ABSTRACT

After the discovery of NiO, a correlated electron system with unusual ground state properties, the grand edifice of band theory became inadequate. The thesis entitled "Density Functional Description of the Electronic structure of Some Correlated Electron Systems" is an attempt to understand primarily the validity of density functional theory (DFT) when applied to strongly correlated systems and also to understand the correlation effect through doping studies. In this connection a series of such systems has been chosen and a detailed study has been made to see exactly when and where DFT fails. Ground state properties such as magnetic moment, equilibrium lattice parameter and cohesive energy have also been calculated for some of these compounds.

The electronic levels of atoms broaden out to be bands when they are placed in the lattice (solids) due to the inter-atomic interactions. There exists several methods for calculating the electronic structure or band structure of a solid. Linear methods, in general, are the most advantageous as they use minimal basis sets with desired accuracy. Since the present work involves systems with many atoms per cell the linear muffin-tin orbital (LMTO) and the tight-binding linear muffin-tin orbital (TB-LMTO) methods turn out to be a good choice.

The band structure calculations of all the systems described in this thesis have been carried out using the above linear methods within the atomic sphere approximation and the ground state properties have been calculated within DFT in its local density approximation (LDA). Self consistency in energy for all the systems studied was achieved to an accuracy of $10^{-5}$ Ry with 75 or more k-points within the irreducible part of the Brillouin zone. The details of the work carried out are the first ever calculations and are as follows.

To start with, the electronic structures of the antiferromagnetic (AF) $KMF_3$ ($M=\text{Mn,Fe,Co and Ni}$) systems are presented. Strongly correlated insulating systems can be classified as charge transfer (CT) type and Mott-Hubbard (M-H) type depending on the values of the onsite Coulomb repulsion ($U$) and the CT energy ($\Delta$) by the Zaanen-Sawatzky-Allen scheme. These systems fall into the former type with $\Delta < U$. All these systems were found to be AF insulators with type G magnetic ordering. A further interest in them is that they crystallise in the cubic perovskite structure at room temperature which is the structure of many of the parent compounds of the high $T_c$. The charge state of the $M$ atom is $2^+$. All of them have partially filled $d$-bands and hence their insulating property
The band structures were computed using the conventional LMTO method. The calculations provide a fairly good description of the electronic states in these systems. The crystal field (\(CF\)) splitting of the \(M-3d\) bands into two fold triplets (\(t_{2g}\)) and doublets (\(e_g\)) is significant and more so is the larger exchange splitting of these bands into up and down spin bands.

The calculations bring out the insulating property of the \(M=Mn\) and \(Ni\) systems which have completely filled \(t_{2g}\) or \(e_g\) bands, though they are strongly correlated systems. whereas the \(M=Fe\) and \(Co\) systems were shown to be metallic contradicting the experimental observations. Still, the other ground state properties calculated, especially the local magnetic moment of the \(M\) cation, were found to be consistent with experiment as anticipated for \(3d\) systems, for which the spin-orbit coupling is less than the \(CF\) splitting. Apart from this the calculated density of states (DOS) for all the systems shows an excellent agreement with that of the other calculations and also with photoemission spectra. The present study leads to the conclusion that the DFT description of the electronic structure is not a complete failure; it is successful whenever either the \(t_{2g}\) or \(e_g\) \(3d\) bands happen to be completely filled (for the \(M=Mn\) and \(Ni\)) as it is in the case of the \(3d\) monoxide series.

A similar type of calculation has been performed using the TB-LMTO method for the perovskite oxide systems \(LaMO_3\) (\(M=Sc, Ti, V, Cr, Mn, Fe, Co\) and \(Ni\)). These systems are of further interest because they show magnetic, non-magnetic and insulator-metal phase transitions as a function of \(M\). It is also the purpose of this work to understand this variation in the magnetic and insulating properties in these systems and to compare the quantitative results with those of Goodenough's (1955, 1971) qualitative classification of them. The system \(LaMnO_3\) is of particular interest as it shows Jahn-Teller (\(J-T\)) distortion. Total energy calculations for these systems confirm their respective high and low spin configurations observed at low temperature. The \(J-T\) distortion present in \(LaMnO_3\) has been exactly identified. The calculations correctly account for the insulating gap in the \(M=Sc, Cr, Fe\) and \(Co\) systems and the values agree fairly with the experiments whereas it fails for \(M=Ti, V\) and \(Mn\) (with octahedral symmetry) basically due to the failure of spin DFT (SDFT) in providing the required splitting within the \(t_{2g}\) and \(e_g\) bands of the \(M\) atoms. However, for \(LaMnO_3\) with its tetrahedral environment, though the correlation in the \(3d\) band persists, the calculations open up an energy gap of about 0.75 eV against an experimental value of 1 eV. These quantitative results for this system further
confirm the earlier conclusions regarding the $KMF_3$ systems showing that the charge state of the $M$ atoms (2$^+$ in $KMF_3$, 3$^+$ in $LaMO_3$) is not relevant. In addition, it becomes clear that $SDFT$ fails in only accounting for the insulating property of the strongly correlated systems when the $M$ atoms with octahedral coordination have partially filled $t_g$ or $e_g$ bands. This is perhaps due to the lack of the correlation effect in lifting the degeneracy present in the $t_g$ or $e_g$ bands. Other properties such as the calculated magnetic moments (which is quite natural for localised 3$d$ band systems with partially filled d shells - the crystal field splitting being very much larger than the spin-orbit coupling), $p$-$d$ band separations and the $DOS$ agree fairly well with experiments.

Furthermore, high pressure studies made for the $M$=$Sc, Cr, Fe$ and $Co$ systems confirm the $Sc$ system to be a direct band insulator and the $Co$ system to be a 'CT' insulator. In the case of $M$=$Cr$ and $Fe$, however, our studies show them to be $M$-$H$ insulators though they are CT insulators. The calculated bulk modulus ($B_0$) and cohesive energies of these compounds are yet to be confirmed by experiments.

The insulator to metal transition ($IMT$) under high pressure in the $LaRhO_3$ system has been calculated and compared with that in its 3$d$ counterpart $LaCoO_3$. The basic reason for this work is to understand the difference in the correlation effect when a 3$d$-$Co$ atom is replaced by a 4$d$-$Rh$ atom. The computed band structures at ambient pressure show that the 4$d$ band width is larger than that of the 3$d$ band suggesting that the correlation effect in the former is less than that in the latter. The pressure studies further confirm the 4$d$ system to be a conventional band insulator which becomes a metal for a volume reduction of about 10%. This is very small compared to that of the 3$d$ system and this feature is consistent with the larger value of $B_0$ obtained for the 3$d$ system. The calculated equilibrium lattice parameter for $LaRhO_3$ deviates from the experimental value by 1.9%. The calculations suggest that strong correlations are not responsible for the insulating nature of $LaRhO_3$ and an explicit calculation of $U$ may confirm the obtained result.

The study of the doping effect on the electronic structure of the $Sr_{1-x}La_xTiO_3$ ($x=0,0.25,0.50,0.75,1$) systems has been carried out. This work also measures the effect of correlation within the framework of $DFT$. Recently Tokura et al. (1993) have done extensive studies on this system with a view to understand the band filling dependence of the electronic properties of correlated narrow band systems for which this material is ideally suited. $SrTiO_3$ is a closed shell band insulator
and electrons are added into the Ti-3d bands with the substitution of Sr by La. This material undergoes a transition from a band insulator (SrTiO$_3$) to a metal with negligible correlations, then to a correlated metal (for 0.95 < x < 0.5) and finally to a M-H insulator (LaTiO$_3$). The calculated band gap for x=0 and the metallic phase obtained for x=0.25 are in excellent agreement with experiment. The system continues to be metallic for 0.25 < x < 0.75 and goes to the AF phase for x=1 and these features also agree well with experimental observations except for the failure in opening up the gap in LaTiO$_3$. As the p-d gap remains almost the same throughout it is clear that the substitution of Sr by La just adds electrons into the conduction 3d bands, agreeing very well with the Hall measurements. Fermi surface studies at x =0.9 as well as at other x values may, however, give a better understanding of the M-H transition.

A similar work on Sr$_{2-x}$La$_x$TiO$_4$ leads to similar conclusions. In addition, pressure studies of Sr$_2$TiO$_4$ reveal that the IMT is due to the overlap of the Ti-3d and the O 2p bands. In this sense the origin of metallisation due to pressure differs from that by doping effects; in the latter case electrons are just added into the d bands of Ti without altering the O-p bands. The pressure parameters were also calculated for Sr$_2$TiO$_4$. Total energy calculations show that the end product for x=2 is an AF system with very low magnetic moment as in the case of LaTiO$_3$.

As a whole the quantitative DFT description of the electronic structures of the KMF$_3$ (M=Mn to Ni) and LaMO$_3$ (M=Sc to Ni) systems reveal precisely that SDFT in its LDA fails to account for the insulating property of the correlated electron systems with an octahedral environment, irrespective of the charge state of the M cations, when the $t_{2g}$ or $e_g$ bands happen to be partially filled. Even for these systems the other ground state properties were found to be reasonable. Specifically, the failure is due to LDA which is incapable of lifting up the degeneracy present in the $t_{2g}$ or $e_g$ bands. This may be remedied by introducing corrections to LDA in the form of self interaction correction (SIC) or by LDA + U calculations. It may also be of interest to know whether the 3d atoms in the 4+ charge state as in Sr$_2$MO$_4$ (M=Ti to Co) can lead to a better understanding of DFT.