Encapsulation of small magnetic clusters in fullerene cages: A density functional theory investigation within van der Waals corrections
Encapsulation of small magnetic clusters in fullerene cages: A density functional theory investigation within van der Waals corrections

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The encapsulation of magnetic transition-metal (TM) clusters inside carbon cages (fullerenes, nanotubes) has been of great interest due to the wide range of applications, which spread from medical sensors in magnetic resonance imaging to photonic crystals. Several theoretical studies have been reported; however, our atomistic understanding of the physical properties of encapsulated magnetic TM 3d clusters is far from satisfactory. In this work, we will report general trends, derived from density functional theory within the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE), for the encapsulation properties of the TMn@Cn (TM = Fe, Co, Ni; m = 2−6, n = 60, 70, 80, 90) systems. Furthermore, to understand the role of the van der Waals interactions in the physical properties, we employed the empirical Grimme’s correction (PBE + D2). We found that both PBE and PBE + D2 functionals yield almost the same geometric parameters, magnetic and electronic properties, however, PBE + D2 strongly enhances the encapsulation energy. We found that the center of mass of the TMn clusters is displaced towards the inside Cn surfaces, except for large TMn clusters (m = 5 and 6). For few cases, e.g., Co3 and Fe4, the encapsulation changes the putative lowest-energy structure compared to the isolated TMn clusters. We identified few physical parameters that play an important role in the sign and magnitude of the encapsulation energy, namely, cluster size, fullerene equatorial diameter, shape, curvature of the inside Cn surface, number of TM atoms that bind directly to the inside Cn surface, and the van der Waals correction. The total magnetic moment of encapsulated TMn clusters decreases compared with the isolated TMn clusters, which is expected due to the hybridization of the d-π states, and strongly depends on the size and shape of the fullerene cages.

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I. INTRODUCTION

Transition-metal (TM) particles composed of a few (cluster) to 1000 (nanoparticle) atoms have been considered as potential candidates for a wide range of applications. For example, Rh, Pd, and Pt particles supported on oxides such as CeO2 (Refs. 1 and 2) and Al2O3 are widely used in catalysis. An nanorods have been studied for selective release of drugs. Rh nanoparticles (NPs) confined inside carbon nanotubes (CNTs) have been studied for ethanol production from syngas, and Co NPs inside CNTs have been studied for tailoring the band gap of CNTs. Furthermore, magnetic iron-oxide NPs and rare-earth atoms have been investigated as contrast agents for magnetic resonance imaging, which is important for cancer therapy.

All those studies can be separated into three groups, namely, TM particles supported on oxides, protected by ligands, and encapsulated inside fullerenes and CNTs. Thus, for real applications, clusters and NPs are in direct contact with an external environment, which can affect their atomic structure, relative stability, magnetic moments, and optical properties compared with isolated TMn clusters. Furthermore, it is important to mention that TM particles can directly affect the chemical and physical properties of the environment, which can be used as a mechanism to tune the physical and chemical properties of different systems.

Experimental studies using spectroscopic ellipsometry measurements of Co clusters inside CNTs (Ref. 7) reveal a drastic change in the dielectric response, which suggests that Co clusters can be used to tailor the optical properties of CNTs. High-resolution transmission electron microscopy (HRTEM) experiments have suggested that large Co particles inside CNTs have face-centered-cubic (fcc) structures, instead of stable hexagonal-close-packed (hcp) structures; i.e., the interaction of Co surface atoms with the inside CNT surfaces induces a structure phase change.

Recently, several theoretical studies have been reported for the encapsulation of TM atoms and clusters inside fullerenes and CNTs. For example, Garg et al. using density functional theory (DFT), studied the encapsulation of 3d atoms inside small fullerenes, Cn (n = 20–36). They found that the Cn size plays an important role in the magnetic interactions, i.e., the system changes from ferromagnetic (FM) to antiferromagnetic (AFM). Ivanovskaya et al., employing tight-binding DFT calculations, found strong changes in the magnetic moments for Fe nanowires and clusters encapsulated inside CNTs. Using DFT calculations, Javan et al. found similar trends for Co(n = 2−7) inside C60 and C82, i.e., large reduction in the magnetic moments, which was attributed to the strong Co-C hybridization. Furthermore, they found that Co9@C60 and Co9@C82 are energetically favorable for n = 2−7, except for Co7@C60. Javan et al. also studied the encapsulation of Fe(n = 2−7) inside C60 and C80. For both Fe9 and Co9 clusters in gas phase, Javan et al. found highly symmetric TM configurations, which are substantially different from previous results, i.e., previous DFT calculations found distorted structures for Fe9 and Co9 in gas phase. Furthermore, there is no explanation why the encapsulation energies for Co9@C60 and Fe9@C60 are so different, e.g., positive (unstable) even...
for the diatomic Fe₂ molecule, while it is negative (stable) for Co₆ inside C₆₀.

Therefore, while the theoretical study of isolated TMₘ clusters and NPs has been reported for a long time (see, e.g., Refs. 20–34), first-principles study of TMₘ clusters inside Cₙ and CNTs is relatively recent, and hence, our understanding of the general trends that drive the stabilization of TMₘ inside Cₙ and CNTs is far from satisfactory.

In this work, we will address the problem of encapsulation of magnetic TMₘ (TM = Fe, Co, Ni; \( m = 2–6 \)) clusters inside fullerene cages, Cₙ (\( n = 60, 70, 80, 90 \)) employing first-principles DFT calculations. It is well known that DFT within local or semilocal functionals cannot correctly describe the van der Waals interactions, which are present for TMₘ encapsulated inside fullerenes. In order to improve our description, we will employ an empirical correction to take into account the van der Waals interactions. Our aim is to obtain a better atomistic understanding of the effects of the encapsulation on the structure, stability, and magnetic properties of TMₘ clusters. Furthermore, we expect that our results for TMₘ@Cₙ can also help to understand the encapsulation of TMₘ clusters inside CNTs, as well as the role of the van der Waals interactions for encapsulation of TMₘ clusters inside fullerenes.

II. THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

Our calculations are based on spin-polarized DFT35,36 within the generalized gradient approximation37 (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE).38 and employing the all-electron projected augmented wave39,40 (PAW) method as implemented in the Vienna \textit{Ab initio} Simulation Package41,42 (VASP). To improve the description of the van der Waals interactions, which might play an important role in the interaction of TMₘ clusters inside fullerenes, we employed the empirical approach proposed by Grimme (DFT + D₂),43 which has a lower computational cost and is currently implemented in VASP. In this approach the total energy, \( E_{\text{DFT}+\text{D}_2} \), is obtained by the sum of the usual self-consistent DFT total energy with the van der Waals dispersion correction, \( E_{\text{disp}} \), i.e.,

\[
E_{\text{DFT}+\text{D}_2} = E_{\text{DFT}} + E_{\text{disp}},
\]

where

\[
E_{\text{disp}} = \frac{s_6}{2} \sum_{i} \sum_{j} C_{ij}^6 R_{ij} f_{\text{dmp}}(R_{ij}).
\]

where \( i \) and \( j \) runs over the atoms in the unit cell. \( C_{ij}^6 \) denotes the dispersion coefficient for atom pair \( ij \) (\( C_{ij}^6 = \sqrt{C_{ij}^6 C_{ji}^6} \)), \( s_6 \) is a global scaling factor that only depends on the exchange-correlation functional (\( s_6 = 0.75 \) for PBE), \( R_{ij} \) is the distance between the \( i \) and \( j \) atoms, and \( f_{\text{dmp}}(R_{ij}) \) is a damped function to avoid near singularities for small distances. All the parameters employed in the DFT + D₂ (PBE + D₂ from now) framework are reported and discussed in Ref. 43.

For all PBE and PBE + D₂ calculations, we employed a plane-wave cutoff energy of 400 eV within a cubic box of 22 Å and the \( \Gamma \) point for the Brillouin zone integration. The equilibrium geometries of all atomic configurations (fullerenes, TMₘ, and TMₘ@Cₙ) were obtained once the atomic forces on every atom are smaller than 0.025 eV/Å.

The search for the lowest-energy configurations of TMₘ clusters encapsulated inside Cₙ is a challenging problem due to the large number of local minimum configurations and the interaction of the TM atoms with the inside Cₙ surface.

In this work, we employed a sequence of steps to obtain a putative set of lowest-energy configurations for the TMₘ@Cₙ systems, which are summarized as follows: (i) Selection of spherical and ellipsoid (prolate) fullerene structures that obey the isolated pentagon rule, i.e., there are no adjacent pentagons,44 which avoid strain induced by pentagon-pentagon contact. (ii) A large number of TMₘ configurations were selected from previous studies for small TMₘ clusters,17–22 which include low coordination structures (open), high coordination structures (compact), and broken-symmetry structures. Furthermore, we selected several snapshots from first-principles simulated annealing (SA) simulations, which were initiated with a given structure with lower symmetry at high temperature (1000 K) and reduced to about 0 K in 10 picoseconds. (iii) The lowest-energy configurations obtained for TMₘ in gas phase were placed at the center or near to the inside Cₙ surfaces to generate several initial TMₘ@Cₙ configurations. This procedure was repeated also for slightly higher energy TMₘ configurations. (iv) Structural crossover was performed among the TMₘ@Cₙ configurations as suggested in Ref. 32, i.e., lowest-energy configurations identified for Feₘ@Cₙ were considered as candidates for Coₘ@Cₙ and Niₘ@Cₙ and vice versa. (v) Different spin-magnetic configurations were considered for TMₘ and TMₘ@Cₙ.

III. RESULTS

A. Fullerenes

Among a large number of Cₙ with different size, shape, and number of isomers,44–46 we selected a set of Cₙ systems with four different sizes, namely, \( n = 60, 70, 80, 90 \) (Fig. 1). There is one isomer for C₆₀, one for C₇₀, seven for C₈₀, and 46 for C₉₀, i.e., different cage shapes are available for particular Cₙ sizes (\( n = 80, 90 \)). To obtain a better understanding of the cage shape in the TMₘ@Cₙ properties, we selected two spherical fullerenes, C₆₀-Iₘ (Refs. 44,46–48 and C₈₀-Iₘ,46,48,49 and two prolate fullerenes, C₇₀-D₅₈ (Refs. 44,46–48, and 50) and C₉₀-D₉₀.46,51 As a consequence of the Euler theorem, there are twelve pentagons in the C₆₀, C₇₀, C₈₀, and C₉₀ cages, and the
number of hexagons close to the fullerene cages are 20, 25, 30, and 35, respectively. We would like to mention that $C_{60}$, $C_{70}$, $C_{80}$, and $C_{90}$ fullerences have been widely observed experimentally, while $C_{60}$-$D_3h$ was only recently identified by single-crystal x-ray diffraction, and has very interesting properties between fullerenes and CNTs.

The four selected $C_n$ structures were optimized using the PBE and PBE + D2 functionals and employing symmetry constraint, i.e., $I_h$ for $C_{60}$ and $C_{80}$, and $D_3h$ for $C_{70}$ and $C_{90}$. We found that the PBE + D2 functional does not affect the geometry of the fullerenes. From our PBE results, we can estimate an average diameter for the spherical cages, namely, 7.10 Å for $C_{60}$ and 8.13 Å for $C_{80}$, while two parameters are necessary for the prolate fullerenes, i.e., the equatorial radii (along the $x$ and $y$ axes) $a$, and the polar radius (along the $z$ axis) $c$. For $C_{70}$, $a = 7.09$ Å and $c = 7.94$ Å, while for $C_{90}$, $a = 6.95$ Å and $c = 10.55$ Å. We estimated the cage volume ($V = \frac{4}{3} \pi a^2 c$, $a = c$ for spherical shape) as 1499, 1672, 2251, 2294, 228, and 4268 Å$^3$, respectively; however, for $C_{70}$ and $C_{90}$, the volume increases from $C_{60}$ to $C_{70}$ to $C_{90}$, which is expected to play an important role for TM encapsulation. The C-C bond lengths in $C_n$ are from 1.39 to 1.45 Å, which is consistent with experimental results, and substantially smaller than the TM-TM bond lengths, which might affect the binding of the TM$_m$ clusters to the inside $C_n$ surfaces.

B. Isolated transition-metal clusters

For the isolated TM$_m$ clusters, several configurations were calculated using PBE and PBE + D2 for each system, and there is no significant difference between the PBE and PBE + D2 results. Thus, only the lowest-energy PBE TM$_m$ structures are shown in Fig. 2. For the structural analysis of the TM$_m$ clusters, we employed the effective coordination concept, which yields the effective coordination number for all atoms, ECN, and the respective weighted bond length, $d_{av}$. In this work, ECN and $d_{av}$ indicate the average results over all atoms in the TM$_m$ cluster. This analysis has been employed in several TM cluster studies, and has very interesting properties between fullerenes and CNTs.

At their crystalline phases, Fe, Co, and Ni form compact structures, namely, body-centered cubic (bcc), hexagonal close-packed (hcp), and face-centered cubic (fcc), respectively. However, the lowest-energy TM$_m$ structures are not as compact as the well-known compact Lennard-Jones clusters (LJ). For example, for LJ$_m$ structures, ECN = 1.0 (dimer), 2.0 (triangle), 3.0 (tetrahedral), 3.6 (trigonal bipyramid), and 4.0 (tetragonal bipyramid) for $m = 2, 3, 4, 5, 6$, respectively. However, for $m = 5$, we found ECN = 3.38 (Fe$_5$), 2.85 (Co$_5$), and 3.20 (Ni$_5$), while it is 3.36 for LJ$_5$ (Fig. 2). Furthermore, there is a large deviation for Co$_4$, i.e., ECN = 2.10, instead of 3.0 (LJ$_4$). Thus, there is a strong tendency of the magnetic TM$_m$ clusters for lower symmetry structures, which helps to increase their energy stability due to splitting of the highest occupied states.

From the ECN results, Fig. 2, the Ni$_m$ clusters are much more compact than the Fe$_m$ and Co$_m$ structures, and hence, we expect that this trend can affect the stability of the TM$_m$@$C_n$ systems, i.e., noncompact structures would occupy large volumes inside the fullerene cages. Except for TM$_2$, $d_{av}$ increases slightly as a function of the TM$_m$ size, e.g., 2.13 Å (Co$_2$) and 2.27 Å (Co$_5$). For TM$_2$, $d_{av}$ has the smaller value, which is expected due to the lowest coordination (ECN = 1). Our lowest-energy structures are consistent with previous calculations based on DFT within semi-local functionals.

The isolated Fe$_m$, Co$_m$, and Ni$_m$ clusters are ferromagnetic as their respective bulk phases. The total magnetic moments $m_T$ of the TM$_m$ clusters increase almost linearly as a function of cluster size, except small deviations, e.g., for Co$_6$ and Ni$_2$. As expected from results for the bulk phases, $m_T$ decreases from Fe to Ni clusters. For example, for Fe$_5$, Co$_6$, and Ni$_6$, $m_T = 3.33, 2.33$, and $1.33 \mu_B/\text{atom}$, which is larger than for the bulk systems, i.e., $m_T = 2.21, 1.62$, and $0.64 \mu_B/\text{atom}$, for Fe, Co, and Ni bulk, respectively. Our results and trends are in good agreement with previous results.

C. TM$_m$ at $C_n$

We calculated about 450 configurations for the TM$_m$@$C_n$ systems employing the PBE functional and following the procedure online in Sec. II with the aim to identify the best set of putative lowest-energy structures. All relaxed PBE geometries were reoptimized using the PBE + D2 functional.

1. Geometric parameters

We found only slight changes in the atomic structure of the TM$_m$@$C_n$ systems due to the van der Waals corrections, i.e., the changes in the ECN and $d_{av}$ of the encapsulated TM$_m$ clusters are between 2% and 5% for all cases. Thus, only the lowest PBE structures are shown in Fig. 3 along with the results for ECN and $d_{av}$, which we will use to identify the structural changes due to the encapsulation of the TM$_m$ clusters inside $C_n$ cages.
We found that the center of mass of the TM\(_m\) (\(m = 2 - 4\)) clusters displaces towards the inside \(C_n\) surface, which indicates an attractive interaction of the TM\(_m\) clusters by the inside \(C_n\) surface; however, large TM\(_m\) clusters (\(m = 5\) and \(6\)) are nearly located at the center of the cages due to the cluster and cage sizes. For all TM\(_m@C_n\) systems, the smallest TM-C distances are in the range from 2.08 to 2.30 Å, which is typical for the bond lengths of Fe, Co, and Ni atoms with C atoms in metal complexes, e.g., 2.06 Å for Fe-C in Fe(C\(_5\)Cl\(_5\)).\(^{38}\) For most cases, the TM atoms bind to the center of the hexagonals or pentagonals, which maximizes the coordination number of the TM atoms.

From the results reported in Figs. 3 and 2, we can observe the following effects on TM\(_m\). Except for Fe\(_5\) and Fe\(_6\) inside C\(_60\) and C\(_70\), \(d_{av}\) increases for all clusters, e.g., changes from 2.01 Å for Fe\(_2\) in gas-phase to 2.27, 2.16, 2.42, and 2.17 Å for Fe\(_2\) inside C\(_60\), C\(_70\), C\(_80\), and C\(_90\), respectively. Similar changes can be observed for the other systems. The compression of the Fe\(_5\) and Fe\(_6\) bond lengths inside C\(_60\) and C\(_70\) can be explained by the small cage sizes of the C\(_60\) and C\(_70\) fullerenes as there is no similar compression for Fe\(_6\) inside C\(_80\). We would like to mention that the compression of the bond lengths occurs only for Fe\(_m\) clusters, which can be explained by the atomic radii differences between the TM atoms, i.e., Fe is slightly larger than Co and Ni, while Co and Ni have a similar atomic size. For example, using our calculated average weighted bond lengths for the bulk systems, the atomic radius (\(d_{av}/2\)) of Fe, Co, and Ni are 1.27, 1.25, and 1.24 Å, respectively, which is consistent with atomic radius reported in the literature, i.e., 1.32, 1.26, and 1.24 Å, for Fe, Co, and Ni, respectively.\(^{11,39}\)

We noticed that most of the TM\(_m\) clusters increase their average effective coordination number inside fullerene cages, and hence, the TM\(_m\) clusters are more compact. For few cases, we found that the TM\(_m\) clusters change their lowest-energy structure upon the encapsulation, e.g., the Co\(_5\) structure changes from trigonal bipyramid (isolated) to tetragonal upon the encapsulation in C\(_70\), C\(_80\), and C\(_90\) cages. The same effects happen also for Fe\(_4\). Thus, this result indicates that not only the lowest-energy structures in gas phase should be considered
for encapsulation inside \( C_n \) cages. In Fig. 4, we summarize the number of TM atoms that binds directly to the inside fullerene surfaces as a function of the TM size. It can be seen that the number of atoms binded directly to the inside surfaces increases almost linearly with few deviations, which is expected to affect the encapsulation energy and magnetic properties.

### 2. Encapsulation energy

The encapsulation energy \( E_{\text{enc}} \), which measures the energy gain due to the encapsulation (\( \text{TM}_m + C_n \rightarrow \text{TM}_m @ C_n \)), can be calculated by the following equation:

\[
E_{\text{enc}} = E_{\text{tot}}^{\text{TM}_m @ C_n} - (E_{\text{tot}}^{C_n} + E_{\text{tot}}^{\text{TM}_m}),
\]

where \( E_{\text{tot}}^{\text{TM}_m @ C_n} \) is the total energy of the \( \text{TM}_m @ C_n \) system. \( E_{\text{tot}}^{C_n} \) and \( E_{\text{tot}}^{\text{TM}_m} \) are the total energies of the \( C_n \) and \( \text{TM}_m \) systems, respectively. A positive or negative value for \( E_{\text{enc}} \) indicates an energetically unfavorable or favorable system. Thus, it is important to obtain the range of values for \( m \) and \( n \) for which \( E_{\text{enc}} \) is negative. The PBE and PBE + D2 results for \( E_{\text{enc}} \) are shown in Fig. 5.

In contrast with the structural parameters (ECN, \( d_{av} \)), the van der Waals correction strongly affects the encapsulation energy. For example, the dispersion correction to the PBE functional increases the stability of all systems by about a factor of 2, which is a substantial change; however, it is important to take into account that the magnitude of the change depends strongly on the magnitude of the \( C^6_j \) parameters. Recent theoretical studies have suggested that Grimme’s \( C^6_j \) parameters in the PBE + D2 framework might be overestimated, which contributes to increase the van der Waals corrections to the binding energy. We would like to point out that both PBE and PBE + D2 functionals yield similar dependence of the encapsulation energy as a function of \( \text{TM}_m \) size for a particular \( C_n \).

For a given \( \text{TM}_m \) size, the encapsulation energy gets more negative (increase stability) from \( C_{60} \rightarrow C_{70} \rightarrow C_{90} \rightarrow C_{80} \). For example, for Co \( (\text{Co}_6) \), \( E_{\text{enc}}^{\text{PBE}} = -0.17 \) (1.42), \( -0.70 (-0.01) \), \( -0.97 (-0.77) \), and \( -1.63 \) eV \((-3.13 \) eV) for \( C_{60} \), \( C_{70} \), \( C_{90} \), and \( C_{80} \), respectively. The same trend is also observed for the PBE + D2 results. We would expect this dependence for large \( \text{TM}_m \) clusters, but not for small diatomic molecules such as TM. We found that PBE (PBE + D2) yields a positive (negative) encapsulation energy for TM inside \( C_{60} \), and the stability of the \( \text{TM}_m @ C_n \) increases by increasing the \( C_n \) cage size, which is intuitively expected. For TM inside \( C_n \), we found that TM adsorbs perpendicular to the hollow sites of the hexagonal rings for \( C_{60} \), \( C_{70} \), and \( C_{90} \), i.e., only one TM atom directly binds to the C atoms; however, TM adsorbs parallel to the surface inside \( C_{80} \), and hence, two TM atoms bind directly to the surface, which increases the binding energy. Therefore, our results and analysis indicate that the curvature of the inside \( C_n \) surfaces affects directly the

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**FIG. 4.** (Color online) Number of transition-metal atoms binded directly to the inside fullerene surfaces of the lowest-energy TM@C\(_n\) configurations (TM = Fe, Co, Ni; \( m = 2,3,4,5,6 \); \( n = 60,70,80,90 \)).

**FIG. 5.** (Color online) Encapsulation energy of the \( \text{TM}_m \) clusters inside \( C_n \). \( \text{TM}_m @ C_n \) (TM = Fe, Co, Ni; \( m = 2,3,4,5,6 \); \( n = 60,70,80,90 \)).
Results for TM

For a particular Cₙ size and both PBE and PBE + D2 functionals, the encapsulation energy starts at a particular value for TM₂, and increasing the cluster TMₙ size, the encapsulation energy turns more negative (increases stability) to reach a limit in which the stability decreases for large TMₙ clusters. Thus, there is a minimum in the encapsulation energy of TMₙ inside Cₙ as a function of the TMₙ size for a particular value of n. For TM₉₀, our encapsulated TMₙ clusters were not large enough to reach a minimum in the encapsulation energy; however, our results indicate that the same trends can be obtained. These results lead to the following question: Why is the stability larger for TM₃ and TM₄ than for TM₂? From our analysis, we found that the number of TM atoms that bind to the inside Cₙ surface plays a crucial role in increasing the stability of the TMₙ@Cₙ systems.

3. Magnetic properties

We found that the total magnetic moments are not affected by the van der Waals corrections, and hence, only the PBE results will be discussed below. The total magnetic moments of the lowest-energy TMₙ@Cₙ configurations are shown in Fig. 6 along with the results for the TMₙ clusters in gas phase. The following trends can be observed: (i) Except for a few cases, the total magnetic moments decrease for encapsulated TMₙ clusters compared with TMₙ in gas phase, in particular, for large TMₙ clusters inside small Cₙ cases, e.g., m = 5,6 inside C₆₀, C₇₀, and C₉₀. Therefore, our results indicate that the ratio between cluster and cage size plays a key role in the magnetic properties of encapsulated magnetic systems. (ii) For few Ni₉@C₉₀ systems, e.g., Ni₃@C₆₀, we found that the magnetic solutions change from ferromagnetic to antiferromagnetic or ferrimagnetic phases. (iii) For most of the systems, we observed a large number of atomic configurations with similar total energies, i.e., differences smaller than 5.0 meV per TM atom, and slightly different magnetic moments. This result indicates that at real experimental conditions one of the magnetic configurations might be more favorable or a wide range of magnetic configurations might exist, and experimental techniques might access only the average results.

4. Density of states

To obtain a better understanding of the electronic properties of the TMₙ@Cₙ systems, we calculated the total and local density of states (TDOS, LDOS). The PBE and PBE + D2 functionals yield very similar TDOS and LDOS as both functionals yield very similar structural geometries for TMₙ systems. To improve our analysis, we calculated the total and local density of states (TDOS, LDOS) of the TMₙ@Cₙ system. The vertical red-dashed line (zero energy) indicates the energy of the highest occupied state.
and minority spins are strongly affected by the size of the TM states upon the encapsulation, which is expected due to the clusters. For example, for TM$_6@C_{60}$, the largest shift occurs for Fe$_6@C_{60}$ due to the parallel orientation of Fe$_2$ with respect to the inside C$_{60}$ surface. There is no clear trend in the magnitude of the shift of the center of gravity and the magnitude of the encapsulation energy. Similar results are observed for Co$_m@C_n$ and Ni$_m@C_n$, however, with smaller magnitudes. For almost all configurations, the center of gravity of the d states shifts down upon the encapsulation.

IV. CONCLUSIONS

In this work, we performed PBE and PBE + D2 (empirical Grimme’s correction for van der Waals interactions) calculations for TM$_m@C_n$ (TM = Fe, Co, Ni; m = 2–6; n = 60, 70, 80, 90). From a large number of calculations, we obtained a set of putative lowest-energy configurations for TM$_m@C_n$, which were used to calculate the encapsulation energy, total magnetic moments, density of states, and center of gravity of the occupied d states. From our results and analysis, the following trends were identified.

The van der Waals corrections strongly affect the encapsulation energy, while the structural parameters and magnetic moments are affected slightly. We would like to point out that the dispersion correction to the PBE functional increases the stability of all the TM$_m@C_n$ systems by about a factor of 2, which might be related with the overestimation of the $C_6^2$ parameters in Grimme’s PBE + D2 framework. Thus, our results suggest that the correct values of the encapsulation energies depend on the correct treatment of the correlation effects, which might require theoretical approaches such as the quantum Monte Carlo approach.

The center of mass of the TM$_m$ clusters is displaced towards the inside C$_n$ surfaces, except for large TM$_m$ clusters (m = 5–6), which are almost located at the center of the C$_n$ cages due to the cluster and cage sizes. The effective coordination number and average bond lengths of TM$_m$ clusters increase inside fullerenes. For particular cases, e.g., Co$_4$ and Fe$_4$, the encapsulation changes the lowest-energy structure compared with the gas phase, i.e., the lowest-energy configuration depends on the environment. The total magnetic moments of the TM$_m$ clusters inside fullerenes decrease, in general, compared with TM$_m$ in gas phase, in particular, for large clusters inside small C$_n$ cages.

We identified three key parameters that play an important role in the sign and magnitude of the encapsulation energy: (i) The TM$_m$ size and volume of the C$_n$ cage. (ii) The curvature of the inside C$_n$ surfaces. (iii) The number of TM atoms that bind directly to the inside C$_n$ surface. Therefore, these three terms play a crucial role in the minimum of the encapsulation energy curve as a function of TM$_m$ cluster size for a particular C$_n$. Thus, we believe that our conclusions can help to improve the understanding of encapsulation of TM clusters inside fullerenes.

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