The Noncollinear Magnetism in 3d – 5d zigzag nanowires

If an electrical charge is suddenly moved, its effect is delayed and the electromagnetic field contains the momentum; the sum of field momentum and particle momentum is conserved.

-Richard Feynman

In the previous chapter, we have investigated the collinear magnetic properties of Au/Ni bimetallic nanowires. The systems we investigated so far have either ferromagnetic or paramagnetic ground state. If the system exhibits broken inversion symmetry, it can give rise to the magnetic ground state which is neither ferromagnetic nor antiferromagnetic, but one where, spins are rotating under strong spin orbit coupling. It is possible to calculate the ground state energy of such rotating/canted spin structures which can give rise to “Dzyaloshinskii-Moriya Interaction (DMI)”. Experimentally, such ground states are observed, which invoke interest in the theoretical investigations of such phenomenon.[272]

So why is the magnetism in 3d – 5d zigzag chains, with one magnetic and one non-magnetic element so interesting and challenging? It can be expected that, the 3d magnetic element such as, Fe and Co has ferromagnetic ground state in its respective bulk system, whereas 5d element (Ir, Pt, Au) is non-magnetic. However, the 5d element can become spin polarized in the presence of Fe or Co due to hybridization of d orbitals. The 5d elements have heavy nuclei and hence exhibit strong spin orbit interaction in comparison to Fe or Co atoms, hence spin orbit interactions induced effects like magnetic anisotropy energy and Dzyaloshinskii-Moriya Interaction are likely to be observed in these systems. *Ab initio* calculations allow to estimate the magnitudes of the different effects and hence can help to investigate such antisymmetric exchange interactions. In this chapter, we discuss about the different approximations used for calculation of canted spin structures, DMI and magnetocrystalline anisotropy energy.

The chapter is organized as follows: In the next section, we describe the structure of 3d – 5d chain and the structural properties as well as magnetic moments at equilibrium. Then we discuss the isotropic exchange interaction without considering spin orbit
Structural Properties and Magnetic Moments

Figure 5.1 – Structure of the $3d-5d$ transition metal nanowires. The lattice parameter $a$ denotes the equilibrium bond length between two consecutive $3d$ (or $5d$) atoms. The symbol $d$ represents the distance between the $3d-5d$ atoms and $\alpha$ is the angle spanned by the $5d-3d-5d$ atoms.

coupling under different exchange-correlation potential and with different methods. We also discuss the effect of spin orbit coupling on the canted spin structures along with the magnetocrystalline anisotropy energy. In order to understand the effect of hybridization on the strength of the DMI, we have developed a trimer model analogous to $3d-5d$ chain.

5.1 Structural Properties and Magnetic Moments

We have modeled free standing bi-atomic $3d-5d$ nanowire as shown in Fig. 5.1. The structural optimization of the geometry was performed using VASP package. The structural parameters were verified by self consistent calculations using FLEUR code. The FLEUR was used further to calculate all magnetic properties. The $3d-5d$ nanowire structure is quasi-one dimensional and infinite in $X$-direction. We have optimized the lattice parameter $a$, corresponding to the unit cell length in $X$-direction and the bond length $d$ within GGA-rPBE functionals. The bi-atomic nanowires shown in Fig. 5.1 exhibit broken inversion symmetry due to lack of the reflection along the $XZ$ plane.

Figure 5.2 shows the total energy with respect to the lattice constant $a$ in the upper panel. For completeness, we have listed the optimized bond length, bond angles and the magnetic moment on two kinds of atoms in Table-5.1. It can be observed from Fig. 5.2 that, all the bi-atomic nanowires give well defined, unique minima in total energy curve against lattice parameter. The values of $a$ and $d$ indicate that the bi-atomic nanowires do not form equilateral triangles, but isosceles triangles similar to gold and nickel zigzag nanowires. The optimized isosceles structures are due to reduced symmetry along the direction perpendicular to the wire direction.

We have also investigated the variation of the total magnetic moment in the unit cell\(^1\) as a function of the lattice constant $a$ and shown this in the lower panel of Fig. 5.2. The magnetic moment of $3d$ atoms is enhanced in comparison with the $5d$ atoms. The $5d$ atoms show small induced magnetic moment, which depends weakly on the choice of $3d$ atom. In general, it can be seen from Table-5.1 that, the magnetic moment is larger for smaller atomic number ($Z$). The trend of enhanced magnetic moment in Fe-$5d$ chains than that of Co-$5d$ chains is valid for larger range of the lattice parameter

\(^1\)The total magnetic moment is a sum of the magnetic moments per atom, reported in Table 5.1, and the magnetization in the interstitial region.
Figure 5.2 – The upper panel shows the total energy plotted as a function of lattice constant $a$. In the lower panel, the magnetic moment as function of $a$ is displayed.

<table>
<thead>
<tr>
<th>System</th>
<th>$a$ (Å)</th>
<th>$d$ (Å)</th>
<th>$\alpha$ (in $^\circ$)</th>
<th>$M$ (µB/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ir</td>
<td>2.41</td>
<td>2.35</td>
<td>61.83</td>
<td>3.11</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>2.55</td>
<td>2.44</td>
<td>63.08</td>
<td>3.27</td>
</tr>
<tr>
<td>Fe-Au</td>
<td>2.62</td>
<td>2.59</td>
<td>60.76</td>
<td>3.26</td>
</tr>
<tr>
<td>Co-Ir</td>
<td>2.45</td>
<td>2.37</td>
<td>62.07</td>
<td>2.06</td>
</tr>
<tr>
<td>Co-Pt</td>
<td>2.50</td>
<td>2.43</td>
<td>62.02</td>
<td>2.18</td>
</tr>
<tr>
<td>Co-Au</td>
<td>2.59</td>
<td>2.57</td>
<td>60.42</td>
<td>2.15</td>
</tr>
</tbody>
</table>

Table 5.1 – Structural parameters of the optimized zigzag $3d - 5d$ metallic chains. $a$ is the lattice constant, $d$ represents the $3d - 5d$ distance and $\alpha$ is the angle between the $5d$-$3d$-$5d$ atoms (cf. Fig. 5.2). The magnetic moment $M$ on the $3d$ and $5d$ atoms are also listed.
5.2 Isotropic Exchange Interaction

We consider a homogeneous spin spiral (as shown in Fig. 2.6) for bi-atomic 3d – 5d zigzag nanowires, which is defined by a spin spiral vector \( q \) and a rotation axis. The details of the properties of spin spiral vector are described in Sec. 2.8.2 of Chapter-2. Here we describe the self consistent total energy calculations of spin spirals with the scalar relativistic approximation (without SOI) using two functionals, viz., GGA-rPBE and LDA-VWN. We choose the rotation axis along the Z-direction. The spin spiral energy is calculated within a generalized Bloch theorem, which allows for a calculation of spin spirals in a chemical unit cell rather than supercell. Figure 5.3 shows spin spiral energy calculated using LDA and GGA exchange correlation energy functional for Fe-Pt nanowire as an example. The energy of the ferromagnetic state (corresponding to \( q = 0 \)) is set to zero.

It can be observed from Fig. 5.3 that, the dispersion energy curve has approximately the same behavior for LDA and GGA functionals as a function of spin spiral vector \( q \). The Fe-Pt chain shows ferromagnetic state as energetically more stable than the antiferromagnetic state, however quantitatively spin spiral dispersion energy (i.e, \( E(q = 0) - E(-q = 0.5) \)) shows difference for LDA and GGA functionals. This difference can be attributed to the change of basis set used in the exchange correlation energy functionals for LDA and GGA. For completeness, we compared the energy difference between ferromagnetic and anti-ferromagnetic state configuration of the spin spiral calculated from noncollinear calculation and collinear supercell calculations. The energy difference is shown in Table-5.2. It can be seen from Table-5.2 that, LDA-VWN exchange-correlation functionals give better agreement between collinear and spin spiral calculations. The energy difference is of order of 1 meV/cell and is maximal for Fe-Au nanowire (4 meV/cell). However, the GGA-rPBE exchange-correlation energy

\[ E(q) = E(q=0) - E(-q = 0.5) \]

Figure 5.3 – The spin spiral dispersion energy for Fe-Pt nanowire without SOI as a function of spin spiral vector \( q \) shown for LDA nd GGA exchange correlation energy functional.

a. With an increase in \( a \), the magnetic moments increase as the wave function tends to become more localized (atomic). This variation in the magnetic moment is comparatively larger in Fe-5\( d \) chains than that of Co-5\( d \) chains. The variation in the magnetic moment decreases, as the lattice parameter increases. When the lattice constant is close to 2 Å, the magnetic moment of Fe-5\( d \) chain decreases abruptly, indicating the possibility of a magnetic transition during compression of the lattice.
Table 5.2 – Energy difference in eV between ferromagnetic and anti-ferromagnetic states for 3d – 5d chains. Collinear calculations are performed using a supercell approach, whereas the spin spiral calculations are performed exploiting the generalized Bloch theorem.

<table>
<thead>
<tr>
<th>System</th>
<th>Collinear (GGA-rPBE)</th>
<th>Spin-Spiral (GGA-rPBE)</th>
<th>Collinear (LDA-VWN)</th>
<th>Spin spiral (LDA-VWN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ir</td>
<td>0.092</td>
<td>0.105</td>
<td>0.117</td>
<td>0.121</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>0.112</td>
<td>0.126</td>
<td>0.162</td>
<td>0.170</td>
</tr>
<tr>
<td>Fe-Au</td>
<td>0.119</td>
<td>0.061</td>
<td>0.185</td>
<td>0.181</td>
</tr>
<tr>
<td>Co-Ir</td>
<td>0.154</td>
<td>0.348</td>
<td>0.294</td>
<td>0.296</td>
</tr>
<tr>
<td>Co-Pt</td>
<td>0.146</td>
<td>0.155</td>
<td>0.182</td>
<td>0.186</td>
</tr>
<tr>
<td>Co-Au</td>
<td>0.171</td>
<td>0.168</td>
<td>0.212</td>
<td>0.213</td>
</tr>
</tbody>
</table>

The calculated spin spiral dispersion energy for all 3d – 5d chains is shown in Fig. 5.4. In this case, the spin spiral energy is an even function of the spin spiral vector (i.e., $E^0(q) = E^0(-q)$). In most of the 3d – 5d chains, the ferromagnetic state is more stable, except for Fe-Pt and Co-Pt nanowires which show a spin spiral ground state. Co-Pt nanowire has lower energy than the ferromagnetic state by 4.41 meV/cell at the...
5.3 Effect of Spin-orbit Interaction on Magnetism

<table>
<thead>
<tr>
<th>System</th>
<th>Easy Axis</th>
<th>$E^1$ (meV/cell)</th>
<th>$E^2$ (meV/cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ir</td>
<td>X</td>
<td>2.40</td>
<td>5.26</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>X</td>
<td>0.76</td>
<td>7.28</td>
</tr>
<tr>
<td>Fe-Au</td>
<td>Y</td>
<td>1.81</td>
<td>2.08</td>
</tr>
<tr>
<td>Co-Ir</td>
<td>X</td>
<td>15.84</td>
<td>20.65</td>
</tr>
<tr>
<td>Co-Pt</td>
<td>Y</td>
<td>0.17</td>
<td>12.32</td>
</tr>
<tr>
<td>Co-Au</td>
<td>Y</td>
<td>1.41</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table 5.3 – Magnetic anisotropy energy in meV/cell. $E^1$ represents energy difference between the easy axis and its perpendicular conjugate in the plane of the chain. $E^2$ is the energy difference between the easy axis and z axis.

...spin spiral vector $\mathbf{q} = \pm 0.07$ (corresponding to an angle of 25.20° between the adjacent unit cells.) Whereas, in Fe-Pt nanowire, the energy is minimum at spin spiral vector $\mathbf{q} = \pm 0.03$ (corresponding to an angle of 10.79°) by 1.42 meV/cell than the ferromagnetic state.

The shape of the spin spiral dispersion energy in Fig. 5.4 exhibits interesting features. Co-5$d$ nanowires show a typical parabolic behavior around the ferromagnetic ($\mathbf{q} = 0$) and the anti-ferromagnetic ($\mathbf{q} = 0.5$) state. In Fe-5$d$ chains, an irregular dip around $\mathbf{q} = \pm 0.03$ is observed. Fe-Ir nanowire shows a more pronounced irregularity. These irregularities however do not influence the magnetic ground state of 3$d$–5$d$ nanowires.

5.3 Effect of Spin-orbit Interaction on Magnetism

5.3.1 Magnetocrystalline anisotropy energy

The magnetocrystalline anisotropy energy (MAE) is the major contribution to the total energy due to spin-orbit interaction. It competes against the DMI energy by tending to align the magnetic moments along the easy axis of the system in collinear fashion. In short, the MAE competes against any noncollinear structure, because in noncollinear state, the magnetic moments when pointed away from easy axis increase the energy.

We have extracted the magnetocrystalline anisotropy energy from the total energy self consistent calculations of the ferromagnetic states with the magnetic moments along the three high symmetry directions. Our results show that, in all 3$d$–5$d$ nanowires, the easy axis lies in the plane that is spanned by the nanowire (Table-5.3). In our coordinate system, this plane is XY-plane and the X-axis is the wire axis (Fig. 5.1). It can be seen from the Table-5.3 that, the Fe-5$d$ nanowires prefer axial magnetization (i.e., along the X-axis), except for Fe-Au nanowire. In contrast, Co-5$d$ nanowires prefer Y-axis to be the easy axis, except for Co-Ir nanowire. Based on this information about the easy axis (either X or Y), we denote $E^1$ for the difference between the energies of these two (X and Y) directions and let $E^2$ be the difference in energies along the Z-axis and the easy axis. Any homogeneous, flat spin spiral rotating in the XY-plane will have an average MAE per atom of $\frac{1}{2}E^1$. Our results for all 3$d$–5$d$ nanowires show that, $E^1 < E^2$. This indicates that, a very large amount of energy is required to rotate the magnetization from the easy axis to the axis out of the plane of the nanowire. The 3$d$-Pt nanowires exhibit smallest $E^1$, whereas, 3$d$-Ir nanowires exhibit very large $E^1$. 

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Our results presented in Table-5.3 reveal that 3d – 5d nanowires exhibit very large MAE due to reduced dimensions in comparison with the values found for typical bulk structures.\cite{273–275}

We have also calculated the energy due to shape anisotropy which originates from the dipole dipole interactions, using the magnetic moments listed in Table-5.1. Our results show that the wire axis direction is the easy direction for all 3d – 5d nanowires. However the shape anisotropy energy is about 2 – 3 orders of magnitude smaller than that of the magnetocrystalline anisotropy and hence does not have significant influence on magnetic properties of 3d – 5d nanowires.

5.3.2 Dzyaloshinskii-Moriya Interaction Energy

The second energy contribution from SOI leads to Dzyaloshinskii-Moriya interaction (DMI) energy, which takes the form as discussed in detail in Sec. 2.8.2 of Chapter 2,

$$E_{DM}(q) = \sum_{i,j} D_{ij} \cdot (S_i \times S_j)$$ \hspace{1cm} (5.1)

Due to the cross product of the two magnetic moments, canted spin structures are favored by the above energy term. The energy of the DMI is calculated from Eq. 2.164 as, $E_{DM} = \sum_{k,l,j} \delta \epsilon_{k,l,j}(q)$. Since each level exhibits the symmetry, i.e., $\delta \epsilon_{k,l,j}(q) = \delta \epsilon_{l,k,j}(q)$, this antisymmetric behavior will be inherited by sum, $E_{DM}(q) = -E_{DM}(-q)$. The sign of the DM vectors determines the preferred handedness of the moments. It lifts the degeneracy of the sense of rotation of the spin spirals. For the zigzag 3d – 5d nanowires, it can be derived from the symmetry arguments that, the DM vector is pointing along the Z-direction, hence it prefers the spin spirals with the rotation in the XY-plane. In order to investigate the DMI, we have used the generalized Bloch theorem and have included spin orbit interaction within the first order perturbation. This method is described in detail in Sec. 2.7.8 of Chapter-2. The calculated DMI for positive and negative spin spiral vector is shown in Fig. 5.5. It can be observed from the Fig. 5.5 that, the DMI has non-monotonous behavior and is antisymmetric with $q$. At the extremes, the $E_{DM}(q)$ has the value of the order of 10 – 30 meV. In the vicinity of the collinear states, i.e., $q = 0$ or $q = 0.5$, DMI exhibits strong dependence on the atomic number of the 5d element.

The total energy $E(q)$ of the spin spiral is calculated by adding the DMI contribution $\Delta E_{DM}(q)$ (Fig. 5.5) to the isotropic spin spiral dispersion energy $E^0(q)$ (Fig. 5.4). In Fig.
Figure 5.6 – The isotropic exchange interaction contribution and Dzyaloshinskii-Moriya interaction (DMI) contribution to the total energy of the $3d - 5d$ chains as a function of $q$. The blue triangles represent the energy $\Delta E(q)$ due to inclusion of SOI in the system. The red filled circles show the spin spiral energy without SOI ($E^0(q)$). The total energy $E(q)$ is shown by filled black squares. In each figure, we have shown the magnified view of the spin spiral energy, DMI energy and the total energy in the vicinity of ferromagnetic state in the inset.

5.6, we show $E^0(q)$, $E_{\text{DM}}(q)$ and total energy $E(q)$. The inset in each figure is shown to magnify the qualitative behavior of the dispersion energy in the neighborhood of ferromagnetic state. We describe the noncollinear magnetic properties of $3d - 5d$ nanowires based on the presence of magnetic element.
Effect of Spin-orbit Interaction on Magnetism

System \( \frac{1}{2}E^1 \) (meV/cell) DMI (meV/cell)

Fe-Ir 1.200 0.500
Fe-Pt 0.380 8.540
Fe-Au 0.905 0.130
Co-Ir 7.092 0.000
Co-Pt 0.085 19.690
Co-Au 0.705 4.670

Table 5.4 – The comparison of magnetic anisotropy energy \( E^1 \) with the energy due to Dzyaloshinskii-Moriya interaction. The DMI energy has to overcome the \( \frac{1}{2}E^1 \) to have a stable ground state.

5.3.2.1 Fe-5d nanowires:

In the absence of spin orbit interaction, the spin spiral calculations show that, Fe-Ir and Fe-Au nanowires are ferromagnetic (Fig. 5.6(a) and 5.6(c)), whereas Fe-Pt nanowire shows degenerate ground state at \( q = \pm 0.03 \) (Fig. 5.6(c)). The energy of Fe-Pt nanowire at \( q = \pm 0.03 \) is lower by 1.42 meV/cell than the corresponding ferromagnetic state. The DMI lifts the degeneracy and changes the ferromagnetic state of Fe-Ir nanowire to a left handed spin spiral at \( q = -0.02 \) with an additional energy gain of 0.5 meV/cell (Fig. 5.6(a)). In Fe-Pt nanowire, DMI lifts the degeneracy in the spin spiral ground state (Fig. 5.6(b)) leading to a right handed spin spiral rotation with a significant energy gain of 7.09 meV/cell. Similarly, in Fe-Au chains the DMI prefers left-handed spin-spirals (Fig. 5.6(c)), but an energy gain of 0.1 meV/cell with respect to the ferromagnetic state is too small to compete against the MAE. In Fe-5d nanowires, Fe-Ir and Fe-Au systems exhibit very weak energy due to DMI in comparison with their respective MAE, hence spin spiral states cannot be stable. The situation leads to ferromagnetic ground state. Fe-Pt nanowire has a strong DMI energy with respect to its MAE (Table-5.4), hence the systems preserves its right handed spin spiral ground state at \( q = 0.5 \).

5.3.2.2 Co-5d nanowires

Fig. 5.6(d)-5.6(f) show the total energy for Co-5d nanowires. It can be seen from the figures that, Co-Ir and Co-Au nanowires show ferromagnetic ground state without addition of the DMI energy. The DMI does not influence the ground state of Co-Ir and Co-Au nanowires, in effect maintaining these nanowires ferromagnetic. The Co-Pt nanowire, however has degenerate spin spiral ground state at \( q = \pm 0.07 \), in the absence of SOI. The DMI lifts the degeneracy of the spin spiral ground state of Co-Pt nanowire (Fig. 5.6(e)) and the system exhibits right handed spin spiral at \( q = 0.07 \) with an additional energy gain of 15.29 meV/cell. The energy gain due to DMI in Co-Pt is very strong in comparison with MAE of 0.085 meV/cell (Table-5.4). Hence, Co-Pt nanowire has a noncollinear spin spiral ground state.

In order to investigate the effect of spin orbit interaction and the degree of hybridization on the strength of DMI, we have investigated the shift of energy bands due to SOI at a fixed spin spiral vector \( q = 0.15 \), as shown in the first three panels of Fig. 5.7(a) and 5.7(b). It can be observed that, the SOI influences different parts of the Brillouin zone. The effect of SOI is seen to vary even within a single band with a simultaneous occurrence of positive (red) or negative (blue) shift in the energy.
The spin orbit coupling effects are seen to penetrate deep into the occupied states, in contrast to the effect due to MAE which is near the Fermi energy.

The shift in the band energy eigenvalues due to SOI is observed in large number of occupied states, and can be seen from the colored circles with significantly larger radii in comparison with the bands in the rest of the Brillouin zone (Fig. 5.7). This region of the band structure is highlighted by open square.

The effect due to spin orbit interaction is enhanced and shifts down gradually from the Fermi energy with an increase in the atomic number of 5d element in the nanowire.

The energy separation between the hybridizing orbitals increases with the increase in the atomic number of 5d element in the nanowire except in the case of Fe-Pt. The separation between the orbitals is marked for one such case by an open circle in the band structure plot for visual understanding.

The fourth panel of Fig. 5.7(a) and 5.7(b) shows the contribution due to DMI, when integrated over the entire Brillouin zone and plotted against the energy spectrum of the band structure with the Lorentzian functions. The result for DMI distribution is shown only for Fe-Au and Co-Au chains in Fig. 5.7(a) and 5.7(b). The last panel of Fig. 5.7 shows the $D_{SOI}$ values which are calculated from positive and negative shifts in the energy eigenvalues due to SOI. It can be observed that, the DMI has the largest contribution where the shift in the energy eigenvalues is maximum due to SOI.

In order to understand which states hybridize in the energy band structure at the points where the strength of SOI is maximum, we have performed a site projected and orbital resolved fat band analysis. The orbital character projected energy band structure is shown in Fig. 5.8 for Fe and Au atom in the Fe-Au nanowire. The energy bands which show maximum spin orbit interaction in the energy band structure are $d_{xy}$, $d_{xz}$ and $d_{yz}$ hybridizing orbitals. It can be concluded that, the effective DMI contribution is maximum where the spin orbit interaction as well as the orbital hybridization are maximum.

\[ l(\epsilon, \epsilon_n) = \frac{1}{\pi b} \frac{b}{(\epsilon - \epsilon_n)^2 + b^2} \]  

[2] The Lorentzian distribution $l$ can be written as,
Figure 5.7 – The electronic band structure with the inclusion of SOI is shown for a spin spiral with $q=0.15$ for (a) Fe-5$d$ chains, and (b) Co-5$d$ chains. The red circles indicate the positive difference and the blue circles indicate the negative difference between the eigenvalues with and without SOI. For visual clarity, the radius of the circle is magnified 140 times of the actual difference in eV. The highlighted square shows the area in the band structure exhibiting the maximum SOI effect. The energy levels with SOI along with the Lorentzian distribution are shown for Fe-Au and Co-Au zigzag chains with the SOI density of states in the first Brillouin zone. The fourth panel shows the positive difference between eigenvalues with spin orbit coupling ($\delta \epsilon_{k,j} > 0$) indicated by red curve, and negative difference ($\delta \epsilon_{k,j} < 0$) is indicated by blue curve, whereas the fifth panel is the addition of the positive and negative differences in SOI density of states.
Figure 5.8 – The orbital character of the energy band structure on each site shown for the Fe-Au chain, with the Fermi energy set to zero. In this figure, we have shown only $s$ and $d$-projected orbitals. The majority spins are highlighted by red circles, whereas minority spins are shown by blue circles. The radius of the circle at each $\mathbf{k}, j$ is directly proportional to the respective orbital character. The band structure without SOI is labeled as ‘bare’. The highlighted square shows the area in the band structure where maximum SOI effect is observed.
The physical origin of the DMI is in the spin orbit interaction in the non-inversion symmetric systems. Investigations so far of various transition metal structures have yielded that the DMI has a significant contribution in the formation of chiral magnetic orders. However, not much information is available on what affects the strength and the sign of the DMI. Therefore we have investigated the DMI in the simplest possible system within a tight binding approach to get a very general understanding of the occurrence of the DMI. The simplest system showing non-vanishing DMI is a trimer, which consists of two magnetic atoms and one non magnetic atom with enhanced SOI. Such trimer is shown in Fig. 5.9, which lies in the XY-plane. At the beginning, we assume that, the non-magnetic sites do not have nonzero exchange splitting. However, upon hybridization with the magnetic sites, the induced spin polarization may lead to nonzero exchange splitting on the non-magnetic site. We can safely ignore the SOI in the magnetic atom due to low atomic number, whereas nonmagnetic site exhibits significant SOI.

In order to reduce the complexity, we restrict the theoretical description for the $d_{xz}$ and $d_{yz}$ orbitals only within the tight binding approach, since these orbital give the main contribution to the DMI in infinite length $3d-5d$ bi-atomic nanowire, as discussed in the previous section. The Hamiltonian consists of three parts:

$$ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{mag}} + \mathcal{H}_{\text{SOI}}. $$

(5.3)

$\mathcal{H}_0$ describes the spin-independent hopping elements and onsite energies of the system, $\mathcal{H}_{\text{mag}}$ describes the magnetic interaction within the Stoner model$^{[276, 277]}$ and $\mathcal{H}_{\text{SOI}}$ introduces the SOI. The onsite energies are denoted as $E_i$ and they do not depend on the type of the orbital instead only on the type of the atom.$^3$ The onsite energy difference ($\Delta E$) between magnetic and non-magnetic site has a significant effect on the hybridization. The hopping elements of $\mathcal{H}_0$ are described via the Slater-Koster parametrization scheme,$^{[278]}$ hence three types of parameters are needed, viz., $V_{dd\pi}$ and $V_{dd\delta}$ to describe hopping elements of the magnetic and the non-magnetic site. We do not need $V_{dd\sigma}$, since our geometry lies in the XY plane. We do not use direct hopping between one magnetic site to another magnetic site in the model, as they are

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$^3$That makes the states $t_{2g}$ and $e_g$ undifferentiated!
not useful to obtain the DMI.

The magnetic Hamiltonian is described by the Stoner model as well as the non-collinear magnetism.[279, 280]

\[ \mathcal{H}_{\text{mag}} = -\frac{I_i}{2} \mathbf{m}_i \cdot \sigma, \]  

(5.4)

where, \( I_i \) is the Stoner parameter of the \( i^{th} \) atom, \( \mathbf{m}_i \) is the magnetic moment of \( i^{th} \) site, and this is independent of the orbital \( \mu \). The vector \( \sigma \) describes Pauli matrices. Since the geometry lies in the \( XY- \) plane, the symmetry of the structures that gives DMI leads the moments to rotate in the \( XY- \) plane. Hence the magnetic moment can be written as,

\[ \mathbf{m}_i = |m_i| (\cos \varphi \cdot \mathbf{e}_x \pm \sin \varphi \cdot \mathbf{e}_y) \]  

(5.5)

The plus sign is for \( i = 1 \), whereas the minus sign is for \( i = 2 \), respectively. We call the angle within the \( XY- \) plane with respect to the \( X \) axis, by \( \varphi \).

Since DMI is mainly due to SOI, it is important to write the SOI matrix which contains the term \( \mathbf{L} \cdot \sigma \) in the atomic orbital representation. Here, we introduce the parameter \( \xi \) for the the non magnetic site as:

\[ [\mathcal{H}_{\text{SOI}}]_{\mu \alpha}^{\nu \sigma} = \frac{1}{2} \xi_i \cdot \langle \mu \sigma | \mathbf{L} \cdot \sigma | \nu \sigma' \rangle \cdot \delta_{ij}. \]  

(5.6)

The SOI martix in representation of \( (d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}) \) orbitals can be given as following:

\[ [\mathcal{H}_{\text{SOI}}]_{\sigma}^{\sigma} = \pm \frac{1}{2} \xi_i \begin{pmatrix} 0 & 0 & 0 & 2i & 0 \\ 0 & 0 & -i & 0 & 0 \\ 0 & i & 0 & 0 & 0 \\ -2i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \]  

(5.7)

We write \( \sigma = \uparrow \) for plus sign and \( \sigma = \downarrow \) for negative sign. The spin flip contribution of the SOI matrix can be written as:

\[ [\mathcal{H}_{\text{SOI}}]^{\uparrow \downarrow} = \frac{1}{2} \xi_i \begin{pmatrix} 0 & -i & 1 & 0 & 0 \\ 1 & 0 & 0 & -1 & \sqrt{3} \\ -1 & 0 & 0 & -i & -i\sqrt{3} \\ 0 & 1 & i & 0 & 0 \\ 0 & -\sqrt{3} & i\sqrt{3} & 0 & 0 \end{pmatrix}, \]  

(5.8)

The \([\mathcal{H}_{\text{SOI}}]^{\uparrow \downarrow}\) can be written as the complex conjugate of the above matrix.

We calculate the DMI within the first order perturbation by diagonalizing the Hamiltonian \( (\mathcal{H}_0 + \mathcal{H}_{\text{mag}}) \). We use the eigenvalues \( \varepsilon_n \) and eigenvectors \( \Psi_n \) to determine the contributions in the first order perturbation

\[ \Delta \varepsilon_n = \langle \Psi_n | \mathcal{H}_{\text{SOI}} | \Psi_n \rangle \]  

(5.9)

The DMI can be evaluated by the expression:

\[ E_{\text{DMI}} = \sum_n \Delta \varepsilon_n \cdot f(\varepsilon_n, E_f), \]  

(5.10)
where \( f(\epsilon, E_f) \) displays the Fermi-Dirac occupation function and \( E_f \) is the Fermi energy. Note that the SOI-matrix is local on the sites, therefore only matrix elements of the same site can contribute to \( \Delta \epsilon_n \). Additionally, due to \( \xi_i = 0 \) for the magnetic sites only the matrix elements between the states of the non-magnetic site can contribute to \( \Delta \epsilon_n \). The matrix elements \( \langle \mu \sigma | \mathbf{L} - \sigma \mathbf{\nu} \mathbf{L}' \rangle \) of Eqs. 5.7 and 5.8 restrict the contributions to a couple of transitions. It is insightful to use the \( x \)-axis instead of the \( z \)-axis as global spin quantization axis, because it allows for a deeper insight using the spin-resolved LDOS. Therefore \( \uparrow \) and \( \downarrow \) refer to the spin up and spin down components pointing along the \( x \)-direction henceforth. As a consequence, before the large spin-conserving contribution \( d^\sigma_{xz} \rightarrow d^\sigma_{yz} \) of Eq. 5.7 in representation of \( z \) as spin quantization axis vanishes, whereas the spin-flip contribution \( d^\uparrow_{xz} \rightarrow d^\downarrow_{yz} \) and vice versa are giving a large contribution to the system of Fig. 5.9 in representation of \( x \) as spin quantization axis.\[281\] In the simplified model of only two orbitals on the non-magnetic site this is the only transition, which can contribute to the DMI.

Now the following questions arise: what role does the non-collinear magnetic structure play, if only the non-magnetic states enter \( \Delta \epsilon_n \)? Why is the breaking of the inversion-symmetry important? Which properties determine the sign of \( \Delta \epsilon_n \)? We discuss these questions by analyzing the SOI contributions \( \Delta \epsilon \) with the help of the LDOS of the unperturbed system.\[4\]

For the calculation of the LDOS, broadened Lorentzian functions have been used to improve the visibility. The LDOS can be presented site-, orbital- and spin-resolved to allow for a detailed analysis. First the role of magnetism is discussed by comparing the LDOS of the ferromagnetic case with the maximally canted case of \( \varphi = 45^\circ \) as displayed in Fig. 5.10. If the magnetic moments of the magnetic sites are ferromagnetically aligned as in Fig. 5.10(a), no DMI can be observed.\[5\] \( \Delta \epsilon \) vanishes, because each eigenenergy has either \( d_{xz} \)- or \( d_{yz} \)-character of the non-magnetic site but not both. Due to the artificial Lorentzian broadening of about 25 meV, the eigenenergies 1 and 2 around the Fermi energy in Fig. 5.10(a) seem to contribute largely to the DMI. However, a more closer look should reveal, that eigenenergy 1 exhibits only \( d^\uparrow_{xz} \)- and eigenenergy 2 only \( d^\downarrow_{xz} \)-character. Therefore their eigenfunctions can not contribute to DMI. In contrast, the case of \( \varphi = 45^\circ \) of Fig. 5.10(b) shows that the non-collinearity of the magnetic sites is crucial to obtain non-vanishing DMI. The \( d_{xz} \)-orbitals of the magnetic sites hybridize with the orbitals of the non-magnetic site and induce spin-polarization. In the non-collinear case this hybridization differs in the spin-channels, which leads to non-vanishing \( (d^\sigma_{xz} \leftrightarrow d^\sigma_{yz}) \)-contributions.

The SOI contributions in Fig. 5.10(b) show an interesting characteristic behavior. Each contribution comes along with an energetically slightly shifted contribution of opposite sign. Therefore the DMI vanishes automatically for the maximum occupation number of 8 electrons. In the above case of 6 electrons, where the Fermi edge lies in between the contributions of opposite sign, asymmetric exchange can occur. Due to the complicated nature of \( \Delta \epsilon(E) \), it is understandable why the amplitude and the sign of the asymmetric exchange could be very sensitive to the number of electrons, i.e. the specific elements.

\[4\] If not mentioned explicitly, we have used following parameters for the calculations: the onsite energies of the magnetic sites are \( E_m = 0 \) eV and the onsite energy for the non-magnetic site is \( E_n = 1 \) eV. As hopping parameters from the magnetic to the non-magnetic sites and vice versa, we have chosen \( V_{ddn} = 0.9 \) eV and \( V_{ddm} = -0.1 \) eV. The exchange splitting of the magnetic sites is \( 1.152 \) eV. The SOI-parameter \( \xi \) of the non-magnetic site is \( 0.6 \) eV.

\[5\] For the antiferromagnetic alignment the asymmetric exchange vanishes due to a two-fold degeneracy of each eigenenergy.

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5.4 $d$-orbital Tight Binding Model of The Dzyaloshinskii-Moriya Interaction in the zigzag Trimer

Figure 5.10 – The site-, orbital- and spin-resolved LDOS of the trimer is displayed for the cases (a) $\varphi = 0^\circ$ and (b) $\varphi = 45^\circ$. In each case the 8 eigenenergies are displayed in an upper panel above the LDOS. The corresponding spin-resolved LDOS with the X-axis as global spin quantization axis is displayed for both cases with the red curve showing the LDOS of the magnetic site (m) in the $d_{xz}$-orbital, whereas the black solid curve and the black dashed curve display the LDOS of the $d_{xz}$- and $d_{yz}$-orbital of the non-magnetic site (nm). Note that the LDOS of the non-magnetic site has been enhanced by a factor of 5. In the case of $\varphi = 45^\circ$ the first-order SOI contribution $\Delta \varepsilon(E)$ is shown depending on the energy using the same Lorentzian broadening of 25 meV as for the LDOS. To prevent misunderstandings, for the two eigenenergies 1 and 2 around the Fermi energy in case (a), either $d_{xz}^\uparrow$- or $d_{yz}^\downarrow$-character is indicated in the figure. Therefore they do not contribute to DMI.

Figure 5.11 – The site-resolved LDOS of the trimer within the two- $d$-orbital tight-binding model is shown for two different onsite energy differences $\Delta E$: (a) $\Delta E = 3$ eV and (b) $\Delta E = 0.5$ eV. The maximally canted case with $\varphi = 45^\circ$ has been considered. The 8 eigenenergies of the system are displayed in the upper panel for each case. The site-resolved LDOS is displayed above, where the red curve shows the LDOS of the magnetic sites (m) and the black curve the LDOS of the non-magnetic site (nm). The energy-resolved first-order SOI contribution $\Delta \varepsilon(E)$ is shown in the lower panels. The inset displays the onsite energy difference between the non-magnetic site and the magnetic sites (black: nonmagnetic, red: magnetic). A reasonable bandwidth of about $1 - 2$ eV is indicated by the boxes.
Beside the non-collinearity, the breaking of the inversion-symmetry is also crucial for the appearance of DMI. Contrary to the non-inversion-symmetric trimer as in Fig. 5.10(b) in the inversion-symmetric trimer (i.e. the geometrically collinear arrangement of the sites) the LDOS shows no hybridization between the $d_{yz}$-orbital of the non-magnetic site and the $d_{xz}$-orbital of the magnetic sites. Therefore DMI can not occur. Again it could be observed that the hybridization between the orbital of the magnetic sites and the orbitals of the non-magnetic site is crucial. This can be also observed in the ab-initio results of several zig-zag chains reported in this chapter. There the largest contribution to the DMI occurs in the vicinity of the crossing points in the band structure, where the hybridization is the largest, as it can be seen in Fig. 5.7.

It is interesting to take a look at the DMI depending on the difference in the onsite energies $\Delta E$. The degree of hybridization between the magnetic sites and non-magnetic site is strongly connected to their difference in the onsite energies. Therefore the DMI should become larger in amplitude for smaller $\Delta E$, as it can be observed in Fig. 5.11. In the case (a) the orbitals of the non-magnetic site and the magnetic sites are almost separated due to a large onsite energy difference of $\Delta E = 3\text{eV}$. Therefore the DMI is smaller than the case (b) with $\Delta E = 0.5\text{eV}$, where the orbitals are strongly hybridizing with each other.

The DMI turns out to be a very delicate quantity even in the simplified two-$d$-orbital trimer model described within a tight-binding scheme. The model displays the simplest possible system with a non-vanishing DMI. We can not deduce a “simple equation” describing the sign and the amplitude for the general case. However, some general features of the DMI could be successfully observed in the trimer regarding the symmetries and the amplitude. DMI can only occur in non-inversion-symmetric, non-collinear magnetic systems and its driving force is the hybridization between the orbitals of the magnetic and non-magnetic sites (i.e., the elements exhibiting strong SOI).

5.5 Summary

In summary, we have systematically investigated the noncollinear magnetic properties of infinite length $3d - 5d$ bi-atomic nanowires. The $3d - 5d$ nanowires show induced magnetization due to the hybridization of the magnetic $d$ orbitals with the orbitals of the non-magnetic atom. The induced magnetization is seen to decrease with an increase in the atomic number of the $5d$ atom in the nanowire. The spin spiral calculations reveal that, the dispersion energy curve is parabolic near the ferromagnetic state ($\mathbf{q} = 0$). Our results for energy difference of ferromagnetic and anti-ferromagnetic calculations performed with spin spiral calculations and collinear supercell calculations agree very well with each other for LDA-VWN and GGA-rPBE exchange correlation functionals. The Fe-Pt and Co-Pt nanowires exhibit degenerate spin spiral ground state at $\mathbf{q} = \pm 0.07$ and $\mathbf{q} = \pm 0.03$ respectively when the spin orbit interaction is not included. With the inclusion of energy due to DMI, the degeneracy is lifted. All nanowires have nonzero DMI, however not all nanowires show noncollinear ground state. This is due to strong MAE competing against DMI. Our results reveal that, only Fe-Pt and Co-Pt nanowires show very strong DMI in competition with the MAE, leading to noncollinear ground state. The MAE dominates over DMI in Fe-Ir and Fe-Au nanowires, and hence show ferromagnetic ground state. However, DMI as well as MAE has no effect on the ground state of Co-Ir and Co-Au nanowires. The energy band structure
in the presence of SOI show that, SOI effect penetrates deep into the occupied states and it is shifted downwards from the Fermi energy as the atomic number of the 5d atom in the nanowire is increased. In order to understand the effect of the d orbital hybridization on the strength of DMI, we have modeled a trimer consisting of two magnetic atoms and one non-magnetic atom. The model shows that, symmetry plays very important role in determining the occurrence of DMI. The degree of hybridization between the magnetic and non-magnetic atoms is crucial to have strength of DMI in the system. We compared the characteristics exhibited by the trimer model with the infinite length 3d – 5d bi-atomic zigzag chain. The general features agree very well with the calculations in infinite zigzag chains.