Summary

This dissertation presents the results of theoretical investigations of the electron distribution in crystals. Electronic and magnetic properties can be investigated using the theory of quantum mechanics developed at the beginning of the 20th century. The increased power of computational tools enables nowadays the treatment of more and more accurate models to simulate electron motion in crystals or molecules and complement experimental observations and interpretations. Crystals containing transition metal elements are studied in many laboratories for the complex behavior of electrons leading in some cases to intriguing properties like superconductivity or magnetoresistance. These properties are often intimately connected to the open shell character of the transition metal ions, which are susceptible to adopt different electronic configurations and oxidation states depending on their environment. This dissertation focuses on the distribution of electrons between transition metal and ligands and discusses various definitions of oxidation state and charges for the transition metal ions and compares with estimates on the basis of different experimental techniques.

The perovskite oxides treated in this work present some crystal distortions at low temperature. We described the crystals within the embedded cluster approach and also compared with the periodic approach. Much information can be extracted using the quantum mechanical methods that are briefly described in Chapter 2. These methods are aimed at approximating the solutions of the Schrödinger equation, which cannot be solved exactly for such extended systems. However, experience has shown that by choosing the correct approximate quantum mechanical treatment one is able to recover many of the experimental observables. The analysis of the factors that enable to reproduce these observables is of
great importance to guide the design of new materials. In the embedded cluster model, a limited number of transition metal ions and nearest anions are considered to represent the material. To introduce the effect of the rest of the crystal this cluster is embedded in a set of point charges to account for long range electrostatic interactions, whereas the nearest ions around the cluster are represented by model potentials. This cluster (or ”molecular”) material model allows the use of advanced \textit{ab initio} quantum chemical methods that accurately describe the electron distribution in the cluster region including strong local electron correlation. In this thesis the complete active space self consistent field (CASSCF) model is used to find the approximate wave functions. The CASSCF expansion of the N-electron wave function is constructed by distributing a limited number of electrons over a set of relevant valence orbitals, the so-called active space. All other electrons are in doubly occupied orbitals, the inactive orbitals. CASSCF is able to give a reasonable description of the distribution of the electrons of the cluster, but it fails in many cases to reproduce accurately the relative energies of the different electronic states, because the method only partially includes the effects of so-called dynamical electron correlation. This can be improved with the use of many body perturbation theory. In this thesis we employ complete active space second-order perturbation theory (CASPT2). The weak point of the embedded cluster approximation is the size of the considered clusters. We obtained complementary information from calculations in a periodic model. These calculations are based on one-electron band theory, with a simpler wave function model. A crystal can be viewed as a regular array of atoms (or molecules) which follows crystallographic symmetry rules. Bulk properties can be investigated by applying periodic boundary conditions, which are briefly introduced in Chapter 2. In the thesis periodic unrestricted Hartree-Fock (UHF) and hybrid density functional theory (DFT) (B3LYP) calculations are used to determine one-electron properties that lead to few points of comparison with experiment like the band gap and the electron charge distribution.

Chapter 3 is devoted to finding a relation between the observed Mössbauer isomer shifts and computed electronic distribution of transition metal compounds containing iron. Motivation for this study is that it is common practice to relate the Mössbauer isomer
shift with the oxidation state of Fe in the compounds. Multiconfigurational N-electron wave functions are calculated for a series of Fe complexes. We find a linear correlation between the experimentally determined $^{57}$Fe Mössbauer isomer shift and the calculated electron density at the Fe nucleus. However, the analysis of the wave function in terms of valence bond terms shows that there is no straightforward relation between the density at the nucleus, the so-called contact density, and the charge or oxidation state of the iron atom in the complexes. The analysis of the CASSCF wave function expressed in localized orbitals shows that the isomer shift is very sensitive to the weight of charge transfer configurations and hence to the covalency. It gives a measure of the deviation from the formal charge rather than of absolute charge.

Many perovskite oxides exhibit orbital and/or magnetic ordering. Some transition metal oxides are believed to also show charge ordering. However, the ordering of the charge is still not well understood. This points the interest on CaFeO$_3$, which contains according to the ionic model high valent Fe$^{4+}$ (d$^4$) Jahn-Teller (JT) active ions but shows, instead of JT distortions, an alternative type of distortion interpreted as charge disproportionation at low temperature. In chapter 4 we use the embedded cluster approach to study the ground state of CaFeO$_3$ and the pressure induced spin transition observed in this material. Ab initio calculations have been performed to clarify the character of the ground state of the high temperature phase of CaFeO$_3$ at different external pressures. The analysis of the correlated N-electron wave function of properly embedded [FeO$_6$] clusters in terms of optimal atomic orbitals clearly establishes the character of the ground state as being dominated by ligand-to-metal charge transfer configurations. For all pressures, the number of Fe-3d electrons is around five and the Fe should be considered as a Fe d$^5$ ion. We find a S=2 to S=1 transition around 25 GPa external pressure in the CaFeO$_3$ crystal.

In Chapter 5 three perovskite oxides that undergo different type of distortion for decreasing temperature, are investigated. The character of the ground state is determined with accurate CASSCF wave functions for LaMnO$_3$, CaMnO$_3$ and CaFeO$_3$ crystals. Distortion in the octahedral environment is performed to investigate the evolution of the eigenvalues for the corresponding wave function. These artificial distortions explain why
the LaMnO$_3$ crystal, well know to show orbital ordering, prefers to go through a collective Jahn-Teller distortion while the Fe ions in CaFeO$_3$ avoid the particular d$^4$ electronic configuration and undergo a different type of distortion.

We finally investigate in Chapter 6 two different crystals, CaFeO$_3$ and YNiO$_3$, characterized by a type of distortion that is commonly interpreted as charge disproportionation. The transition metal ions are predicted to keep the same charge for decreasing temperature using either embedded cluster or periodic approaches. The analysis of periodic solutions using UHF and hybrid DFT (B3LYP) demonstrates that there is no reason to consider different oxidation state or charge for the TM ions in these compounds at low temperature. Embedded cluster calculations agree with an almost identical charge on Fe ions in CaFeO$_3$ and Ni ions in YNiO$_3$ crystals in the low-temperature phase. The results from Chapter 3 are used to show that the difference in Mössbauer isomer shift of the two Fe sites in CaFeO$_3$ is not a direct proof of charge disproportionation. The two isomer shifts can also be explained by the somewhat more covalent oxygen metal bond in the large octahedron in comparison to the small one.