CHAPTER- 3
ELECTRONIC AND MAGNETIC PROPERTIES OF RARE EARTH ELEMENTS AND HEXABORIDES
Electronic and magnetic properties of rare earth elements and hexaborides

In this chapter, calculations of density of states (DOS), energy band structures and magnetic moments of rare earth elements will be presented. The rare earth elements considered for the study are La, Ce, Pr, Nd, Gd and Lu. Wherever possible, the calculated results will be compared with the experimental results available and also with previously calculated data. This will also be followed by the results of DOS, energy band structures and magnetic moments on the case of rare earth hexaborides like RB$_6$ (where R = La, Ce, Pr, Nd and Sm).

3.1 Rare earth elements:

The calculations are performed (Sandeep et al., 2010a) in the frame work of DFT as stated by Hohenberg and Kohn (1964). The LDA+U (Anisimov et al., 1997) calculations were performed in the parametrization of Perdew and Burke (1996) for the exchange-correlation potential to include the effects of 4f-state electrons which is not determined in LDA or GGA approximations. $R_{MT} \times K_{MAX}$ will calculate the LAPW basis functions for the expansion of the charge density and the potential in the interstitial region and lattice harmonics for the expansion inside the muffin-tin spheres (where $R_{MT}$ is the average radius of the muffin-tin spheres and $K_{MAX}$ is the maximum value of the wave vector $\mathbf{K} = \mathbf{k} + \mathbf{G}$). The dependence of the total energy on the number of $k$ points in the irreducible wedge of the first Brillouin zone has been explored within the linearized tetrahedron scheme (Bloch et al., 1994). Core states will be treated in a fully relativistic manner and the valence states are treated semi-relativistically. No shape
approximations has been made for the potential and the charge density. A convergence criteria using self-consistent field was achieved by considering a number of FP-LAPW basis functions with $R_{MT} \times K_{MAX}$. The use of the full-potential ensures that the calculation is completely independent of the choice of the sphere radii, inside the muffin-tins. An energy cut-off of -122.4 eV is taken to separate the core states from the valence states. Self-consistency is achieved by setting the convergence of both the total energy and the eigen values to be smaller than $10^{-4}$ eV. WIEN2k code (Blaha et al., 2008) is employed for the computation of DOS and bandstructures of La, Ce, Pr, Nd, Gd and Lu. The lattice parameters were taken to be $a = b = 3.75$ Å and $c = 6.07$ Å for La, $a = b = 3.65$ Å and $c = 5.96$ Å for Ce, $a = b = 3.67$ Å and $c = 5.92$ Å for Pr, $a = b = 3.66$ Å and $c = 5.90$ Å for Nd, $a = b = 3.64$ Å and $c = 5.78$ Å for Gd and $a = b = 3.50$ Å and $c = 5.55$ Å for Lu (Wyckoff, 1963; Spedding et al., 1956). All the rare earth elements considered in the present work are studied in their hexagonal structure with space group $P6_3/mmc$. The lattice co-ordinates used for rare earth atom is $(1/3, 2/3, 1/4)$. There was 1 independent atom with a total of 2 atoms per unit cell for all the elements. The radius for the muffin tin sphere was chosen to be 2.5 a.u. for all the elements. The $R_{MT} \times K_{MAX}$ is taken to be 7.00 with $G_{min} = 5.6$ and $G_{max} = 12$.

The values of various parameters used in the calculations are given in Table 3.1. Theoretical lattice constants for each system are calculated by volume optimization method (Murnaghan, 1944) using experimental lattice constants. $R_{MT}$ values are chosen in such a way that the charges do not leak out of the spheres.
Table 3.1: Parameters used for the calculations of DOS and band structures of rare earth elements under study.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Element</th>
<th>Space group</th>
<th>Our calculated Lattice constants (Å)</th>
<th>RMT X KMAX</th>
<th>k-points</th>
<th>GMAX</th>
<th>RMT (a.u.)</th>
<th>Our calculated Magnetic Moment (µB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>La</td>
<td>P6_3/mmc</td>
<td>a=b=4.22 c=6.88</td>
<td>7.0</td>
<td>560</td>
<td>12</td>
<td>2.5</td>
<td>0.72</td>
</tr>
<tr>
<td>2.</td>
<td>Ce</td>
<td>P6_3/mmc</td>
<td>a=b=4.22 c=6.88</td>
<td>7.0</td>
<td>560</td>
<td>12</td>
<td>2.5</td>
<td>1.78</td>
</tr>
<tr>
<td>3.</td>
<td>Pr</td>
<td>P6_3/mmc</td>
<td>a=b=4.22 c=6.88</td>
<td>7.0</td>
<td>459</td>
<td>12</td>
<td>2.5</td>
<td>3.09</td>
</tr>
<tr>
<td>4.</td>
<td>Nd</td>
<td>P6_3/mmc</td>
<td>a=b=4.22 c=6.88</td>
<td>7.0</td>
<td>563</td>
<td>12</td>
<td>2.5</td>
<td>4.43</td>
</tr>
<tr>
<td>5.</td>
<td>Gd</td>
<td>P6_3/mmc</td>
<td>a=b=4.22 c=6.88</td>
<td>7.0</td>
<td>652</td>
<td>12</td>
<td>2.5</td>
<td>7.22</td>
</tr>
<tr>
<td>6.</td>
<td>Lu</td>
<td>P6_3/mmc</td>
<td>a=b=3.66 c=5.98</td>
<td>7.0</td>
<td>761</td>
<td>12</td>
<td>2.5</td>
<td>0.24</td>
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</tbody>
</table>
Chapter 3

3.1.1 Results and discussions

In this section, we will present the calculated results (Sandeep et al., 2010b) of the density of states (DOS) and energy band structures in the case of rare earth elements in hexagonal phase. The rare earth elements include Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Gadolinium (Gd) and Lutetium (Lu). In hexagonal phase the rare earth elements were found to have 2 atoms in the unit cell. The magnetic moments were contributed by the two atoms of the rare earth and the interstitial magnetic moment.

(a) Lanthanum

In Fig 3.1, we have shown the spin up and down band structures along with the DOS. Sharp peaks were observed in both the spin up and spin down channel at energy 1.0 eV due to the 4f states of La atom. A small contribution towards of the total DOS was also observed from the interstitials in the h.c.p. structure of La atom not shown in the plots. The valence bands were more dispersive than the conduction band. The results were in qualitative agreement to those obtained by Lang et al. (1981) in their XPS and BIS spectra. The peak in the conduction region was observed at 5.5 eV by Lang et al. (1981) (Fig. 3.7). The contributions at and around the $E_F$ in the valence region were found to agree satisfactorily. The magnetic moment of La was observed to be 0.72 $\mu_B$ contributed by the atoms as well as the interstitials. For La the flat bands at 1.0 eV were observed in both spin channels along all the symmetry directions supplementing the DOS results (Fig 3.1)
Chapter 3

Figure 3.1: Spin up band structure (left), total DOS (middle) and Spin-down band structure (right) of La. \((E_F=0\text{ eV corresponds to the Fermi level})\)

Figure 3.2: Spin up band structure (left), total DOS (middle) and Spin-down band structure (right) of Ce. \((E_F=0\text{ eV corresponds to the Fermi level})\)
(b) Cerium

A similar DOS is observed for Ce in the hexagonal phase in terms of contribution from its 4f-state electrons towards the total DOS. Unlike La, the DOS for Ce has a peak at 0.4 eV in the spin up channel and 0.8 eV in the spin down channel. The XPS and BIS measurements of Lang et al. (1981) have found peaks at 4.0 eV (BIS) and around $E_F$ (XPS). A qualitative agreement was found except for the fact that the BIS peaks were located at a higher level (Fig. 3.7). An exchange splitting of 0.6 eV was observed and the magnetic moment for Ce was due to this splitting in the spin up and down channel. The value of total magnetic moment 1.78 $\mu_B$ calculated in the hexagonal phase of Ce is composed of moments from the moments of Ce atom and the interstitial moment. The magnetic nature of the system is indicated by the total magnetic moment. The band structures for Ce also produces the regions around 0.49 eV in the spin up and 0.8 eV in the spin down channel with close lying energy bands to support the calculated DOS for the system (Fig 3.2). A typical metallic character is observed from the band structures for both La and Ce.

(c) Praseodymium

The total DOS for the Pr atom shows an unsymmetrical DOS peaks in the spin-up and spin-down configurations. The spin up DOS is distributed mainly at the Fermi level, DOS peaks were observed at -0.35 eV, -1.5 eV, 0.2eV and 0.6 eV. In the spin down configuration, DOS contributions were observed mainly in the conduction region with two peaks at 1.55 eV and 1.8 eV in the spin down channel. Lang et al. (1981) have
Chapter 3

Figure 3.3: Spin up band structure (left), total DOS (middle) and Spin-down band structure (right) of Pr. ($E_F=0$ eV corresponds to the Fermi level)

Figure 3.4: Spin up band structure (left), total DOS (middle) and Spin-down band structure (right) of Nd. ($E_F=0$ eV corresponds to the Fermi level)
Chapter 3

reported qualitatively similar results with peaks at -3.0 eV (XPS) and 2.0 eV and 4.0 eV (BIS) (Fig. 3.7). These DOS features are mainly due to the 4f-states of the Pr-atom. An exchange splitting of the order of 0.7 eV was observed which was responsible for the net magnetic moment of the Pr atom. The calculated magnetic moment for Pr atom was 3.09 $\mu_B$. The spin-up and spin-down band structures shown in Fig. 3.3 for Pr also have supported for the metallic nature of the Pr. Further, the spin–up band structure complements the peaks observed in the DOS with flat bands lying at and above the Fermi level. In the spin-down configuration, bands were seen mostly at 1.6 eV. A ferromagnetic nature of Pr was interpreted from the DOS and band structures plots.

(d) Neodymium

Fig. 3.4 showed that the total contributions of the DOS as given by the 4f-state electrons of Nd atom. In the spin-up configuration, sharp peak at $E_F$ was observed. In the spin down configuration, peaks at 2.1 eV and 2.3 eV were noted. Negligible DOS contributions were observed near the Fermi level in the spin down channel. Lang et al. (1981) have shown peaks at -5 eV (XPS) and 2 eV and 4 eV (BIS) in their results (Fig. 3.7). Heden et al. (1971) presented XPS have shown sharp peaks at $E_F$ and -4.0 eV which qualitatively supports our DOS results in the spin up channel. The exchange splitting between the spin up and spin down channels were observed to be of the order of 2.3 eV to give a high magnetic moment of Nd. The magnetic moment calculated for Nd is 4.43 $\mu_B$ including the contribution from the interstitial. This supports the magnetic nature of the element Nd in the h.c.p. structure. The spin-up and spin-down band structures for
Nd in Fig. 3.4 also showed similar results. Spin-up configuration reveals the bands interacting at the Fermi level which are due to the $4f$-bands observed in the DOS plot. The spin-down configuration shows number of bands at 2.2 eV supporting the results observed from the DOS for Nd. This also indicated a FM ground state for Nd.

(g) **Gadolinium**

In the spin up channel, the total DOS contribution is contributed by $4f$ state electrons at -4.7 eV below $E_F$ (Sandeep et al., 2009). The spin down channel showed a peak at $E_F$ due to $4f$ state electrons of Gd-atom. From the total DOS the majority (spin up) electrons do not contribute near the Fermi energy ($E_F$) whereas the minority electrons (spin down) contribute near $E_F$. The total DOS is almost reproduced by the $4f$ state DOS plot as shown in Fig. 3.5. This shows that near the Fermi level total contribution is mainly due to $4f$ states. We have found that LDA+U do not produce significant change in the energy positions of $4f$ states when compared to Shick et al. (2000). Lang et al. (1981) have shown sharp peaks at -2.0 eV (XPS) in the valence and 4.0 eV (BIS) in the conduction region. The calculated band structures showed flat energy bands at -4.7 eV and at $E_F$ supplementing the calculated band structures. The magnetic moment for Gd was calculated to be 7.22 $\mu_B$.

(f) **Lutetium**

In case of Lu (Fig. 3.6), both spin-up and spin down channel showed peaks at -7.8 eV below $E_F$. These peaks were due to Lu-$4f$ state electrons. DOS contributions near $E_F$
Chapter 3

Figure 3.5: Spin up band structure (left), total DOS (middle) and Spin-down band structure (right) of Gd. ($E_F=0$ eV corresponds to the Fermi level)

Figure 3.6: Spin up band structure (left), total DOS (middle) and Spin-down band structure (right) of Lu. ($E_F=0$ eV corresponds to the Fermi level)
Figure. 3.7: Experimental results of Lang et al. (1981) for rare earth elements: combined XPS and BIS spectra (points) with the fitted (full and broken) curves.
Chapter 3

were negligible and were not contributed by the 4f state electrons. Lang et al. (1981) have calculated the experimental spectra and the sharp peaks were noted at -7.0 eV and -8.5 eV in XPS result (Fig. 3.7). The band structures also revealed that the contributions of the Lu-4f with flat bands at -7.8 eV in both spin channels (Fig. 3.6). The magnetic moment of Lu was calculated to be 0.24 $\mu_B$. 


3.2 Rare earth hexaborides:

The calculations were performed (Rai et al., 2010) by using the theoretically optimized lattice parameters and the atomic positions (Wyckoff, 1965) for RB₆. RB₆ have the CaB₆ type crystal structure and may be viewed as a CsCl-type lattice with the Cs replaced by a R ion and the chlorine by a B₆ octahedron. The atomic arrangement is described in terms of the space group $Pm\bar{3}m$. Since R 4f-orbitals are rather localized, the 4f-electron correlations are expected to be strong. Consequently, the LSDA+U calculations (Anisimov et al., 1997) have been chosen to include the on-site Coulomb interaction. The values of on-site Coulomb energies (U) used are 5.00 eV for LaB₆ and CeB₆ (Gschneider et al., 1995), 6.00 eV for PrB₆ and NdB₆, 7.00 eV for SmB₆ (Antonov et al., 2002) and the exchange parameter (J) 1.00 eV was chosen fixed as the usual value for R respectively. The density plane cut-off $R_{MT}*K_{MAX}$ is chosen to be 7.0, where $K_{MAX}$ is the plane wave cut-off and $R_{MT}$ is the muffin-tin radii. This amounts 419, 407, 408, 413 and 416 plane waves for LaB₆, CeB₆, PrB₆, NdB₆ and SmB₆ respectively. To provide a reliable Brillouin zone integration, a set of 120, 84, 165, 120 and 120 $k$ points for LaB₆, CeB₆, PrB₆, NdB₆ and SmB₆ respectively in the irreducible wedge of the Brillouin zone (IBZ) were used. The self-consistency was better than 0.0001 e/a.u.³ for charge density. The stability was better than 0.01 mRy for total energy per cell.
### Table 3.2: Lattice constant and total magnetic moment of rare earth hexaborides

<table>
<thead>
<tr>
<th>RB₆</th>
<th>Space group</th>
<th>Our calculated Lattice constants (Å)</th>
<th>Previous Lattice constants (Å)</th>
<th>Magnetic moments (µ₅B)</th>
<th>Magnetic moments (µ₅B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental</td>
<td>Theoretical</td>
<td>Our results</td>
<td>Previous Total</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rare earth</td>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaB₆</td>
<td>Pm3m</td>
<td>4.176</td>
<td>4.156❯</td>
<td>4.185†</td>
<td>0.00</td>
</tr>
<tr>
<td>CeB₆</td>
<td>Pm3m</td>
<td>4.144</td>
<td>4.141❯</td>
<td>4.084†</td>
<td>0.88</td>
</tr>
<tr>
<td>PrB₆</td>
<td>Pm3m</td>
<td>4.151</td>
<td>4.121❯</td>
<td>-</td>
<td>2.28</td>
</tr>
<tr>
<td>NdB₆</td>
<td>Pm3m</td>
<td>4.157</td>
<td>4.128❯</td>
<td>-</td>
<td>3.38</td>
</tr>
<tr>
<td>SmB₆</td>
<td>Pm3m</td>
<td>4.172</td>
<td>4.133❯</td>
<td>4.156†</td>
<td>5.67</td>
</tr>
</tbody>
</table>

❯ Wyckoff (1965); † Gupta et al. (2010); † † Singh et al. (2007); * Leger et al. (1985); ** Biasini et al. (1997).
Chapter 3

3.2.1 Results and Discussions

The magnetic moments of RB\textsubscript{6} are tabulated in table 3.2. We have observed zero magnetic moment for LaB\textsubscript{6} as was reported by earlier studies of Gupta et al. (2010) and Singh et al. (2007). The magnetic moment for CeB\textsubscript{6} was calculated to be 1.03 µ\textsubscript{B} which is also in agreement with the results of Singh et al. (2007). This was found to agree qualitatively side when compared with the value obtained by Biasini et al. (1997) and Gupta et al. (2010). The moment for PrB\textsubscript{6} was calculated to be 0.09% less than the value reported by Singh et al. (2007). The NdB\textsubscript{6} moment was calculated to be 0.15% higher than the value reported by Singh et al. (2007). The SmB\textsubscript{6} was found to have a moment of 5.87 µ\textsubscript{B} which agrees well with the result obtained by Gupta et al. (2010) and is higher than the moment calculated by Singh et al. (2007) by 4.2%.

From the DOS plots of LaB\textsubscript{6}, we obtained various peaks in both spin channels [Fig 3.8 (a)]. The peaks at -17.5 eV is due to La-5\textit{p} electrons, -15.5 eV is due to B-2\textit{sp} electrons [Fig 3.8 (b, d)]. The extending DOS between -10.75 eV to -1.9 eV in the valence region is observed. The DOS of La-5\textit{d} electrons [Fig 3.8 (c)] cuts the E\textsubscript{F} in both spin channels showing the metallic behavior of the system. Sharp peak at 1.25 eV in the conduction region is found due to La-4\textit{f} electrons [Fig 3.8 (d)]. We also observe hybridization between La-5\textit{d} and B-2\textit{sp} electrons [Fig 3.8 (b-c)] above 1.25 eV for both spin channels. The total and partial DOS shown in [Fig. 3.8 ] is in qualitative agreement with Singh et al. (2007). The band structure plots of LaB\textsubscript{6} are shown in Fig. 3.9 (a-b) for
Figure 3.8: DOS plots of (a) LaB₆ total DOS, (b) B-2s and B-2p DOS, (c) La-5deₐ and t₂g and (d) La-5p and La-4f. (Eₐ=0 eV corresponds to the Fermi level)
Figure 3.9 (a-b): Spin polarized band structure of LaB$_6$: (a) majority spin (b) minority spin. (E$_F$=0 eV corresponds to the Fermi level)
spin up and spin down configurations along various symmetry directions. The lowest lying bands at -17.5 eV in both the spin channels were due to La-5p electrons. The energy bands at -15.5 eV were due to B-2sp electrons. The groups of bands formed from -10.75 eV to -1.9eV were due to B-2sp electrons. The conduction bands were less dispersive than the valence bands and the bands at 1.25 eV were due La-4f states in both spin channels. Above 1.25 eV in the conduction region, energy bands are due to La-5d electrons with few B-2sp states. The energy bands at $E_F$ along $\Gamma M$ direction are due to the hybridization of B-2sp and La-5d bands. This was also reported by Hossain et al. (2005) in their plane wave pseudopotential energy calculation method as the existence of electron pocket.

The total and partial DOS plots of CeB$_6$ are shown in Fig. 3.10 (a-d) for spin up and spin down configurations. Sharp peaks were observed at -15.5 eV due to B-2sp electrons. The DOS extending from -9.9 eV upto 2.3 eV in the valence region are due to B-2sp electrons with few Ce-5d electrons. We observe that Ce-5d and 4f electrons cuts the $E_F$ level with peaks at 0.0 eV and 0.3 eV in spin up channel. While in spin down channel, sharp peak was observed at 1.0 eV due to Ce-4f electrons in the spin down channel. We observe an exchange splitting of Ce-4f states in spin up and spin down with an energy difference of 0.8 eV. The magnetic moment value is contributed by this splitting of the Ce-4f state electrons. Hybridization between Ce-5d and B-2sp electrons for both the channels were seen in the conduction region beyond 1.2 eV. From the total and partial DOS plots we observe that B-sp states [Fig 3.10 (b)] slightly changes with
Figure 3.10: DOS plots of (a) CeB₆ total DOS, (b) B-2s and B-2p DOS (c) Ce-5de₉ and t₂g and (d) Ce-5p and Ce-4f. (Eᵥ=0 eV corresponds to the Fermi level)
results of Singh et al. (2007). It is also observed that the peak occurring at -2.5 eV of spin up channel in their calculation is contradicting to our result as we observe a peak at 0.0 and 0.3 eV due to Ce-4f electrons in spin up channel. In addition to B-5sp and Ce-5d contributions at $E_F$, we have also seen Ce-4f contributions at $E_F$ in the spin up channel which was not observed earlier. The 4f bands were noted with much higher DOS states when compared to other electronic states (B-2sp, Ce-5p and Ce-5d) unlike results provided by Singh et al. (2007) where the intensity of Ce-4f DOS were shown comparable. The band structures plots for spin up and down channels for CeB$_6$ are shown in Fig 3.11 (a-b) along various symmetry directions. The bands in the core and semi core regions were contributed by B-2sp and Ce-5p as were contributed in the case of LaB$_6$. The qualitative difference noted for CeB$_6$ was the position of Ce-4f bands at and above the $E_F$ in the spin up and spin down channels respectively. The bands in the conduction regions were due to Ce-5d, B-2sp state electrons.

Fig 3.12 (a-d) shows the total and partial DOS plots of PrB$_6$ in spin up and spin down configurations. The peaks at -15.1 eV in both the spin channels were contributed by B-2sp and Pr-5p state electrons. The DOS of Pr-5d with few B-2sp electrons are contributing in the conduction region above 2.0 eV in both spin channels. In spin up channel, DOS due to Pr-4f was seen to contribute exactly at $E_F$ whereas in the spin down channel Pr-4f were found to contribute in the conduction region with peak situated at 1.65 eV [Fig. 3.12 (d)]. The magnetic moment of PrB$_6$ was due to the occurrence of exchange
Figure 3.11 (a-b): Spin polarized band structure of CeB₆; (a) majority spin (b) minority spin. (Eₓ=0 eV corresponds to the Fermi level)
Figure 3.12: DOS plots of (a) PrB₆ total DOS, (b) B-2s and B-2p DOS (c) Pr-5dₑ₉ and t₂g and (d) Pr-5p and Pr-4f. (Eₚ=0 eV corresponds to the Fermi level)
Figure 3.13: (a-b): Spin polarized band structure of PrB$_6$: (a) majority spin (b) minority spin. ($E_F=0$ eV corresponds to the Fermi level)
splitting which is of the order of 1.5 eV between the Pr-4f state electrons in spin up and down channel [Fig. 3.12 (d)]. Two DOS peaks were noted by Singh et al. (2007) in the spin up channel below and at $E_F$. This contradicts our findings as there is a sharp peak at $E_F$ in our result due to Pr-4f state electrons. In the spin down channel of the conduction region, Singh et al. (2007) have reported the peak due to Pr-4f at 10 eV and the localized nature is less pronounced when compared to our results.

Fig 3.13 (a-b) shows the band structures of PrB$_6$ in the spin up and down channels along various symmetry directions. The band at -15.1 eV was due to B-2sp and Pr-5p electrons. In the semi core and valence regions, bands were due to the B-2sp and Pr-d electrons. These bands were seen more dispersive than the conduction region bands as was also noted in the case of LaB$_6$ and CeB$_6$. In the spin up region, bands at $E_F$ were seen to be due to Pr-4f and in the spin down the bands were noted at a slightly higher energy (1.65 eV). The energy bands in the conduction region are due to B-2sp and Pr-5d state electrons mostly above 2.0 eV for both spin channels.

Fig 3.14 (a-d), shows the total and partial DOS plots of NdB$_6$ in spin up and spin down configurations. From the total DOS we have observed peaks at -15.1 eV due to B-2sp state electrons [Fig. 3.14(b)]. Energy ranging between -10.25 eV to -1.38 eV, the DOS contributions are due to B-2sp and Nd-5d electrons [Fig. 3.14 (b-c)]. At $E_F$, sharp peak due to Nd-4f was observed for spin up channel, while it observed at 2.25 eV in the conduction region for spin down channel [Fig. 3.14 (d)]. The exchange splitting of the Nd-4f bands was of the order of 3.5 eV which is responsible for the magnetic nature of
Figure 3.14: DOS plots of (a) NdB₆ total DOS, (b) B-2s and B-2p DOS (c) Nd-5de₈ and t₂₅ and (d) Nd-5p and Nd-4f. (E₉=0 eV corresponds to the Fermi level)
Figure 3.15 (a-b): Spin polarized band structure of NdB₆; majority spin (a) minority spin (b). (Eₚ=0 eV corresponds to the Fermi level)
NdB₆. DOS contribution above 3.5 eV were mainly due to the Nd-5d electrons. The Nd-4f peak was found to occur at -7.5 eV in the spin up channel by Singh et al. (2007) which is contradicting the peak in our result. In the spin down channel Singh et al. (2007) have shown the peak due to Nd-4f occurring at similar energy value above E_F. The band structures of NdB₆ are shown in Fig 3.15 (a-b) for spin up and spin down configurations along various symmetry directions. The bands at -17.5 eV were due to Nd-5p electrons. The bands at -15.0 eV in both spin channels are contributed mainly by B-2sp electrons. Energy ranging between -10.25 eV and -1.38 eV, energy bands were contributed by both B-2sp and Nd-5d state electrons. The bands at E_F in the spin up channel were due to Nd-4f state electrons, while in spin down it is observed at 2.25 eV of the conduction region. In the conduction region bands were seen less dispersive in nature and were contributed by B-2sp and Nd-5d electrons. The position of the sharp peak at E_F in the spin up channel is contradicting to the results reported by Singh et al. (2007) whereas it agrees with the peak above E_F in the spin down channel. The bands in the conduction regions were seen comparatively less dispersive when compared to those of Singh et al. (2007).

The total and partial DOS plots of SmB₆ in both spin channels are shown in Fig. 3.16 (a-d). The DOS contributions were seen at -15.0 eV and between -10.25 eV to -1.0 eV are due to B-2sp electrons below E_F [Fig. 3.16 (b)]. Sharp peak in the spin up channel at -0.5 eV, -0.25 eV and 0.1 eV due to Sm-4f electrons are observed. Similarly, for spin down case peaks due to Sm-4f electrons are noted at 3.0 eV and 3.9 eV respectively in the conduction region. The exchange splitting of the Sm-4f state electrons were noted to
Figure 3.16: DOS plots of (a) SmB$_{6}$ total DOS, (b) B-2$s$ and B-2$p$ DOS (c) Sm-5$d$-e$_{g}$ and $t_{2g}$ and (d) Sm-5$p$ and Sm-4$f$. ($E_{F}$=0 eV corresponds to the Fermi level)
Figure 3.17 (a-b): Spin polarized band structure of SmB₆; majority spin (a) minority spin (b). \( E_F = 0 \text{ eV} \) corresponds to the Fermi level.)
be 4.0 eV which is the origin of its magnetic ground state. In the conduction region, DOS contributions were mainly due to Sm-5d [Fig. 3.16 (d)] and B-2p state electrons [Fig. 3.16 (b)]. The Sm-4f peak was found to agree with Singh et al. (2007) in the spin up region while for spin down, the peak observed by them are lower in energy. The band structures plots of SmB$_6$ for spin up and spin down channels are shown in Fig. 3.17 (a-b) along various symmetry directions. The energy bands at -14.75 eV is due to B-2sp state electrons. The bands occurring between -10.25 eV and -1.0 eV are mostly contributed by B-2sp and few Sm-5d electrons. In the vicinity of the Fermi level, energy bands are contributed by Sm-4f electrons in spin up channel, while energy bands due to them in spin down occurs between 3.0 eV and 3.9 eV. Above $E_F$, the bands were less dispersive and were mainly contributed by Sm-5d and B-2p state electrons. Thus, the full potential spin polarized electronic and magnetic properties were calculated for RB$_6$ with the calculations of the optimized value of the lattice constants. For this purpose, we have the LSDA + U method. Metallic ground states with band overlap (R-5d and B-2p) at the X symmetry point were indicated by the band structures. More importantly, the overlap of spin up and spin down is the same. The value of the total magnetic moment increases from LaB$_6$ to NdB$_6$. We have presented calculations for the rare earth hexaborides in the FM, because most of the rare earth hexaborides are ferromagnetic at low temperatures. The main reason behind the contradictions noted in our studies when compared to the results of Singh et al. (2007) must be due the variance in lattice parameters which were optimized in the present case. Also the $k$ points were chosen such that the corresponding
self consistent field energy value remains almost constant. We have provided the band structure plots for RB₆ in addition to DOS which were not shown by Singh et al. (2007) except for LaB₆, NdB₆ and GdB₆. In our studies we have shown each of the partial DOS for the description of $s$, $p$, $d$ and $f$ states of the atoms forming the compounds. The $4f$ DOS contributions were found to have higher intense DOS when compared to those reported by Singh et al. (2007).