}

The electronic properties of TM@C_{n} complexes are investigated in terms of the HOMO (Highest occupied molecular orbital)- LUMO (Lowest unoccupied molecular orbital) gap as well as the electronic density of states (EDOS).

The HOMO-LUMO gap for both spin up (↑) and spin down (↓) states as a function of 3d TMs with increasing atomic number is plotted in Figure 4.4. The spin ↑ gap shows a sharp decrease from V to Cr and vice versa in spin ↓ gap with an oscillatory pattern thereafter in C_{20}. For TM@C_{28} complex, the spin ↑ gap shows a sharp increase from Cr to Mn and nearly constant thereafter whereas spin ↓ gap
Figure 4.4: HOMO-LUMO gaps for spin up and spin down states for all $TM@C_{20}$, $C_{28}$, $C_{32}$ and $C_{36}$. 
decreases sharply from Mn to Fe and an oscillatory pattern after that but decreases
to 0.36 eV for Cu. For $C_{32}$, the spin $\uparrow$ gap decreases from 1.41 eV in pure $C_{32}$ to
0.68 eV in $Fe@C_{32}$ and shows sharp increase from Fe to Co and then decrease for
Cu. The spin $\downarrow$ gap shows similar pattern as spin $\uparrow$ gap but it increases sharply from
Mn to Fe and then decreases for Co and further increase for Cu. In $C_{36}$, the spin $\uparrow$
gap decreases from 0.83 eV for pure $C_{36}$ to 0.41 eV in $V@C_{36}$ which increase to 0.76
eV (Cr) and then gradual decrease to 0.73 eV (Cu). The spin $\downarrow$ gap shows almost
similar behavior as spin $\uparrow$ gap with only exception being Co which has a very small
gap of 0.12 eV.

The EDOS of $TM@C_{2n}$ complexes are plotted in Figure 1.5 which shows polarized
EDOS for $C_{2n}$ at fermi level ($E_f$) even without encapsulating TMs. On encapsulation
with Ti and V, the EDOS is modified significantly near ($E_f$) with spin $\downarrow$ EDOS greater
than spin $\uparrow$ EDOS. The EDOS of $C_{2n}$ show occupied states within the range -1.0 to
-2.0 eV in contrast to Ti and V which show unoccupied states. In $Cr@C_{36}$ complex,
spin $\uparrow$ and spin $\downarrow$ EDOS are almost equal with 0.85 eV of HOMO-LUMO gap.

The Mulliken charge analysis shows an interesting pattern of the charge redis­
tribution in $TM@C_{2n}$ complexes. Ti, V, and Cr donates $\approx 0.36-0.55$ electrons to
the $C_{2n}$ cage structure. Mn and Fe gain 0.12 electrons from nearby C atoms whereas
Co, Ni and Cu show no charge transfer. Apart from the external charge transfer in
all the complexes, the internal transfer of electrons takes place from $1s$ to $3d$ and $4p$
orbitals significantly.

The EDOS for $TM@C_{2n}$ complexes are plotted in Figure 4.6. EDOS for $C_{2n}$ is
equal for both spin $\uparrow$ and spin $\downarrow$ electrons. However, with the encapsulation of TMs
the EDOS show significant change at and below the ($E_f$). Ti shows finite spin $\uparrow$
states at ($E_f$) and modified spin $\uparrow$ and $\downarrow$ EDOS upto -4.0 eV below ($E_f$). V shows
similar behavior as Ti with the only difference being the finite spin $\uparrow$ EDOS near
($E_f$). For Mn, there is an equal HOMO-LUMO gap for spin $\uparrow$ and spin $\downarrow$
electrons with unoccupied states at ($E_f$). For Fe and Ni, the EDOS show almost similar
behavior at and near ($E_f$) with equal HOMO-LUMO gap.

To further elucidate the origin of FM the projected density of states (PDOS)
for both Ti and Ni inside $C_{2n}$ cage are plotted in Figure 4.7 as the former behaves
as acceptor and the latter behaves as donor with respect to neighboring carbon
atoms. Figure 4.7 represents PDOS for Ti which show that the electronic states in
the vicinity of $E_f$ come mainly from up $3d$ states with empty down $3d$ states. In
Ni, spin $\downarrow$ DOS are finite and gives significant contribution at and near $E_f$ whereas
Figure 4.5: Spin-up and spin-down electronic density of states (EDOS) for $C_{20}$, $Ti@C_{20}$, $V@C_{20}$, and $Cr@C_{20}$. The dotted line shows the position of Fermi level ($E_f$).
Figure 4.6: Spin-up and spin-down EDOS for $C_{28}$, $Ti@C_{28}$, $V@C_{28}$, $Mn@C_{28}$, $Fe@C_{28}$, and $Ni@C_{28}$. The dotted line shows the position of $E_f$. 
up 3d states show finite contribution within the region -3.0 to -1 eV. For both Ti and Ni, 4s and 4p states do not show any contribution near $E_f$ and whereas all 3d up and 3d down components lie in its vicinity.

For $TM\alpha C_{28}$ complexes, Ti gains $\approx 0.30$ electrons from $C_{28}$ cage and Ni loses $\approx 0.72$ electrons to surrounding C atoms. 4s orbital of Ni has lost 0.2 electrons to 3d orbital, 0.7 electron to 4p orbital and 0.7 electron to $C_{28}$ cage with 0.32 electrons remaining in 4s orbital. Therefore, there is an internal conversion as well as donation of electron takes place from 4s.

For $C_{32}$ cage, the spin $\uparrow$ and spin $\downarrow$ EDOS are equal with unoccupied states at $E_f$. Ti shows an increased spin $\uparrow$ EDOS whereas V shows more contribution from spin $\downarrow$ EDOS as shown in Figure 4.8. At $E_f$, Mn and Fe show similar behavior and below $E_f$ upto -4.0 eV, there is a significant change in EDOS. For Ni, the complex shows half-metallic behavior with finite spin $\downarrow$ EDOS and very small spin $\uparrow$ EDOS near $E_f$. Inside $C_{32}$ cage, all the 3d TMs behave as donors by donating $\approx 0.11$-0.86 electrons to the surrounding cage C atoms. Like all the other cages considered, 4s orbital loses charge to the cage as well as undergo internal conversion of electrons with 3d and 4p orbitals.

EDOS for $TM\alpha C_{36}$ complexes show almost similar behavior as shown by $TM\alpha C_{32}$ complexes (Figure 4.9) with the small change in the EDOS at the $E_f$ which is depicted in HOMO-LUMO gap (Figure 4.4). The difference in the spin $\uparrow$ and spin $\downarrow$ EDOS for $TM\alpha C_{n}$ complexes is because of the presence of strong electronic polarization arising due to transfer of charges. The Mulliken charge analysis predict that V, Cr and Cu inside $C_{36}$ cage act as donors by losing $\approx 0.4$-0.76 electrons to the surrounding C atoms.

To study the evolution of magnetic properties of $C_n$ fullerenes, we calculated the total (MMs) of $TM\alpha C_{n}$ complexes and the local magnetic moments (LMM) of TMs (Figure 4.10). The local MM at 3d TM site along with the individual contributions of 3d, 4p and 4s orbitals are tabulated in Table 4.4. Due to the Jahn-Teller distortion and strong hybridization between s and p orbitals of carbon atoms and d orbitals of TM ions, a significant amount of MM is induced on the C atoms of host cage. The MM in complexes is not only localized at TM sites but also a considerable amount is induced on carbon atoms of $TM\alpha C_{20}$ complexes.

$C_{20}$ with $I_h$ symmetry has an intrinsic MM of 2 $\mu_B$ which is consistent with [42] and in $TM\alpha C_{20}$ complexes, the MM varies from 2 $\mu_B$ for $Ti\alpha C_{20}$ to 5 $\mu_B$ in $Cu\alpha C_{20}$ whereas for $Cr\alpha C_{20}$, the MM gets quenched (Figure 4.10). In $TM\alpha C_{20}$ complexes,
Figure 4.7: Projected density of states (PDOS) for \( \text{Ti@C}_{28} \) and \( \text{Ni@C}_{28} \) with their 4s and 3d contributions. The dotted line shows the position of \( E_f \).
Figure 4.8: EDOS for C32, Ti@C32, V@C32, Mn@C32, Fe@C32 and Ni@C32. The dotted line shows the position of $E_f$.
Figure 4.9: Spin-up and spin-down EDOS for $C_{36}$, $Ti@C_{36}$, $V@C_{36}$, $Mn@C_{36}$, $Fe@C_{36}$ and $Ni@C_{36}$. The dotted line shows the position of $E_f$. 
Figure 4.10: Total magnetic moments and local MMs at TM site with respect to the 3d TMs for all fullerenes i.e. $C_{20}$, $C_{28}$, $C_{32}$ and $C_{36}$.

Table 4.4: The magnetic moments at TM site inside $C_{20}$ and $C_{28}$ cages, $\mu_{TM}$, and the individual contributions of 3d, 4p, 4s orbitals of TM atoms, $\mu_{3d}$, $\mu_{4p}$ and $\mu_{4s}$, are tabulated respectively.

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<tr>
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<td>3.08</td>
<td>0.06</td>
<td>0.02</td>
<td>4.87</td>
<td>4.64</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe</td>
<td>3.45</td>
<td>3.33</td>
<td>0.14</td>
<td>0.04</td>
<td>3.82</td>
<td>3.71</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>Co</td>
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<td>0.12</td>
<td>0.04</td>
<td>2.73</td>
<td>2.65</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>1.39</td>
<td>1.54</td>
<td>0.11</td>
<td>0.04</td>
<td>2.29</td>
<td>1.61</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu</td>
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<td>0.45</td>
<td>0.12</td>
<td>0.04</td>
<td>0.20</td>
<td>0.01</td>
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</table>
Table 4.5: The magnetic moments at TM site inside C_{32} and C_{36} cages, $\mu_{TM}$, and the individual contributions of 3d, 4p, 4s orbitals of TM atoms, $\mu_{3d}$, $\mu_{4p}$ and $\mu_{4s}$, are tabulated respectively.

<table>
<thead>
<tr>
<th>TM</th>
<th>$\mu_{TM}$</th>
<th>$\mu_{3d}$</th>
<th>$\mu_{4p}$</th>
<th>$\mu_{4s}$</th>
<th>$\mu_{TM}$</th>
<th>$\mu_{3d}$</th>
<th>$\mu_{4p}$</th>
<th>$\mu_{4s}$</th>
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</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2.00</td>
<td>1.99</td>
<td>0.05</td>
<td>0.03</td>
<td>2.13</td>
<td>2.03</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>V</td>
<td>3.24</td>
<td>3.08</td>
<td>0.09</td>
<td>0.06</td>
<td>3.43</td>
<td>3.38</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>Cr</td>
<td>4.65</td>
<td>4.43</td>
<td>0.12</td>
<td>0.09</td>
<td>4.82</td>
<td>4.60</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>Mn</td>
<td>5.04</td>
<td>4.80</td>
<td>0.12</td>
<td>0.11</td>
<td>5.10</td>
<td>4.86</td>
<td>0.12</td>
<td>0.12</td>
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<tr>
<td>Fe</td>
<td>3.92</td>
<td>3.76</td>
<td>0.07</td>
<td>0.08</td>
<td>3.93</td>
<td>3.80</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Co</td>
<td>2.42</td>
<td>2.34</td>
<td>0.04</td>
<td>0.04</td>
<td>2.77</td>
<td>2.69</td>
<td>0.05</td>
<td>0.04</td>
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<tr>
<td>Ni</td>
<td>1.17</td>
<td>1.11</td>
<td>0.02</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The LMM is not fully localized at TM site but also a significant amount is induced at the nearest neighboring C atoms. The magnetic interaction between TM impurities at the endo position and the surface C atoms is ferromagnetic (FM) in nature. The 20-60% of the total MM is contributed by TM which is due to unpaired 3d electrons.

The $C_{28}$ cage structure possesses zero MM, however, when encapsulated with TMs, it acquires finite MM. In $TM@C_{28}$ complexes, MM is mainly localized at the TM site (Figure 4.10) with a small amount of MM induced on surrounding C atoms. The total MM ranges from 2 $\mu_B$ in $Ti@C_{28}$ to 1 $\mu_B$ in $Cu@C_{28}$. However, the total MM of $Cr@C_{28}$ increases to 4 $\mu_B$ from 0 $\mu_B$ in $C_{28}$ cage. In $Cu@C_{28}$, the MM of 0.2 $\mu_B$ of total 1 $\mu_B$ is localized at the Cu atom. The magnetic interaction of Ti, V, Mn, Fe, Co and Cu with the surrounding C atoms is of FM nature except for Ni which shows anti-ferromagnetic (AFM) interactions.

The $C_{32}$ and $C_{36}$ fullerene structures are non-magnetic in their ground state. However, when encapsulated with TMs, the resultant complex becomes magnetic. Similar to the trend observed in the smaller fullerenes, $C_{32}$ and $C_{36}$ also have MM localized mainly at the TM sites as shown in Table 4.5 except Co, Ni and Cu (Figure 4.10). Interestingly, Ni@C_{32} and Ni@C_{36} show zero MM. The LMM at Ni site in Ni@C_{32} is 1.17 $\mu_B$ with a major contribution from 3d orbital electrons whereas in Ni@C_{36} complex, LMM is zero. The surrounding C atoms interact AFM with Ti, V, Cr, Mn, Co and Ni. The $Cu@C_{32}$ complex shows a MM of 1 $\mu_B$ but nearly no contribution from TM and all MM is contributed by the cage C atoms.

Inside $C_{36}$ the TMs show a mixed behavior as Ti, V, and Mn show AFM interac-
tions where as Cr, Fe, Co and Cu show FM interactions with the cage C atoms. In TM@C_{26} complexes, the majority contribution to MM is localized at the TM site with maximum contribution from 3d orbitals apart from Cr and Cu (Table 4.5).

The MMs of TM@C_{n} complexes are dependent on nature of TM and size of encapsulating fullerenes. The atomic MMs of 3d TMs are altered to a large extent inside the fullerene cage. For Cr, the MM increases from 0.0 μ_B in C_{20} to 5.99 μ_B in C_{30}. Interestingly for Mn, the MM is constant in all fullerenes from C_{20} to C_{30}. For Fe, the MM decreases from 8.0 μ_B in C_{20} to 3.99 μ_B in C_{30}. For Co, the MM decreases from 7.0 μ_B in C_{20} to 1.0 μ_B in C_{32} and then increases to 3.0 μ_B in C_{36}. There is a small induced MM on nearest C atoms in all fullerenes which aligns FM for n < 32 and AFM for n ≥ 32 with some exceptional cases.

Table 4.6: Average C-C and C=C bond lengths (in Å) for all fullerene cages when encapsulated with 3d-TM.

<table>
<thead>
<tr>
<th>TM</th>
<th>C_{20} C-C</th>
<th>C_{11} C-C</th>
<th>C_{30} C=C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1.45-1.49</td>
<td>1.41-1.44</td>
<td>1.47-1.48</td>
</tr>
<tr>
<td>V</td>
<td>1.46-1.49</td>
<td>1.41-1.44</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Cr</td>
<td>1.46-1.49</td>
<td>1.41-1.43</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Mn</td>
<td>1.46-1.49</td>
<td>1.41-1.44</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Fe</td>
<td>1.46-1.48</td>
<td>1.42-1.43</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Co</td>
<td>1.45-1.49</td>
<td>1.41-1.43</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Ni</td>
<td>1.46-1.48</td>
<td>1.42-1.43</td>
<td>1.46-1.48</td>
</tr>
<tr>
<td>Cu</td>
<td>1.46-1.50</td>
<td>1.41-1.43</td>
<td>1.46-1.49</td>
</tr>
</tbody>
</table>

We have also studied the structural and magnetic properties of TM encapsulated C_{40}, C_{44}, and C_{50} cages. The preliminary structural results are summarized are tabulated in Table 4.6, and HOMO-LUMO gap of spin up and spin down of TM@C_{n} are plotted in Figure 4.11. The HOMO-LUMO gap variation of spin up - spin down shows interesting cross in magnitude with increase in atomic number of dopant.

The effect of various 3d TM in C_{44} at endohedral position on Electronic Density of States (EDOS) is plotted in Figure 4.12. The spin-up and spin-down EDOS plot for TM@C_{44} shows significant polarization near Fermi level and there is no magnetic moment for pure C_{44}. The unequal polarization of spin up and spin down electrons due to TM atom results into a net MM.
Figure 4.11: HOMO-LUMO gaps for spin up and spin down states for all $T M @ G_{\phi}$, $C_{4v}$ and $C_{5v}$. 

$\text{HOMO-LUMO gap (eV)}$

$2.4$

$2.0$

$1.6$

$1.2$

$0.8$

$0.4$

$0.0$

$2.4$

$2.0$

$1.6$

$1.2$

$0.8$

$0.4$

$0.0$
Figure 4.12: Spin-up and spin-down EDOS for $C_{44}$, $Ti@C_{44}$, $V@C_{44}$, $Mn@C_{44}$, $Ni@C_{44}$ and $Cu@C_{36}$. The dotted line shows the position of $E_f$. 
Figure 4.13: Total magnetic moments and local MMs at TM site with respect to the 3d TMs for all fullerenes i.e. $C_{40}$, $C_{44}$, and $C_{50}$.
The total MM and LMM at the TM site are also plotted in Figure 4.13. The MM is induced in all these cages when doped with TM atoms. The magnetic moment of the order of 0.01-0.12 $\mu_B$ is induced on the cage atoms. The MM is quenched for Ni as well as Cu for $n = 40$, 44 and 50.
4.5 Summary and Conclusions

In this chapter we have investigated a possibility of inducing magnetism in small carbon fullerenes $C_{n}$, $n < 50$ by encapsulating magnetic 3d TM impurities using spin polarized DFT. The average diameter of the fullerene cages show a small increase on TM encapsulation. The cohesive energy difference of $TM@C_{n}$ complexes suggest that Ti and V are stable inside all cage structures therefore indicating a strong possibility of their production. $C_{28}$ cage is the smallest fullerene which can encapsulate all 3d TMs except Cr and Cu which can only be encapsulated inside $C_{36}$ cage. Cu is found to be least stable for encapsulation. The MM is induced in all fullerene cages with the introduction of TM impurity at the endohedral site. There is a significant MM of the order $0.12-0.50 \mu_B$ induced on the carbon cage atoms. All the 3d TMs in $C_{20}$ and $C_{28}$ cages interact with C atoms ferromagnetically except $Ni@C_{28}$ which interacts antiferromagnetically. Ti, V, Cr, and Mn show AFM interactions with C atoms of $C_{36}$ cage. Therefore it may be concluded that there is a transition of magnetic interactions from FM to AFM for $n = 32$. The MM is quenched for Ni beyond $C_{32}$. It does not show any change for $Mn@C_{n}$ although FM to AFM change does take place at $n = 32$. Thus, the magnetic behavior of $TM@C_{n}$ complexes is dependent on the size of the fullerene cages, configuration of 3d metals and the type of magnetic interactions between TMs and surrounding C atoms. Therefore, the choice of TM and host fullerenes provides a novel possibility to induce and manipulate magnetism in carbon nanostructures.
Bibliography


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