Delocalized and correlated wave functions for excited states in extended systems
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d-d Excitations and Charge Transfer States in $LaMnO_3$

ABSTRACT — Ab initio embedded cluster calculations are presented on d-d and charge transfer excitations in cubic and orthorhombic $LaMnO_3$. This theoretical approach allows for an independent evaluation of controversial quantities related to the Mn d-d excitations, such as Jahn-Teller and crystal field splitting parameters as well as Mn 3d exchange interaction. We investigate the effect of the JT distortion and tilting of the MnO$_6$ octahedra on the lowest d-d transitions.

We find 1.3 eV for the JT splitting, $\sim$ 2.0 eV for the exchange splitting and 1.8 eV for the crystal field splitting in the orthorhombic compound. Cluster size effects on the calculated d-d transitions are found to be modest. As expected, the computed charge transfer excitations are influenced more significantly by cluster size effects. We find that the changes in the relative energies of the charge transfer states when the [MnO$_6$] cluster is extended are mainly caused by electronic relaxation effects and a change in the external potential. The highest spin quintet state in the Mn 3d$^4$ manifold and the lowest state (a spin septet) in the charge transfer manifold are separated by $\sim$1.3 eV in the model [MnO$_6$] cluster. This separation decreases to $\sim$ 0.4 eV in the largest cluster.

6.1 Introduction

The intriguing physical properties of the Mn-based perovskite materials have been a focus of interest in the physics of strongly correlated condensed matter in the last years. Depending on the composition $A_{1-x}D_xMnO_3$, where $A$ is a rare-earth element, e.g. $La, Nd, Pr$ and $D$ is a divalent ion such as $Ca, Ba, Sr$, these transition metal (TM) compounds show a large variety of interrelated physical phenomena. These include ferromagnetic (FM), antiferromagnetic (AFM) ordering, so-called orbital or-
ordering and charge ordering [1], colossal magnetoresistance (CMR) effect [2] and diverse phase transitions [3]. The $La_{1-x}D_xMnO_3$ series has particularly attracted much attention mainly due to the colossal negative magnetoresistance effect (CMR), observed in this system [4]. This phenomenon has been described as an AFM insulator to FM metal phase transition [4,6,7], induced by a magnetic field. Different physical mechanisms such as the double exchange model [8], the dynamical Jahn-Teller (JT) effect [9], lattice and magnetic polarons [3,18] etc. have been invoked to clarify the complex nature of the charge, magnetic and lattice order in this material. Clearly, understanding the nature of the interrelated phenomena in these systems, requires information about the electronic structure and properties of the end members of the series, i.e., $LaMnO_3$ and $CaMnO_3$. Numerous experimental and theoretical efforts have been dedicated to elucidate the electronic structures of the two compounds [6,10–24]. In particular the electronic structure of $LaMnO_3$ has been intensively studied theoretically within the periodic UHF approach [5,10], the local (spin) density approximation (L(S)DA (+U )) [14], generalized-gradient corrected relativistic full potential method (GGCRFPM)$^a$ [15], etc. GGCRFPM is a DFT approach which employs the full-potential linearized augmented plane wave method including spin-orbit couplings and GGA corrections.

$LaMnO_3$ has orthorhombic symmetry at RT [31,32] with space group $Pnma$ (the equivalent $Pbnm$ system is also used in some studies [30]). The formal electronic configuration of the $Mn^{3+}$ ions is $3d^4$. The $5E_g$ ground state is in a (nearly) $O_h$ site symmetry high spin coupled, characterized by a weak-field electron configuration $t_{2g}e_{g1}^1$. The two-fold orbital degeneracy of the ground state implies a JT type distortion, which splits the degenerate components of $5E_g$ and produces large asymmetric oxygen displacements of the $MnO_6$ octahedra. In addition, the $MnO_6$ octahedra are tilted and the $Mn-O-Mn$ angles are less than $180^\circ$ [30,32].

The valence electronic structure of $LaMnO_3$ contains the local Mn $d$-$d$ excited states and local charge transfer (CT) O $2p$ $\rightarrow$ Mn $3d$ states. Important model parameters associated with the Mn $d$-$d$ excitations are the crystal field (CF) splitting parameter, $10Dq$, the Mn $3d$ exchange splitting and the Jahn-Teller splitting parameter. In a simplistic orbital model the $10Dq$ parameter measures the energy splitting between the Mn $3d$ ($e_g$) and ($t_{2g}$) levels of the $Mn^{3+}$ ion with four $3d$ electrons in the weak, nearly octahedral crystal field of the oxygen ligands. The Mn $3d$ exchange parameter determines the energy splitting between two ($e_g$) levels which differ by a spin flip of the electron. The JT parameter is a measure of the energy splitting of the Mn $3d$ ($e_g$) levels in the distorted structure $^b$. These model parameters have been deduced in several theoretical and experimental studies. In Table 6.1, we have listed these parameters, extracted from some selected studies. We outline briefly some relevant findings in those studies.

The optical conductivity studies performed by Jung et al. [21] suggested that the lowest optical conductivity peak in the spectra should be associated with a transition

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$^a$We adopt the GGCRFPM acronym for future reference

$^b$A description of the crystal structure of $LaMnO_3$ was presented in Chapter 4 in section 4.4. The reader is referred to this section also for the description of the $Mn^{3+}$ configuration.
Table 6.1: CF, JT splitting and Mn 3d exchange parameters, evaluated in some theoretical and experimental studies; The values in the table are in eV;

<table>
<thead>
<tr>
<th>Reference</th>
<th>Approach</th>
<th>JT</th>
<th>exchange</th>
<th>CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jung et al. 21</td>
<td>Optical conductivity spectra</td>
<td>1.9</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>Picket and Singh 5</td>
<td>LAPW</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>Ravindran et al.15</td>
<td>GGCRFPM/FPLAPW(^a)</td>
<td>1.5</td>
<td>3.3</td>
<td>1.1(^a)</td>
</tr>
<tr>
<td>Elfimov, Anisimov et al.20</td>
<td>LSDA +U</td>
<td>1.41</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Satpathy et al.14</td>
<td>LDA +(U)</td>
<td>(\simeq)1.5</td>
<td>(\simeq)3.0</td>
<td>(\simeq)2.0</td>
</tr>
<tr>
<td>Lawler et al.24</td>
<td>Optical transmission spectra</td>
<td>-</td>
<td>-</td>
<td>1.7</td>
</tr>
</tbody>
</table>

across the JT gap which gives rise to a JT splitting parameter of about 1.9 eV. The theoretical study of Allen and Perebeinos [16, 17] within the framework of a model Hamiltonian produces the same JT splitting parameter. To explain the character of the lowest optical conductivity peak in the optical spectrum by Jung [21], Allen and Perebeinos [16, 17] introduced the self-trapped exciton theory within which the lowest electronic excitation is found to be a \(d-d\) transition. This excitation is self-trapped on a single Mn site because the energy gain accompanying a local lattice undistortion (relaxation) is larger then the energy gain associated with an exciton band formation [16,18]. The lattice relaxation leads to a reduction of the energy of the \(d-d\) excited state to about half the energy associated with the maximum intensity of the optical conductivity peak [18].

An alternative interpretation of the optical peak at \(\sim 2.0\) eV is suggested by Quijada and co-workers [59], who studied the temperature dependence of the optical conductivity of \(\text{LaMnO}_3\). These authors found a gradual increase in the oscillator strength of the 2.0 eV feature within the 300-150 K interval [59]. They argued that the dominant contribution to the optical spectral weight of the conductivity peak at \(\sim 2.0\) eV arises from the optical charge-transfer hopping transition between the JT-split \(e_g\) levels at adjacent Mn ions rather than the on-site optical transition of a self-trapped exciton [59].

The density functional band structure (DFBS) studies by Satpathy et al [14] and Elfimov et al. [20] within LD(S)A (+U) yielded a value of \(\simeq\)1.4-1.5 eV for the JT parameter.

Clearly the magnitude of the JT splitting parameter is a question of on-going controversy, so is the interpretation of the optical excitation.

Similar controversy exists with respect to the value of the CF splitting parameter (see the last column in Table 6.1). For instance, Lawler et al. [24] deduced from the optical transmission spectra of \(\text{LaMnO}_3\) a value for the CF splitting parameter of \(\sim 2.0\) eV. The DFBS calculations carried out by Satpathy and co-workers [14] yielded also a value for the CF splitting parameter of \(\sim 2.0\) eV. Ravindran and co-workers [15] obtained within the full potential linearized augmented plane-wave
(FPLAPW) method a twice as small CF parameter.

Contrary to the JT and CF splittings, the estimates of the Mn 3d exchange splitting parameter deduced from experimental and theoretical studies are more consistent. The optical conductivity spectra studies by Jung et al. [21], the GGLSDA band calculations by Ravindran and co-workers [15], the LAPW [19] band calculations by Picket and Singh [6] as well as the \( \text{LDA} + U \) calculations by Satpathy [14] lead to an estimate of the Mn 3d exchange parameter in the range of 3.0-3.5 eV (see Table 6.1). The discussion above indicates that in spite of the numerous studies dedicated to LaMnO\(_3\) the CF spectrum and the magnitude of the CF and JT splittings are still controversial. LaMnO\(_3\) is often cited as a representative of the strongly correlated electron materials. A correct account for the electron correlation effects in these 3d TM compounds is compulsory for obtaining quantitative results.

The model parameters, discussed above, characterize the spectra of the Mn 3d\(^4\) electronic configuration. The d-d excitations which constitute this spectra are excitonic states with a predominantly localized character. A relevant question to be addressed in connection with the valence electronic structure of LaMnO\(_3\) is also the relative position of the hole-electron coupled O 2p \( \rightarrow \) Mn 3d CT states with respect to the d-d excitations. These CT excitations are also considered to be local but not as local as the d-d excitations. In the following discussion, we refer to those hole-electron coupled states as local d-d and CT excitations.

The focus of the present study are some of those excitonic states, which are related to the optical spectra and the optical band gap of the structure. This optical gap is defined at the onset of an intensity increase in the measured optical conductivity, i.e. it is related to a transition at the same \( k \) point of the Brillouin zone. Arima and co-workers [11] carried out an optical conductivity study of 3d TM oxide compounds based on reflectivity spectra measurements and their conductivity data for LaMnO\(_3\) suggested a CT optical gap of \( \sim 1.1 \) eV.

The O 2p \( \rightarrow \) Mn 3d CT excitations have been assigned in the optical conductivity analyses of Jung and co-workers [21] to the high frequency peaks at 4.6 eV and 7.71 eV in the optical conductivity spectra. Quijada et al. [59] show also that the peak centered around 4.0-5.0 eV in their room temperature (RT) conductivity measurements corresponds to CT transitions between the O 2p and Mn 3d (\( e_g \)). The dielectric tensor spectra of the orthorhombic LaMnO\(_3\) obtained by Ravindran et al. [15] within GGRFPM calculations shows also peaks at 4.7 and 8.8 eV associated with O 2p \( \rightarrow \) Mn 3d CT transitions.

In some earlier photoemission spectra analysis by Saitoh and et al. [12], LaMnO\(_3\) has been referred to as a CT insulator with a conductivity band gap of 1.7 eV. They also suggested that the ground state has mixed \( d^4 - d^5 L \) character, i.e. strong covalency of the compound. Chainani, Mathew and Sarma [23] claimed a strong mixing of the Mn 3d and O 2p derived states (from X-ray and ultraviolet photoelectron valence band spectra) and suggested that according to their bremsstrahlung isochromat spectroscopy (BIS) data the conductivity band gap in LaMnO\(_3\) should be about 1.3 eV. Contrary to Saitoh and et al. [12] the analysis of Chainani, Mathew and Sarma [23] placed LaMnO\(_3\) in the Mott -Hubbard insulator regime rather than in the CT regime.
Introduction

Previous studies on related compounds [25–27, 33, 55, 56] have shown that an ab initio quantum chemical study on embedded clusters may provide an accurate determination of the CF and CT excitation energies. Indeed the embedded cluster model combined with a well chosen MC wave function (WF) ensures the proper incorporation of the predominant non-dynamical electron correlation effects and relaxation effects. The dynamical correlation effects are often estimated using the CASPT2 [42] approach. Furthermore the cluster approach allows for extracting information about the validity of the material model, the covalency of the compound, and the degree of localization of the excitation.

In the present study we employ the embedded cluster model combined with the CASSCF / CASPT2 [35] method to investigate the lowest CF and CT excitations in cubic and orthorhombic LaMnO$_3$. A recent similar embedded cluster study on the d-d excitations in cubic and JT distorted LaMnO$_3$, performed by Hozoi et al [33] has shown that the lower part of the valence excitation spectrum is constituted of CF excitations. Hozoi et al [33] have however neglected the tilting of the MnO$_6$ octahedra. The cluster size effects on those d-d excitations have also not been addressed explicitly. Hozoi et al [33] have also not found excitations with predominantly CT character below 3.0 eV. The model cluster employed in their study is a [MnO$_6$] embedded cluster. Taking into consideration that the CT excitations are anticipated to be more delocalized than the CF excitations, the CT energies computed using the small [MnO$_6$] cluster might be overestimated. A recent study on the CF and CT excitations in the related compound CaMnO$_3$, performed by Bordas [56], has demonstrated that indeed the CT energies are affected significantly by the cluster model.

The rest of the chapter is organized as follows. Computational details and structural data for the calculations of the valence electronic structure of LaMnO$_3$ are given in section 6.2. We organize section 6.3 in two parts. In the initial discussion, we focus on the Mn 3d$^4$ CF excitations in the local $O_h$, $D_{2h}$ and $C_i$ symmetries in order to probe the role of the distortions on the CF spectra. We include subsequently the local distortion and the tilting of the MnO$_6$ octahedra. Furthermore the present study allows for an ab initio determination of the model parameters, JT, CF and Mn 3d exchange splitting parameters by relating those parameters to the calculated CF excitation energies. The cluster size effects on the calculated d-d excitations are also discussed. The effect of the cluster expansion on the energy is expected to be insignificant if the excitation is reasonably well localized, which is the case for d-d excitations in many ionic systems.

The second part of section 6.3 is dedicated to the character and relative energies of some lowest local CT excitations. An important question is how localized these CT excitations are. The extent of delocalization is probed by investigating the cluster size dependence of the CT energies. Furthermore the relative position of the lowest CT states with respect to the Mn 3d$^4$ states is addressed.

Finally, we provide an estimate of the error in the excitation energies due to the ideal cubic geometry, used in some calculations, and due to the active space restrictions. We compare our results for the lowest CF excitation energies with the results obtained in other theoretical and experimental works to point out the new
insights in the valence electronic structure of the compound.

### 6.2 Crystal Structure, Material Model and Computational Information

The cooperative JT coupling between the Mn 3d $e_g$ electrons and the oxygen distortions at neighbour $MnO_6$ sites leads to a simultaneous ordering of the octahedral distortions as well as so-called ordering of the occupied $e_g$ orbitals ($d(3x^2-r^2)/d(3y^2-r^2)$ ordering in the ab plane in $Pbnm$ reference system) [43]. To obtain a reliable picture for the Mn 3$d^4$ manifold of the system, the study is carried out for the crystal structure at room temperature. However, we estimate in two separate sets of calculations the influence of the JT distortion and the tilting on the structure of the manifold.

First, we consider the ideal cubic geometry with equal $Mn-O$ distances of 1.95 Å and no tilting. At the next step we take into account the JT distortion, while keeping the tilting angle at 0 degrees. In this JT distorted $MnO_6$ octahedra each $Mn-O_i$ bond length has a value, which is the average between the corresponding experimental $Mn-O_i$ estimate in the tilted geometry and its projection on the $i$ axis, where $i \in \{x,y,z\}$ [33]. Hence, the $Mn-O$ bond lengths have the following values: $d(Mn-O_x)=2.14$ Å, $d(Mn-O_y)=1.90$ Å, and $d(Mn-O_z)=1.95$ Å, where the $z$ direction is along the c axis of the $Pbnm$ reference system. The third step involves accounting for the tilting. At this step we consider the experimental $Mn-O$ distances for the room-temperature tilted structure, which are $d(Mn-O_{x'})=2.18$ Å, $d(Mn-O_{y'})=1.91$ Å, and $d(Mn-O_{z'})=1.97$ Å [30]. Finally, the estimate of the cluster size effect on the computed $d-d$ spectra in the real geometry is discussed. For practical reasons, we choose to investigate the character and relative energies of the CT states and their cluster size dependence in the ideal cubic geometry. We suggest, that this geometry already incorporates the main features of the CT manifold.

In the initial calculations on the Mn 3$d^4$ and CT manifolds, the crystal is modeled with an embedded cluster, centered around a transition metal (Mn) ion: $[MnO_6]^{9−}$. We denote this cluster as [A]. In order to study the cluster size effects on both manifolds, we introduce three types of larger clusters: [B]-$[MnO_6Mn_6]$; [C]-$[MnO_6Mn_6La_8]$ and [D]-$[MnO_6Mn_6La_8O_24]$. In the [B], [C] and [D] clusters the six outer $Mn^{3+}$ ions are represented by $Al^{3+}$. The clusters for the cubic LaMnO$_3$ are illustrated in Figure 6.1. $Al^{3+}$ is a reasonable representation of $Mn^{3+}$, because both ions have equal net charges and similar ionic radii ($r(Al^{3+})=0.67$ Å and $r(Mn^{3+})=0.75$ Å). $Al^{3+}$ is a better representation for $Mn^{3+}$ than a crude point charge representation. The reason for replacing $Mn^{3+}$ by $Al^{3+}$ is, that the number of orbitals in the active space increases significantly with the number of $Mn^{3+}$ ions in the cluster. We note that with our clusters the delocalization of the open Mn-3$d$ orbitals is not possible. The short-range interactions between the cluster oxygen ions and the nearest $Mn^{3+}$ and $La^{3+}$ ions outside the cluster are taken into account by modeling the latter with total ion potentials (TIPs) [46]. There are no basis functions present on these neighbouring ions. The next shells of ions, surrounding the cluster, are represented by a finite
array of point charges (PCs) at lattice positions. The first few shells of PCs have the formal charges of the fully ionic model of the material. The PCs at the outermost shell are optimized to obtain the best representation of the Madelung potential due to the crystal represented by formal ionic charges on a fine grid within the cluster region [33].

The basis sets are atomic natural orbital (ANO) Gaussian-type basis sets. The contraction scheme for each basis set is as follows: Mn (21s15p10d6f)/(6s5p4d), O (14s9p4d/5s4p), Al (17s12p5d4f/3s2p) and O (14s9p4d/3s2p) [45] for the oxygen ions $O^{2-}$ in the largest cluster. In clusters [C] and [D], the core shells up to $(....4d^{10})$ of the $La^{3+}$ ions within the clusters are represented by relativistic ab initio model potentials (AIMPs) [47] with a basis set contraction scheme 13s10p7d/1s2p1d for the valence shell.

The calculations are performed within the CASSCF approach, in which the WF is obtained as a full CI expansion in an active orbital space [35,36]. This WF incorporates to a different extent, depending on the active orbital space, the near-degeneracy correlation and a part of the dynamical correlation effects in the system.

The first estimate of the energies of the $d-d$ excitations is obtained for the cubic geometry by constructing CASSCF WFs in an active space formed by the $e_g$-like and $t_{2g}$-like Mn 3d orbitals and 4 active electrons. Let us denote this minimal active space as CASSCF-d. CASSCF-d accounts for the mixing of the different $d^4 O^{2-}$ configurational state functions (CSFs) in the WF expansions. We extend the active space by adding a set of five correlating virtuals $d'$ of the same symmetry as the Mn 3d-like orbitals: CASSCF-dd'. These virtuals turn out to form a second shell of Mn 3d-like orbitals [40,41]. Previous studies [37,40,41] on local excitations in TM ion compounds have shown that the active space constructed in this manner leads to a variational treatment of a large part of the $d-d$ electron correlation energy. It avoids its overestimation that was obtained within a CASPT2 treatment of this effect [40], based on the CASSCF-d WF as a reference WF.

CASSCF-dd′ accounts for part of the dynamical correlation due to the valence
electrons that are in orbitals which have mainly Mn 3d character [37]. The remaining part of that correlation, plus the correlation effects associated with the semi-core electrons on the TM-ion (Mn-3s, 3p), the ligand O-2s and 2p electrons is accurately treated by CASPT2 [42].

The non-dynamical correlation effects related to CT configurations are accounted for only partially within the CASSCF-dd'/CASPT2 [37]. A better treatment of the differential electron correlation effects on the Mn 3d$^4$ manifold, due to the contribution of CT configurations can be achieved by adding occupied O -2p orbitals to the CASSCF-dd' active space [37]. Some earlier studies [37, 62] on local d-d excitations in bulk NiO and a NiO(100) surface have shown that we can apply a simple criterion in the selection of the O-2p orbitals to be included in the active space. We expect the largest contributions to arise from CT configurations connected to excitations from the O-2p orbitals with the same symmetry character as the Mn 3d orbitals.

The study of low lying CT states also requires extending the active space with occupied ligand O-2p orbitals to CASSCF -(n)pdd'.

The dynamical correlation effect of the valence O-2p electrons can be treated at the CASSCF level, if the active space contains the O-2p orbitals and a set of correlating O $-2p'$ orbitals. However, such an extended active space is too demanding to be handled. Therefore, no ligand O -2p' orbitals are in the active space. Moreover, most of the doubly occupied O-2p are placed in the inactive space. The O-2p orbitals which are relevant either to the CT configurations contributing to the WFs of the Mn 3d$^4$ states or are involved in the CT excitations are kept in the active space. This active space reduction leads to a perturbational treatment of the dynamical correlation of the O-2p electrons, which was shown to be quite accurate [37].

In the study of the CT states, we make a further reduction of the active space by removing the Mn $-3d'$ orbitals from the active space. The resulting active space CASSCF -(n)pd is sufficient to account for the mixing of the various $d^4O^{2-}$ and $d^5O^{1-}$ CSFs in the CASSCF WF of a CT state. However, the large dynamical correlation effect of the valence Mn 3d electrons is no longer accounted for by this CASSCF WF, but treated perturbationally and overestimated by CASPT2 [40]. The correlation effects for the CT states are expected to be larger than for the d$^4$ states, because the $d^5O^{1-}$ states have a larger number of Mn 3d electrons. Therefore, the CT excitation energies obtained with CASPT2 within this active space, should be considered with care. They appear to be lower due to the overestimation of the dynamical correlation, which is different for the ground and the CT states. Taking into consideration all effects of the active space, we provide an estimate of the error in the quantitative results. It is expected that the character and relative order of those transitions is predicted correctly within the CASSCF-(n)pd/CASPT2 approach. Furthermore, CASPT2 accounts for the main orbital relaxation effects accompanying the CT excitations. In the following paragraph, we present a detailed description of the active space, used in the study of the CT states.

The CASSCF active space for the CT states is denoted as CASSCF -(n)pd, where n is the number of active O-2p orbitals. We perform the calculations in $D_{2h}$ symmetry. CASSCF -(n)pd has only active O-2p orbitals in the irreducible representations, where
the $O-2p$ hole resides. There are $n$ $O-2p$ active orbitals in that symmetry species. The value of $n$ is determined by the number of low lying CT states in that particular irreducible representation. For instance, the CASSCF -(3)pd for the ungerade CT states of $T_{1u}$ and $T_{2u}$ symmetry contains 3 $O-2p$ active orbitals in either $b_{1u}$, $b_{2u}$ or $b_{3u}$ in $D_{2h}$. The configurational mixing of the $d^4O^2-$ CSF in the WFs of the CT states is discussed in section 6.3.2. In order to obtain a balanced description of the relative energies of the CT states, the ground state WF is expressed in the active space of only 5 Mn 3d orbitals. The study of the cluster size effects on the CT manifold is carried out also within CASSCF -(n)pd.

In this paragraph, we briefly comment on some details in the calculation of the CASSCF WFs for both manifolds. Some states could not be obtained by optimizing the orbitals for the CASSCF WF of that particular state in a ”single state” calculation. This is due to the fact, that the character of the state for which the WF is optimized changes in each iteration and thus no convergence can be achieved. This optimization problem occurs when the state of interest and another state of the same spatial symmetry and multiplicity as the state required become near-degenerate, when the WF of the other state is expressed in the orbitals of the state of interest. In those cases, we perform an orbital optimization for an average of states. The outcome of this optimization are states WFs expressed in one set of the average orbitals. The lack of a fully optimized orbital set for each state, leads to an increase in the states energies. To obtain the closest approximation to the single state calculation, we increase the weight of the state of interest to the maximum possible value which still leads to a convergent solution [37,62]. This technique has been applied successfully by Geleijns et al. in the calculations on the local electronic (d-d and CT) transitions at the NiO (100) surface [62].

In some calculations on the CT manifold the CASPT2 approach failed to give a correct estimate of the dynamical electron correlation. In those cases, the weight ($\omega$) of the zero-order CASSCF WF in the first-order corrected WF is low compared to the corresponding $\omega$ of the ground state. We considered $\omega$ to be too low if it showed a deviation of more than 4 % compared to the reference $\omega$ of the ground state. This breakdown of CASPT2 is sometimes caused by the appearance of intruder states in the first-order WF [51]. If the Hamiltonian matrix element between this intruder state and the reference WF is not large, the intruder state can be artificially shifted up in energy by adding an arbitrary value to the expectation value of the zero-order Hamiltonian of this intruder state. This approach to avoid the breakdown of CASPT2 is known as level shift technique [49]. Geleijns et. al. [62] have given a justification of this method. However, in some cases the technique applied to shift the energy of an intruder state can introduce another singularity in the energy denominator in the expression for the second-order correction to the energy. N. Forsberg and P.-Å. Malmqvist have introduced an ”imaginary” level shift technique which avoids new singularities [50]. We apply this approach to recover the CASPT2 breakdown that occurred in some of our results.

The Al-2s and 2p electrons were correlated by CASPT2 in clusters [B], [C] and [D]. This has a minor effect on the results. The reason to correlate those orbitals is
technical and makes no difference for the final conclusions.

All calculations are carried out with the MOLCAS program package [48].

6.3 Results and Analysis

6.3.1 Mn d-d excitations

Attention is focused mainly on the lowest localized excitations because they constitute the low energy optical spectra. We calculate the energies of those lowest excitations in the Mn 3d^4 spectra at three levels of distortion of the octahedra. The summary of the results is presented in Tables 6.2, 6.3, 6.4. All states in \(O_h\) and \(D_{2h}\) geometries are obtained in a single state calculation. The analysis of the main electronic configuration of a particular state is based on Mulliken (spin) population analysis (MSPA) and Mulliken gross population analysis (MGPA) of the active natural orbitals (ACNOs). An inspection of the composition of the CI vector of the WFs confirms as well the electronic configurations established in the other analyses. The simplest model of the system in the present study is cluster [A]: [MnO_6]^{9-}.

Cluster [MnO_6]^{9-}

\(O_h\) geometry - ideal cubic structure

The study in cubic symmetry is performed in parallel with that of the non-tilted and real forms in order to clarify the importance of accounting for the JT effect and the tilting for a realistic theoretical description of the compound. Most of the physical properties are directly related to the valence electronic structure, hence it is relevant to investigate the effects of the distortion on the relative energies and character of the valence excitations.

The \(5E_g\) ground state of the [MnO_6]^{9-} in the ideal cubic structure of \(LaMnO_3\) is high spin coupled and characterized by a weak-field configuration \(t_{2g}^2e_g^1\). The configurational composition and relative energies of the lowest states obtained within CASSCF-d are listed in Table 6.2. These states constitute the lowest part of the CF spectra. The CASSCF-d WF of \(5E_g\) is a restricted open shell HF (ROHF) WF, but the WFs of the triplets and the singlets incorporate some non-dynamical electron correlation. Next, we extend the initial CASSCF-d space with a set of virtual orbitals of the same symmetry character as the Mn -3d orbitals: CASSCF-dd'. The configurational composition of the WFs of all states, of Table 6.2, remains practically unchanged within CASSCF-dd'. The total energies of the CASSCF-dd' WFs are lowered compared to the CASSCF-d WFs, but the effect is not substantial. For instance, the ground state energy is lowered by 0.6 eV. As expected, the CASPT2 energies obtained with CASSCF -dd' are raised compared to those obtained with CASSCF-d. This is due to the overestimation of the Mn 3d dynamical correlation with CASSCF-d/CASPT2 [40]. For all states, except the \(5T_{2g}\) state, the CASPT2 corrections on the relative CASSCF energies lead to a decrease in the energies (see Table 6.2). To analyze whether the CASPT2 correction on the CASSCF energy of the \(5T_{2g}\) state has
Table 6.2: 

<table>
<thead>
<tr>
<th>State</th>
<th>( t_{2g}^3 e_{g}^1 )</th>
<th>( t_{2g}^4 )</th>
<th>( t_{2g}^5 e_{q}^2 )</th>
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<th>CASPT2</th>
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<td>0.00</td>
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<td>2</td>
<td>0.99</td>
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<th>CASPT2</th>
<th>( \omega^a )</th>
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</tbody>
</table>

^a Weight of the reference wavefunction  
^b Crystal-field splitting 10 \( Dq \)
an opposite sign due to atomic–dynamical correlation effects, we perform model calculations on an Mn\(^{3+}\) ion in vacuum. The relative CASSCF-dd’ energy of the Mn\(^{3+}\) ion \(^3H\) state with respect to the relative zero energy of the \(^5D\) ground state is 2.82 eV and increases to 3.01 eV at CASSCF-dd’/CASPT2. The CASPT2 correction on the CASSCF energy of \(^3H\) is of the same magnitude and has the same sign as that for the \(^5T_{2g}\) state in the [MnO\(_6\)] cluster. We conclude, that the increase in the relative energy of the \(^5T_{2g}\) state at CASPT2 is mainly due to atomic correlation effects.

MGPA of the ACNOs of the ground state, \(^5E_g\), shows that the occupied \(e_g\)-type orbital has 92 % Mn-3d character. The \(t_{2g}\) orbitals, compared to the \(e_g\) ones are more localized - 97 % Mn-3d. Analogous analysis for the \(^5T_{2g}\) state points out a \(t_{2g}^2e_g^2\) configuration and the same composition of the \(e_g\)- and \(t_{2g}\)-type orbitals as that in the ground state. The occupied \(e_g\)-type orbital of the \(^3E_g\) state has a quite different character- 88 % Mn-3d while the \(t_{2g}\) orbitals preserve the same composition as for \(^5E_g\).

This MGPA analysis indicates a low covalency of the compound. We note, however that within our cluster approximation, the localization of the occupied Mn 3d \(e_g\) orbital may be overestimated. Moreover, to obtain a reasonable estimate of the covalency of the compound, one also needs to consider the contribution of CT configurations in the WF of the Mn 3d\(^4\) states. A recent study on the CF excitations of ideal and JT distorted LaMnO\(_3\), performed by Hozoi et al [33] have shown that the weight of CT configurations in the CI expansion of the ground state WF is less than 15 %. In the next section, we study the covalency of LaMnO\(_3\) by analyzing the configurational composition of the WF of some Mn 3d\(^4\) states.

The relative energies of the lowest d\(^4\) states obtained in cubic geometry follow the Tanabe-Sugano diagrams [52]. We define the CF splitting parameter (10 \(D_q\)) for local \(O_h\) geometry as the energy difference between the high spin coupled \(^5E_g(t_{2g}^3e_g^1)\) and \(^5T_{2g}(t_{2g}^2e_g^2)\) states. Our calculations within CASSCF -dd’ yield 10 \(D_q\) equal to 2.4 eV. The lowest excitation involves a \(^5E_g(t_{2g}^3e_g^1) \rightarrow 3T_{1g}(t_{2g}^4)\) transition at 0.6 eV (see Table 6.2). Furthermore, the Mn 3d exchange parameter, defined as the energy difference between the \(^5E_g(t_{2g}^3e_g^1)\) and \(^3E_g(t_{2g}^3e_g^1)\) states, has a value of 2.2 eV.

Further studies on the JT distorted and tilted forms are performed within CASSCF-dd’.

\section*{D\(_{2h}\) and C\(_i\) geometry -JT distorted and tilted structures}

When distortions are present in the system all degenerate in \(O_h\) states split up. The JT splitting parameter (\(\Delta_JT\)), defined as the energy difference between the \(^5E_g(t_{2g}^3e_g^1(d_{3x^2−r^2}))\) and \(^5E_g(t_{2g}^3e_g^1(d_{xz}−y^2))\) states has a value of 1.23 eV in the \(D_{2h}\) geometry and changes to 1.32 eV when the tilting of the MnO\(_6\) octahedra is taken into account. These values are the relative CASSCF-dd’/CASPT2 energies of the \(^5E_g(t_{2g}^3e_g^1(d_{3x^2−r^2}))\) state obtained in a state average calculation over the two \(^5E_g\) -like states. The occupied \(e_g\)- type orbital in the \(^5E_g\) ground state of the JT distorted form is directed along the longer \(Mn−O_x\) bond and has predominantly \(d_{3z^2−r^2}\) character.
Table 6.3: \([\text{MnO}_6]^{3-}\) cluster representing LaMnO\(_3\). JT distorted crystal structure. Relative energies (in eV) and configurational composition of some excited states in the \(d^4\) manifold; CASSCF/CASPT2 results; active space CASSCF-\(dd'\); CASPT2 correlates the Mn-3s, 3p, 3d and O-2s, 2p electrons; Notations corresponding to the \(O_h\) symmetry are used;

<table>
<thead>
<tr>
<th>State</th>
<th>(t_{2g}^3e_g^1)</th>
<th>(t_{2g}^2)</th>
<th>(t_{2g}^2e_g^2)</th>
<th>CASSCF-(dd')</th>
<th>CASPT2</th>
<th>(\omega^a)</th>
</tr>
</thead>
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<td>0.00, 1.23(^b)</td>
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<td>0.684</td>
<td></td>
<td></td>
</tr>
<tr>
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<tr>
<td>(^5T_{2g})</td>
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<td>2.21, 2.45, 2.53</td>
<td>2.59, 2.83, 2.91</td>
<td>0.678</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Weight of the reference wavefunction  \(b\) Jahn-Teller splitting, \(\Delta_{JT}\)

For the \(^5E_g\) ground state obtained within CASSCF-\(dd'\), we observe about \(~6\%\) \(O-2p_\sigma\) character mixed in the occupied \(Mn\ 3d\ e_g\) type orbital. Analogous analysis for the \(^5T_{2g}\) and \(^3E_g\)-like states points out \(~6-9\%\) \(O-2p_\sigma\) character of the occupied \(Mn\ 3d\ e_g\)-like orbital. The \(t_{2g}\)-like orbitals have \(~2-3\%\) \(O-2p_\pi\). These results suggest that both \(t_{2g}\)- and \(e_g\)-like orbitals are quite localized and hardly mix with \(O-2p_\pi(\sigma)\).

The optical conductivity analysis of Jung et al. [21] for the real structure of the compound pointed out a strong covalent interaction between the \(e_g\)-like and \(O-2p_\sigma\) orbitals which led to broad \(e_g\)-like bands. Our MGPAs analysis for the real structure suggests a low covalency. However as pointed out above the localization of the occupied \(e_g\)-like orbital might be overestimated within the present cluster and WF model.

For the \(^5E_g\) ground state obtained within CASSCF-\(dd'\), we observe about \(~6\%\) \(O-2p_\sigma\) character mixed in the occupied \(Mn\ 3d\ e_g\) type orbital. Analogous analysis for the \(^5T_{2g}\) and \(^3E_g\)-like states points out \(~6-9\%\) \(O-2p_\sigma\) character of the occupied \(Mn\ 3d\ e_g\) like orbital. The \(t_{2g}\)-like orbitals have \(~2-3\%\) \(O-2p_\pi\). These results suggest that both \(t_{2g}\) and \(e_g\)-like orbitals are quite localized and hardly mix with \(O-2p_\pi(\sigma)\).

The optical conductivity analysis of Jung et al. [21] for the real structure of the compound pointed out a strong covalent interaction between the \(e_g\)-like and \(O-2p_\sigma\) orbitals which led to broad \(e_g\)-like bands. Our MGPAs analysis for the real structure suggests a low covalency. However as pointed out above the localization of the occupied \(e_g\)-like orbital might be overestimated within the present cluster and WF model.

We carried out an analysis of the composition of the WFs of the \(^5E_g\) -like ground state and the \(^5T_{2g}\) -like states in order to obtain an estimate for the covalency of the compound. The WFs of the states are constructed within an active space containing 5 Mn 3d (the \(t_{2g}\)-like and \(e_g\)-like) orbitals and 5 O 2p orbitals :CASSCF-5pd. We found the weight of CT configurations in the CI expansions of the WFs of these \(Mn\ 3d\) states to be less than 10%.

The definition of \(10\) \(Dq\) in the distorted forms requires some attention. In \(D_{2h}\) and \(C_i\) symmetry, the \(^5E_g\) and \(^5T_{2g}\) states split into two and three components, respectively. In these local symmetries, we define parameter the energy difference between two average values. \(10\) \(Dq\) changes from 2.4 eV in \(O_h\) to 2.2 eV in \(D_{2h}\) and finally to 2.0 eV in \(C_i\) symmetry (see Figure 6.1). The values are obtained within CASSCF-\(dd'\)/CASPT2. The configurational composition of the WFs and relative energies of the states are summarized in Table 6.4. We performed for the real structure state average calculations, averaging those states that in \(O_h\) are the degenerate components of a quintet (\(^5E_g\), \(^5T_{2g}\)), or a triplet (\(^3E_g\), \(^3T_{1g}\)) state. This optimization maintains the correct character of the active \(Mn-3d\) orbitals, i.e. \(5d\) and \(5d'\).

The decrease of 0.4 eV in the \(^5E_g(t_{2g}^3e_g^1)\) - \(^5T_{2g}(t_{2g}^2e_g^2)\) splitting (\(10\) \(Dq\)) brings the energies of the \(^5T_{2g}\)-like states, close to those of the \(^3E_g\)-like states. Therefore, in Figure 6.1 we observe no separation of the two sets of states. The Mn 3d exchange
Table 6.4: $[\text{MnO}_6]'^{3-}$ cluster representing LaMnO$_3$. JT distorted and tilted crystal structure. Configurational composition and relative energies (in eV) of some excited states in the $d^4$ manifold; CASSCF/CASPT2 results in active space CASSCF-\text{dd}'; CASPT2 correlates the Mn- 3s, 3p, 3d and O- 2s,2p electrons; Notations corresponding to $O_h$ symmetry are used;

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<th>CASPT2</th>
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<td>1.32$^{JT}$</td>
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<td>2</td>
<td>1.71</td>
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<td></td>
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<td>2.59</td>
<td>2.87</td>
<td>0.681</td>
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$^a$ Weight of the reference function $^{JT}$ Jahn-Teller splitting, $\Delta_{JT}$

Figure 6.2: Valence electronic structure of the Mn$^{3+}$ ion in cubic, JT distorted and real geometries; CASPT2 results. The lowest singlet states are not shown. Their energies are presented in Table 6.2;
splitting parameter, defined as the energy difference $3E_g(t_{2g}^3e_g^{1}) - 5E_g(t_{2g}^3e_g^{1})$ decreases from 2.2 eV in $O_h$ to 2.0 eV in $D_{2h}$ and finally to 1.8 eV in $C_i$. This trend suggests that the prolongation of the $Mn-O_x$ bond in the distorted form allows for a delocalization of the $d_{3z^2-r^2}$ orbital directed along this bond.

Although the state average calculations yield a qualitatively correct order of the excitation energies of the states, we perform single state or weighted state average calculations to obtain also an estimate of the extra relaxation gain when the states WFs are expressed in relaxed orbital sets. The relaxation energy is less than 0.1 eV and about 0.1 eV for the quintets and the triplets, respectively.

The JT splitting parameter increases by less than 0.1 eV within the average calculation, whereas the CF ($10Dq$) and exchange parameters preserve their values of 2.0 eV and 1.8 eV, respectively, in both schemes. The CASSCF energies of the $3E_g$-like and $5T_{2g}$-like states place the triplets above the quintets. At CASPT2, the larger dynamical correlation for the triplets leads to a larger decrease in their energies. This results in similar energies for the sets of non-degenerate $3E_g$-like and $5T_{2g}$-like states. In the JT distorted form the average energy of the quintets differs from that of the triplets by 0.3 eV, in the tilted geometry this energy difference is 0.2 eV.

Scalar relativistic effects are found to affect the relative $d$-$d$ excitation energies by less than 0.01 eV, spin-orbit coupling was not considered.

The splitting of the $5E_g$-like states upon distortion, is an expected and well known effect, but the magnitude of that splitting is still controversial. We find 1.23 eV for the JT splitting in $D_{2h}$. When tilting is introduced in the system, this splitting increases by less than 0.1 eV. The lower energy part of the manifold preserves its structure upon tilting, whereas the higher energy part undergoes moderate changes. We notice that the energy order of the $5T_{2g}$- and $3E_g$-like states in the tilted form is similar to that in the JT distorted structure (see Fig. 1, $C_i$ manifold). The decrease in the energies of the $3E_g$- and $5T_{2g}$-like states upon tilting is less or $\sim$ 0.1 eV. In $C_i$, the $3T_{1g}$-like states increase their relative energies by $\sim$0.1-0.2 eV compared to those in $D_{2h}$. This is due to the smaller value of 10 Dq in the tilted form. Note that, as expected, the CF and Mn 3d exchange parameters undergo only a modest change when the distortions are introduced in the structure. These model parameters can be evaluated rather accurately using an idealized model [MnO$_6$] cluster.

This summary on the change of the Mn 3d$^4$ spectra in $D_{2h}$ and $C_i$ demonstrates, that the main features in the structure of the manifold are already present in the idealized $D_{2h}$ geometry and the tilting adds only moderate corrections to the energies.

**Interpretation of optical excitations determining the model parameters**

Although the theoretical results available in the literature are obtained in model Hamiltonian or DFT based band structure calculations accounting in a different manner for the electron exchange and correlation effects, we compare them with our ab initio results in order to point out the new insights in the valence electronic structure of the compound.

The value of 1.3 eV for the JT splitting calculated within our theoretical approach differs by $\sim$-0.6 eV from the value determined by Jung et al. [21] from their
optical-conductivity analysis. Jung and co-workers obtained the optical conductivity spectrum \( \sigma(\omega) \), using Kramers-Kronig transformation, and expressed further \( \sigma(\omega) \) as a sum of Lorenz oscillator functions. The first oscillator strength in their analysis is smaller by an order of magnitude compared to the second and third ones. Therefore, Jung et al. assigned this first oscillator to the spin allowed transition within the JT split \( e_g \) shell, a transition below the \( O 2p \rightarrow Mn 3d e_g \) transition. This excitation is considered to be intra-atomic, located at \( \sim 1.9 \text{ eV} \) and electric dipole forbidden. The authors suggested, that it becomes optically active due to the strong hybridization of the lower Mn \( e_g \) band with the \( O 2p \) band. This assignment of the optical absorption peak at 1.9 eV to an on-site \( d-d \) electronic excitation across the JT gap was explained by Allen and Perebeinos [18].

In our \textit{ab initio} study of the JT splitting parameter we did not consider the lattice relaxation accompanying the local excitation \( ^5E_g(t_{2g}^3e_g^1(d_{3z^2-r^2})) \rightarrow ^5E_g(t_{2g}^3e_g^1(d_{z^2-y^2})) \) and hence, the calculated excitation energy should, in principle, correspond to the vertical transition in the optical spectra. A relevant question to be addressed in connection with the magnitude of the JT parameter is how sensitive is this quantity to the asymmetric oxygen displacements which occur in the distorted structure. A simple estimate of this effect can be made by varying the lengths of the two bonds which undergo a major change upon distortion by a small amount. We perform this analysis for the JT distorted LaMnO\(_3\), discussed above. The short and long Mn-O bonds in this JT distorted form have lengths of 1.90 Å and 2.14 Å, respectively. We introduce a small displacement outwards of 0.04 Å of the oxygen ions which form the long Mn-O bonds and a displacement inwards of the same magnitude of the oxygen ions which form the short Mn-O bonds. The intermediate Mn-O bond is kept at 1.95 Å. A \([\text{MnO}_6]\) cluster is constructed using these bond lengths. Next the CASSCF -dd’ WF\( s \) of the \( ^5E_g(t_{2g}^3e_g^1(d_{3z^2-r^2})) \) and \( ^5E_g(t_{2g}^3e_g^1(d_{z^2-y^2})) \) states are constructed and the resulting excitation energy, defining the JT parameter, is evaluated to be 1.4 eV. Clearly, the JT parameter is sensitive to the precise value of the oxygen displacements, but by far not sensitive enough to be able to confirm Jung’s interpretation. The three active octahedral distortion modes which enter the expressions for the various model Hamiltonians of the crystals in the model Hamiltonian approaches have to be optimal in order to yield reasonable quantitative estimates of the excitation energies.

The dispersion of the exciton due to the “hopping” of the local excitation between nearest neighbouring Mn sites is studied in a \([\text{Mn}_2\text{O}_{11}]^{16-}\) super-cluster, representing a fully distorted LaMnO\(_3\), using the OF approach, introduced in Chapter 3. The hopping matrix elements associated with this process are found to be less than 1 meV.

As we noted in section 6.1, Quijada and co-workers suggested recently that the feature near 2.0 eV arises from the hopping transition between the JT-split \( e_g \) levels at adjacent Mn ions [59]. According to their analysis, the phonon-assisted on-site electronic transitions, predicted by Allen and Perebeinos [16] are generally much weaker than the optically allowed charge-transfer \( Mn^{3+} \rightarrow Mn^{3+} \) interband transitions, that can be expected in LaMnO\(_3\). We estimated the energy cost for such a hopping transition by using CASSCF results for the smaller \([\text{MnO}_6]\) cluster. The relative energy
of the inter-site excitation is deduced from the following (approximate) relation:

\[ E_{rel} = E(3d \rightarrow \text{adj.} 3d) \approx \{ E(A_{1g}; 3d^3) - E(E_g; 3d^4) \} - \{ E(E_g; 3d^4) - E(^6A_{1g}; 3d^5) \} - E_{\text{Coul.}}(Mn^{3+} \rightarrow Mn^{3+}) \]

The Mn-Mn Coulomb energy is calculated at Mn-Mn distance of 3.99 Å. The energy of the transition is estimated to be 6.63 eV. Dynamical correlation effects are expected to lead to a lowering in the energy of the transition, but their magnitude will not be sufficient to reduce it to 2.0 eV. A justification for the approach adopted here for the estimate of the charge-transfer \( Mn^{3+} \rightarrow Mn^{3+} \) excitations is provided by a recent study on the X-ray Mn K-edge absorption spectra of JT distorted LaMnO\(_3\), performed by Hozoi \textit{et al} [34]. Hozoi \textit{et al} [34] have shown that the relative energy of the 1s→adjacent Mn 3d transition, estimated using the smaller [MnO\(_6\)] cluster in the manner described above, agree well with that obtained in a [Mn\(_2\)O\(_{11}\)] cluster [34]. Note that in our cluster model delocalization of the \( e_g \) orbitals might be underestimated. This delocalization might lead to a relative stabilization of the ground state, and hence to a larger JT gap. Extending the CASSCF-dd' active space by adding \( O^{-2p} \) orbitals is not impossible to lead to an increase in the energy difference between the ground state and the first excited state, which determines the JT parameter. This is a matter of current investigation.

The discussion above has shown that the interpretation of the peak at 1.9 eV in the optical conductivity spectra of Jung [21] is not trivial. Our JT splitting of 1.3 eV compares well with the estimate of 1.4 eV, obtained by Elfmov and co-workers [20] within the LSDA+U approach. Similar values for the splitting of the \( e_g \) -like levels, 1.0-1.5 eV, were obtained from band structure LDA (+U) calculations [14] and analysis of the optical dielectric tensor for the interband transition from the lower Mn \( e_g \) to the upper Mn \( e_g \) band [15]. However, the authors in reference [15] proposed that the peak originates from [Mn \( d_{x^2-y^2}, d_{xz} \); \( O^{-2p} \) hybridized] → [Mn \( 3d; O^{-2p} \)] optical interband transition, based on the considerable amount of \( O^{-2p} \) states present at the top of the VB and the bottom of the CB.

The Mn 3d exchange splitting parameter in our \textit{ab initio} calculations is 1.8 eV, that is \( \sim 1.0 \) eV lower than the estimates, listed in Table 6.1. However the theoretical approaches listed in Table 6.1 do not incorporate important electronic relaxation effects.

The CF splitting parameter in our \textit{ab initio} approach is evaluated to be 2.0 eV in \( C_i \) (2.41 eV in \( O_h \)). This value compares well with the value of \( \sim 2.0 \) eV, deduced from DFT -based BS calculations [14] and optical transmission spectra analysis [24]. The orbital-projected DOS from FPLAPW band calculations, performed by Ravindran \textit{et al.} [15] yielded a value of 1.1 eV.

The comparison of the values of the parameters, obtained in our \textit{ab initio} study, with the values obtained in DFT -based BS calculations showed a significant difference. In the one-electron DFT -based approaches, the electron correlation effects are accounted for by different exchange-correlation functionals and the strong Coulomb interactions are parametrized. In the many-electron WF based methods, the WF type and composition allows to incorporate explicitly those effects. Thus the com-

\( ^c \)The notations correspond to octahedral symmetry, but the actual local symmetry is \( C_i \)
comparison between the results of those semi-empirical methods and our \textit{ab initio} results must be regarded as a check for the results derived within the effective one-electron approaches.

Our calculations on the \textit{d-d} excitations in orthorhombic LaMnO$_3$, based on a CASSCF WF description, suggest a new quantitative picture of the CF valence electronic structure of orthorhombic LaMnO$_3$. The embedded cluster approach, used in our studies, have proved to be a reasonable model for localized excitations in ionic compounds [26,37,54]. The \textit{d-d} transitions are considered to be localized [16,17,33,58], but most of the studies [6, 15, 21] claim a strong covalency between the $e_g$- like Mn 3d states and O -2p$_\sigma$ states, which in addition leads to a broad $e_g$ type VB. We note however that in our approach the lower occupied $e_g$ -like orbital is too localized because the WF of the $^5E_g$ -like ground state is close to a HF WF.

\textbf{Comment on the cluster size effects on the \textit{d-d} excitations in orthorhombic LaMnO$_3$}

The cluster size effects on the \textit{d-d} excitations in orthorhombic LaMnO$_3$ are investigated by considering the changes in the excitation energies of the CF states upon extending the $[\text{MnO}_6]$ cluster, by including extra shells of ions. This enlargement results in clusters [B], [C] and [D]. The cluster size effects are found negligible for the excitation which determines the JT parameter. This is the excitation which involves the two $^5E_g$ -like states. The largest change of about 0.2-0.4 eV in the CASSCF/CASPT2 excitation energies of the $^5T_{2g}$- and $^3T_{1g}$-like states occur upon the cluster enlarging [A]→[B]. The other cluster expansions [B]→[C] and [C]→[D] lead to minor changes in the calculated CASSCF and CASPT2 excitation energies. The $^3E_g$-like energies change by less than 0.01 eV at all cluster expansions. The main effects for all states are already present at CASSCF and almost no extra effects are observed at CASPT2. The cluster size dependence of the \textit{d-d} excitation energies is illustrated in Figure 6.3. The \textit{d-d} excitations show a modest change with the cluster size, which corresponds to a decrease of about 0.2 eV in 10 Dq to 1.8 eV. We can conclude that the \textit{d-d} excitations are indeed quite localized and their energies are negligibly influenced by the size of the cluster.

We also considered the possibility to associate the peak at 1.9 eV in the optical spectra of Jung [21] with the 10 Dq like transition, the transition between the lower $^5E_g$-like state ($a^5A_g$ in the real C$_i$ site symmetry) and the lowest component of the $^5T_{2g}$-like state ($c^5A_g$ in C$_i$ symmetry). However it is found at about 2.5 eV in $[\text{MnO}_6]$ and 2.3 eV in the largest cluster [D]. This makes less probable the hypothesis that the peak at 1.9 eV measured by Jung \textit{et al.} corresponds to a 10 Dq -like excitation.

\textbf{Character of the top of the valence band in LaMnO$_3$}

There have been numerous experimental and theoretical studies of the electronic structure of LaMnO$_3$, addressing in particular the character of the top of the VB. We discussed in detail some of those studies in Chapter 5. From the experimental studies we mention here the photoemission spectra analysis of Saitoh and \textit{et al.} [12]
Results and Analysis: d-d Excitations

Figure 6.3: Illustration of the cluster size dependence of d-d excited states in orthorhombic LaMnO$_3$. The ground state $^5A_g$ relative energy for all clusters is taken at 0.0 eV. The different states for the clusters are depicted with different types of lines.

which led to classifying LaMnO$_3$ as a CT insulator with a band gap of 1.7 eV. See for further details Chapter 5 and the references therein.

To obtain an estimate of the character of the top of the VB in LaMnO$_3$ we performed the following simple analysis. The character of the top of the VB depends on the ionization energies for the Mn 3d and O 2p valence electrons as well as on the width of the bands associated with the Mn 3d and O 2p ionized states. We calculated the relative energies of the lowest Mn 3d and O 2p hole states in [MnO$_6$] cluster, representing orthorhombic LaMnO$_3$. The calculations for the lowest Mn 3d hole state, the ground state $^4A_g$ of [MnO$_6$]$^{8-}$, were carried out within CASSCF-dd’, whereas the WF’s of the two lowest O 2p hole states of symmetries $^6T_{1g}$ and $^6T_{1u}$ in [MnO$_6$]$^{8-}$ were constructed within CASSCF-1p(a$_g$/a$_u$)dd’. The cluster Mn 3d ionization energy as calculated from the CASSCF energies of the $^5E_g$-like ground state of [MnO$_6$]$^{9-}$ and the $^4A_g$ state is 4.78 eV. The lowest O 2p ionized state in [MnO$_6$]$^{8-}$ is the $^6T_{1u}$ state with electronic configuration $t_{2g}^2e_{g}^1t_{1u}^{-1}$. At CASSCF level, this state is 1.0 eV above the $^4A_g$ (d$^3$) state. The dynamical correlation effects are expected to raise the values of the Mn 3d and O 2p ionization energies. Taking into consideration that the relaxation and localization effects are about equal for all O 2p ionized states [28] and that the delocalization effects are dominant, we set the theoretical bandwidth of the O 2p ionization larger than the range of the O 2p orbital energies in [MnO$_6$]$^{9-}$ cluster: 3.0 eV. The band stabilization energy $E_d$ associated with the Mn 3d ionized (hole) state $^4A_g$ is estimated to be about 1.1 eV (see Chapter 4 and Chapter 5). We
expect that formally the localized $O\ 2p$ hole state will be close to the center of the $O\ 2p$ band and hence, the band stabilization energy for this state is at least 1.5 eV.

The close values of the band stabilization energies associated with the $O\ 2p$ and Mn $3d$ ionized states as well as their close ionization energies, makes it difficult to determine the character of the top of the VB with a certainty. However the results indicate that the top of the VB contains contributions of both $O\ 2p$ and Mn $3d$ ionized states.

6.3.2 CT excitations

The study of the CT states is performed with the Mn $6s5p4d2f$ basis, used before, and a smaller $O\ 4s3p2d$ basis set, instead of the $O\ 5s4p2d$ basis. The effects on the energies of the CT excitations are minor and do not have any significance for the outcomes. This survey was carried out with the idealized cubic structure. Although some energetic effects are not accounted for at this level of approximation, the study provides reliable information about the character and relative energies of the lowest CT states at a reduced computational effort. The extra effects are estimated from calculations on the real structure.

CT states in $[\text{MnO}_6]^{9-}$ cluster in $O_h$ geometry

This part of the present study is focused on the character and relative energies of some local $O\ 2p \rightarrow$ to Mn $3d$ CT excitations. The CT states are distinguished as gerade and ungerade. The main configuration of the (un) gerade CT states has an (un) gerade singly occupied oxygen orbital. We are mainly interested in the lower energy part of the ungerade CT manifold, because of its relevance to understanding the nature of the lowest optical excitations. We expect the lowest excitations in the CT manifold to arise from CT states for which the spins in the Mn $3d^5$ shell are high-spin coupled, to $^6A_{1g}$, characterized by an electron configuration $t_{2g}^3e_{g}^2$. If we assume a high-spin coupling in the Mn$3d^5$ shell, then the $O\ 2p$ single electron is coupled to the shell to form either a septet or a quintet. Our choice to study initially those excitations in local $O_h$ geometry (ideal cubic structure) is based on the observation that the relative energies of the lowest states in the Mn $3d^5$ and Mn $3d^4$ spectra follow the same order in all three local geometries (see Figure 6.2 and 6.4). Therefore, the study of the CT manifold in $O_h$ provides reliable information about its structure. As a consequence of carrying out the calculations in the ideal cubic structure, some relaxation energy due to the structural distortion of the octahedra is not accounted for. In addition the use of a CASSCF-(n)pd active space may raise the CASSCF excitation energies while the effect on the CASPT2 estimates has an opposite sign. These additional energetic effects will be estimated in order to probe their significance for the main features of the CT manifold.

First we performed a SCF calculation for a simple $[\text{O}_6]^{12-}$ cluster. The central ion is modeled by a Mn$^{2+}$ TIP. The relative $O\ -2p$- ionization energies obtained for this cluster within the FO approximation are summarized in Table 6.5 and Figure 6.5 gives a pictorial description.
Figure 6.4: Valence electronic structure of a Mn$^{2+}$ ion in cubic, JT distorted and real geometries; CASPT2 results. The lowest singlet states are not shown. The relative energies for the cubic and JT distorted form are taken from reference [33]. Their values are obtained with basis sets Mn-7s6p4d2f and O-6s5p1d. The basis sets in C$_i$ are Mn-7s6p4d2f and O-5s4p2d.

This simplified picture provides a first estimate of the relative order of the O -$2p$ hole states for a cluster with an extra electron on the Mn ion and hence, gives an approximate estimate of the order of the CT states.

Our next studies are performed for an embedded [MnO$_6$] cluster. We apply an active space, described as CASSCF-(n)pd in section 6.2, which differs for the different states in the symmetry character and number of active O -$2p$ orbitals. The complete active space in this scheme contains 5 Mn-3d and n O-$2p$ orbitals. If there is only one CSF in the CI expansion of the WF for a particular CT state, obtained within this active space, this WF is in fact a ROHF type WF. The CASSCF WFs of the lowest ungerade and all gerade CT states are obtained in single state calculations. The optimization of the higher ungerade states is performed in a weighted average of states (see Table 6.6). The active space CASSCF-(n)pd, incorporates some non-dynamical correlation effects for the gerade and ungerade quintet states and leads to a ROHF WF for the septets. Detailed results from the calculations for the gerade and ungerade states in [MnO$_6$] cluster within CASSCF-(n)pd are summarized in Table 6.6 and pictorially presented in Figure 6.6.

All low-lying CT states, correspond to a high-spin coupled Mn 3d$^5$ shell to a $t_{2g}^3e_{2g}^2$ configuration combined with different O -$2p$ hole a $^2T_{1g(u)}$ states. Some of the high-lying states, $^2T_{2g(u)}$ and $^2T_{1g(u)}$ which are not shown in Table (6.6) correspond to
Table 6.5: Oxygen hole states, in an embedded $[O_6]^{12-}$ cluster in $O_h$ symmetry; SCF, Frozen orbital energies;

<table>
<thead>
<tr>
<th>State</th>
<th>State Orbital E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^2T_{1u} (\sigma, \pi)$</td>
<td>0</td>
</tr>
<tr>
<td>$^2T_{2u} (\pi)$</td>
<td>0.61</td>
</tr>
<tr>
<td>$a^{2}T_{1g} (\pi)$</td>
<td>0.69</td>
</tr>
<tr>
<td>$^2E_g (\sigma)$</td>
<td>1.06</td>
</tr>
<tr>
<td>$b^{2}T_{2g} (\pi)$</td>
<td>1.67</td>
</tr>
<tr>
<td>$b^{2}T_{1u} (\sigma)$</td>
<td>1.81</td>
</tr>
<tr>
<td>$^2A_{1g} (\sigma)$</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Figure 6.5: Illustration of the O 2p hole states, obtained in an embedded $[O_6]^{11-}$ cluster in $O_h$ symmetry; SCF, Koopman’s energies;
Table 6.6: Relative energies (in eV) of some low-lying CT states in [A], representing cubic LaMnO$_3$; CASSCF/CASPT2 results; active space CASSCF-(n)pd (5dnp). The electrons within the Mn 3d shell of all states, presented in the Table are high-spin coupled to $^6A_{1g}$ corresponding to the electronic configuration $t^3_2e^2_g$ (only the symmetry of the O hole is pointed out); $t_{x=1g(u)}$ is (x) or (y), (z); $t_{x=2g(u)}$ is ($\xi$) or ($\eta$), ($\zeta$).

<table>
<thead>
<tr>
<th>n</th>
<th>Main Character</th>
<th>State</th>
<th>CASSCF</th>
<th>CASPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Mn ($t^3_2e^2_g$)</td>
<td>$^5E_g$</td>
<td>-1897.5369</td>
<td>-1899.3690</td>
</tr>
<tr>
<td>0</td>
<td>Mn $t^3_2e^1_g$</td>
<td>PS $^5E_g$</td>
<td>-1897.5369</td>
<td>-1899.3685</td>
</tr>
<tr>
<td>2 $t_{1g}$</td>
<td>a $O - \pi$</td>
<td>$^7T_{1g}$</td>
<td>6.46</td>
<td>4.57</td>
</tr>
<tr>
<td>2 $t_{1g}$</td>
<td>a $O - \pi$</td>
<td>$^5T_{1g}$</td>
<td>6.61</td>
<td>4.72</td>
</tr>
<tr>
<td>3 $e_g(\epsilon, \theta, a_{1g})$</td>
<td>O $- \sigma$</td>
<td>$^7E_g$</td>
<td>7.87</td>
<td>5.31</td>
</tr>
<tr>
<td>2 $t_{2g}$</td>
<td>PS b O $- \pi$</td>
<td>$^5T_{2g}$</td>
<td>9.77</td>
<td>6.98</td>
</tr>
</tbody>
</table>

The WF of each $^7,^5T_{1(2)u}$ state is obtained for a weighted average of the three states of the same multiplicity in ratio $(a:T_{2u}:b) - 4:1:1$ for a states, 1:4:1 for $^7,^5T_{2u}$, and 1:1:4 for b states. The gerade states are optimized in a single state calculation. The values in the parentheses are obtained in a single state calculation. PS : Imaginary level shift of 0.3 a.u.
a Mn 3d\(^5\) shell, coupled either to \(^4\)A\(_{1g}\) with a \(t_{2g}^3e_g^2\) configuration or to \(^4\)T\(_{1(2)}g\) with a \(t_{2g}^4e_g^1\) configuration. We concentrate attention in the following discussion mainly on the low-lying CT states. A detailed inspection of the configurational composition of the WFs shows some mixing of the different \(d^5O^-\) CSFs in the CASSCF WFs. For instance, the WF of the lowest quintet- a \(5T_{1u}\) consists of a CSF, described by \(t_{2g}^3e_g^2(6\)A\(_{1g}\)\) a \(O^{T_{1u}}-\sigma(\pi)\) electronic configuration (see Table 6.6) with a weight in the state CI expansion of 89\% and a CSF, described by \(t_{2g}^3e_g^2(4\)A\(_{1g}\)\) a \(O^{T_{1u}}-\sigma(\pi)\) with a weight of 11\%. The gerade quintets show a weight of 89\% of the CSF \(t_{2g}^3e_g^2(6\)A\(_{1g}\)\) a \(O^{T_{1g}}-\pi\). The WFs configurational composition for the higher ungerade and gerade quintets is analogous. A summarized analysis of the results for the \([MnO_6]\) cluster points out that in O\(_h\) the CT states appear above 4.0 eV (see Figure 6.6). We expect some decrease in the CT excitation energies in C\(_i\) due to the lattice relaxation. Furthermore, the energy order of the states shows consistency with the approximate energy order of the O \(-2p\) hole states (see Figure 6.5). The gerade and ungerade spin septet states are with the lower energy in the quintet-septet pairs for each symmetry. The CASPT2 energy difference between the states in a quintet-septet pair is only \(\sim 0.1-0.3\) eV, indicating that the exchange coupling between the spins at Mn and O is rather weak. The magnitude of these energy differences is preserved for all states in the larger clusters except for high-lying \(7.5T_{2g}\) for which it increases by \(\sim 0.6\).

![Figure 6.6: Illustration of the CT manifold in the [A] cluster; CASSCF/CASPT2 results;](image)

In principle, the CT states and the \(d^4\) states, obtained in a CASSCF calculation are not guaranteed to be mutual orthogonal, nor non-interacting. However the lowest gerade quintet CT states are high above the highest gerade quintet \(d^4\) states and thus, no overlap or interaction is expected.
Table 6.7: Change in the CT excitation energies at CASSCF and CASPT2 upon cluster extension

<table>
<thead>
<tr>
<th>State</th>
<th>Cluster Enlarging</th>
<th>△, eV CASSCF</th>
<th>△, eV CASPT2/CASSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a 7,5T_{1u(g)}$</td>
<td>[A]→[B]</td>
<td>~0.76-1.0</td>
<td>~0.8-1.4</td>
</tr>
<tr>
<td></td>
<td>[B]→[C]</td>
<td>~0.1-0.2</td>
<td>~0.5-0.7</td>
</tr>
<tr>
<td></td>
<td>[C]→[D]</td>
<td>~0.02</td>
<td>~0.04</td>
</tr>
<tr>
<td>$7,5T_{2u}$</td>
<td>[A]→[B]</td>
<td>~1.0</td>
<td>~1.4</td>
</tr>
<tr>
<td></td>
<td>[B]→[C]</td>
<td>~0.02</td>
<td>~0.4</td>
</tr>
<tr>
<td></td>
<td>[C]→[D]</td>
<td>~0.02</td>
<td>~0.1</td>
</tr>
</tbody>
</table>

Cluster size effects on the CT manifold in cubic LaMnO$_3$

In this section, we study the constraints which the cluster model implies on the delocalization of the CT excitations. The $[\text{MnO}_6]$ cluster is extended to include more shells of ions. This cluster enlargement results in clusters [B], [C] and [D], discussed before.

The graphs in Figure 6.7a and 6.7b illustrate the change in the excitation energies of some lowest gerade and ungerade CT states, obtained at the CASSCF and CASPT2 level of approximation, respectively. The high-lying ungerade states in the larger clusters could not be obtained in a single state calculation within CASSCF-(n)dp. Therefore, we optimized the orbitals for the WFs of those CT states for a weighted average of states, as in $[\text{MnO}_6]$. The values of the weights are chosen as in $[\text{MnO}_6]$. The WFs of the gerade states are obtained in a single state calculation in all four clusters.

Clearly, there is a systematic lowering in the CT excitation energies with enlargement of the cluster. We also observe that the excitation energies of the lowest CT states converge faster with the cluster expansion, i.e. the excitation energy of a particular low-lying CT state differs by less than 0.05 eV in clusters [C] and [D]. The decrease in the excitation energies may be caused by a gain of electron correlation or, more likely, electron relaxation or a change in the potential within the central regions of the clusters.

In Table 6.7 we have summarized the changes in the CT excitation energies at CASSCF and CASPT2 which occur upon a cluster enlargement. For the lowest CT states the main changes occur at the CASSCF level and for [A]→[B]. The dynamical correlation gain at [A]→[B] is moderate and hence, the energy lowering is determined mainly by extra relaxation effects and/or changes in the external potential. The cluster [C] appears to be the optimal cluster model for the lowest CT excitations. It allows for incorporating the relevant relaxation and electron correlation effects.

We concluded above that the main changes in the CT excitation energies occur at CASSCF and for [A]→[B]. To clarify their origin, we consider the effect of several...
Figure 6.7: Illustration of the cluster size dependence of CT excitation energies in eV in cubic LaMnO₃ at a) CASSCF and b) CASPT2. The ground state $^5E_g$ relative energy for all clusters is taken as 0.0. The order of the states in the right part of the graphics is the order, found in the [MnO₆] cluster. The different states for the clusters are depicted with different types of lines. The second array (from the left to the right site) of states for the [MnO₆Al₆La₈] is obtained, when the La 5p shell is included in the correlation at CASPT2.
model representations of the nearest embedding shell $Mn_6^{3+}$ of [A] on the CT excitation energies. Previous studies [26] on the ionization and excitation energies in CuCl and NiO have shown significant effects of the various embeddings.

First, we represent the nearest embedding shell of 6 $Mn^{3+}$ ions by bare effective core potentials (ECPs) [44] for the $A^{3+}$ core shell. The ECPs for $A^{3+}$ account satisfactorily for the Pauli repulsion between the cluster ions and the nearest neighboring $Mn^{3+}$ cations. This embedding accounts also for the finite size of the ions around the cluster. The exchange and orthogonality interactions are (partially) included in the electronic structure description [26]. The differences in the excitation energies obtained with Al$^{ECP}$ and Mn$^{TIPs}$ with CASSCF are less than 0.05 eV (see Figure 6.8). The use of Mn$^{TIPs}$ instead of bare Al$^{ECP}$ leads to a decrease of 0.2-0.3 eV in the CASPT2 energies.

If the material is an ideal ionic system, the bare ECPs [44] for the Al$^{3+}$ core electrons or the TIPs for the $Mn^{3+}$ ions consitute a reasonable representation of the ions, external to the cluster. The strong orthogonality condition, imposed by TES [60], between the cluster electrons and the electrons of the ions in the nearest embedding, is maintained for these ionic systems. When the cluster WF has non-negligible values outside the cluster region, the strong orthogonality condition can still be maintained by adding basis functions to the ions represented by model potentials [61]. Thus to ensure orthogonality we add (1s1p1d) basis functions to the bare Al$^{ECP}$s to describe the Al valence shell. This embedding brings a decrease in the CASSCF excitation energies by at most 1.0 eV compared to the energies obtained using bare Al$^{ECP}$s. The dynamical correlation contribution to the overall decrease in the energies is in the range of 0.2-0.5 eV.

Finally, we check whether the orthogonality is fully recovered by adding the basis functions to the bare Al$^{ECP}$s. We do so, by including explicitly the electrons associated with the $A_6^{3+}$ in the quantum mechanical treatment$^d$. This results in a further decrease in the excitation energies of the CT states at CASSCF and CASPT2 by less than 0.08 eV. Thus we can conclude that the orthogonality conditions are maintained by the augmented Al$^{ECP}$s.

Next, to distinguish the effects of the relaxation and the change in the potential on the lowest CT energies at [A]$\rightarrow$[B], we consider the changes in the core orbital energies of the ground state of [A] when the nearest ions around the $Mn^{3+}$ ion in [A] are modeled either by bare Al$^{ECP}$s, Mn$^{TIPs}$, augmented Al$^{ECP}$s, or Al$^{3+}$ ions. The changes in those orbital energies indicate changes in the potential close to the nuclei. The difference in the decrease in the energies of the Mn and O core orbitals at different embeddings is related to the change in the external potential. This difference is $\sim$ 0.3 eV for [A]$\rightarrow$[B] and for the augmented Al$^{ECP}$s. The replacement of the Mn$^{TIPs}$ by bare Al$^{ECP}$s introduces only a negligible effect. Thus we can conclude that the total decrease in the CASSCF excitation energies at [A]$\rightarrow$[B] involves a decrease of $\sim$ 0.3 eV, caused by a change in the potential and of $\sim$ 0.7 eV, due to a relaxation energy gain. Similar analysis for the lower-lying CT states at [B]$\rightarrow$[C] indicates that the change in the external potential contributes at most to the overall decrease in the

$^d$in fact this representation of the embedding is equivalent to enlarging the cluster [A]$\rightarrow$[B]
Figure 6.8: Dependence of the CT excitation energies in cubic $LaMnO_3$ on the embedding representation; a) CASSCF and b) CASPT2
CASSCF excitation energies.

An inspection of the charge effects for the states, based on MPA, shows almost no real charge transfer between the Mn$^{3+}$ and O$^{2-}$ ions. The atomic gross charges obtained from MPA point out a transfer of charge between the Mn$^{3+}$ and O$^{2-}$ in the CT states, compared to that in the ground state of $\sim 0.4$ for all clusters.

In summary, the excitation energies of the CT states in cubic LaMnO$_3$ are significantly influenced by the cluster model. For the low-lying gerade and ungerade states, cluster [C] is found to be large enough for an accurate description of the CT states.

Furthermore comparing the estimated energies of the $d$-$d$ excitations and the CT excitation energies obtained in the largest cluster, [D], reveals a small energy gap of $\sim 0.4$ eV between the lowest CT state and the highest $d^4$ state, considered in this study, $^5T_{2g}$. There is no low-lying $^5T_{2g}$ state in the CT manifold, the lowest such state is at about 5.5 eV (CASPT2 result for cluster [C]).

Estimate of the effects of structural distortion and electron correlation

The study of the cubic LaMnO$_3$ elucidated the character and excitation energies of the lowest CT states as well as their cluster size dependence. Next to estimate the effects of structural distortion and Mn 3$d$ dynamical electron correlation on the CT energies, we focus on the lowest CT states, $^7.5T_{1u}$ and $^7.5T_{1g}$, but now obtained in the orthorhombic LaMnO$_3$. We first consider cluster [A].

CASSCF WFs were constructed for the lowest $^7.5T_{1u}$ -like states $a, b, c ^7.5A_u$, and the $^7.5T_{1g}$ -like states, $a, b, c ^7.5A_g$, within an active space containing 5 Mn 3$d$ orbitals and 9 $a_u$ or $a_g$ O -2$p$ orbitals, respectively : CASSCF-9pd. We performed a state average calculation over the three components $a, b, c ^7.5A_u$ or $a, b, c ^7.5A_g$, of each $^7.5T_{1u}$ -like or $^7.5T_{1g}$ -like state. In Figure 6.9 the changes are illustrated when the lattice distortions are introduced in the system.

![Figure 6.9: Lowest CT states. The $^7.5T_{1u}$ -like and $^7.5T_{1g}$ -like CT states in O$_h$ and C$_i$ local geometry. The three components $a, b, c ^7.5A_u(g)$ in C$_i$ of each state are depicted with the same type of lines as the T states.](image)

The decrease in the CASSCF energies of the $^7.5A_g$ states, i.e. the lowest compo-
ments of the $a^{7.5}T_{1g}$-like states, when the distortions are introduced, is $\sim 0.3-0.5$ eV. The energy splittings of the $a^{7.5}T_{1u}$-like states in $C_i$ appear to be somewhat larger and thus, the lowest CT state is the $a^7T_{1u}$-like state, i.e. $a^7A_u$. The energy gain for the $a^{7.5}T_{1u}$-like states is in the range $\sim 0.6-0.9$ eV. At CASPT2 the energy gains for the gerade and ungerade states are vice versa and the lowest CT state appears to be $a^7A_g$. Clearly, the lattice distortions introduce a decrease in the relative excitation energies of the lowest CT states. This is mainly a localization effect.

The configurational composition of the WFs of the septets and ungerade quintets, obtained within CASSCF-9pd shows a mixing of different $3d^5O^-$ CSFs. The WFs of the gerade quintets show some mixing of the different $3d^5O^-$ and $3d^4O^{2-}$ CSFs in addition to the mixing of the various O hole CSFs.

The scalar relativistic corrections to the CASSCF values within CASSCF-9pd for all states are 0.2-0.3 eV. The scalar relativistic corrections are obtained as the energy difference between the non-relativistic energy and the energy with the mass-velocity and Darwin relativistic terms included.

To estimate the extra electron correlation within the $d^5$ shell, CASSCF WFs were constructed for the lowest $a^{7.5}T_{1g}$- and $a^{7.5}T_{1u}$-like CT states in [A] within an active space containing 5 Mn 3d orbitals, a second shell of correlating virtuals $d'$ and 3 $a_g$ or 3 $a_u$ O -2p orbitals, respectively :CASSCF-3pdd’. CASSCF-3pdd’ accounts for the mixing of the different $3d^5O^-$ and $3d^4O^{2-}$ CSFs in the WFs of the CT states as well as for the large Mn 3d dynamical correlation effects [37]. The results are listed in Table 6.8, together with the results (in brackets) obtained within CASSCF-9pd.

An inspection of the CASSCF excitation energies obtained within CASSCF-3pdd’ reveals a decrease of about 0.3-0.4 eV compared to the excitation energies within CASSCF-9pd. As expected, the CASPT2 energies are underestimated within CASSCF-9pd due to an overestimation of the Mn 3d dynamical correlation (see also [40]). The underestimation is $\sim 0.2$ eV.

Finally we estimated the extra orbital relaxation energy associated with expressing each state in its own optimized orbital basis set. The results from these single state calculations are listed in Table 6.9. Note that results, obtained within CASSCF-3pd and within an active space containing 5 Mn3d and only one $O -2p$ (CASSCF -1pd), differ by 3 meV using CASSCF. CASSCF -1pd raises the CASPT2 energy by $\sim 0.05$ eV, compared to that obtained within CASSCF-3pd.

Comparing the excitation energies of $^5A_u$ obtained from the state average calculation (Table 6.8) and the single state calculation (Table 6.9) reveals that the extra relaxation energy is $\sim 0.2$ eV.

Analogous to the analysis, performed for the cubic LaMnO$_3$, we studied the cluster size dependence of the $a^{7.5}T_{1u}$ and $a^{7.5}T_{1g}$-like CT states in [A], [B] and [D] as well as the effect of several model embedding representations of the nearest ions around [A] on those CT states. Because the results of this analysis do not introduce new insights in the effect of the cluster size on the CT manifold, we do not discuss them explicitly here.
**Table 6.8:** Relative energies (in eV) of the lowest CT states in cluster [A], representing orthorhombic LaMnO$_3$; CASSCF/CASPT2 results; active space CASSCF-3p($a_g$ or $a_u$)dd’. The spins in the Mn 3d shell are coupled to $^6A_g$. In brackets are listed the energies obtained within CASSCF -9pd.

<table>
<thead>
<tr>
<th>Main Character</th>
<th>State</th>
<th>CASSCF</th>
<th>CASPT2</th>
<th>$\omega^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Gerade CT states</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{2g}^3e_{g}^1$</td>
<td>$^6A_g$</td>
<td>-1691.5828</td>
<td>-1693.4332</td>
<td>0.686</td>
</tr>
<tr>
<td>$aO^{T_{1g}} - \pi$</td>
<td>$^5A_g$</td>
<td>5.98 (6.35)</td>
<td>4.64 (4.15)</td>
<td>0.655</td>
</tr>
<tr>
<td>$aO^{T_{1g}} - \pi$</td>
<td>$^5A_g$</td>
<td>6.04 (6.41)</td>
<td>4.29 (4.48)</td>
<td>0.652</td>
</tr>
<tr>
<td>$aO^{T_{1g}} - \pi$</td>
<td>$^5A_g$</td>
<td>6.29 (6.71)</td>
<td>4.96 (4.74)</td>
<td>0.656</td>
</tr>
<tr>
<td>$aO^{T_{1g}} - \pi$</td>
<td>$^7A_g$</td>
<td>5.49 (5.92)</td>
<td>4.17 (4.02)</td>
<td>0.661</td>
</tr>
<tr>
<td>$aO^{T_{1g}} - \pi$</td>
<td>$^7A_g$</td>
<td>5.99 (6.41)</td>
<td>4.57 (4.41)</td>
<td>0.658</td>
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<tr>
<td>$aO^{T_{1g}} - \pi$</td>
<td>$^7A_g$</td>
<td>6.07 (6.50)</td>
<td>4.76 (4.57)</td>
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</tr>
<tr>
<td></td>
<td><strong>Ungerade CT states</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$aO^{T_{1u}-\sigma(\pi)}$</td>
<td>$^5A_u$</td>
<td>5.70 (6.01)</td>
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<tr>
<td>$aO^{T_{1u}-\sigma(\pi)}$</td>
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<td>5.76 (6.20)</td>
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<td>0.661</td>
</tr>
<tr>
<td>$aO^{T_{1u}-\sigma(\pi)}$</td>
<td>$^5A_u$</td>
<td>6.16 (6.46)</td>
<td>4.77 (4.66)</td>
<td>0.655</td>
</tr>
<tr>
<td>$aO^{T_{1u}-\sigma(\pi)}$</td>
<td>$^7A_u$</td>
<td>5.41 (5.76)</td>
<td>4.47 (4.28)</td>
<td>0.663</td>
</tr>
<tr>
<td>$aO^{T_{1u}-\sigma(\pi)}$</td>
<td>$^7A_u$</td>
<td>5.56 (5.97)</td>
<td>4.69 (4.40)</td>
<td>0.665</td>
</tr>
<tr>
<td>$aO^{T_{1u}-\sigma(\pi)}$</td>
<td>$^7A_u$</td>
<td>5.81 (6.12)</td>
<td>4.70 (4.57)</td>
<td>0.662</td>
</tr>
</tbody>
</table>

The CASPT2 values are obtained with Imaginary shift of 0.1 a.u.

**Table 6.9:** Relative energy in (eV) for a $^5T_{1u}$ in [A] and [B] clusters, representing cubic and orthorhombic LaMnO$_3$; The results for the orthorhombic form refer to the lowest component of the $^5T_{1u}$ state in $C_i$: a $^5A_u$; CASSCF/CASPT2 results; The results in the parentheses are values with scalar relativistic corrections; The last row lists the result for the corresponding $^7T_{1u}$.

<table>
<thead>
<tr>
<th>Local Symmetry</th>
<th>Active space</th>
<th>Cluster [A]</th>
<th>Cluster [B]</th>
</tr>
</thead>
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<tr>
<td></td>
<td>CASSCF/CASPT2</td>
<td>CASSCF/CASPT2</td>
<td>CASSCF/CASPT2</td>
</tr>
<tr>
<td>$C_i$</td>
<td>CASSCF-1pdd’</td>
<td>5.55 (5.78)</td>
<td>4.87</td>
</tr>
<tr>
<td>$O_h$</td>
<td>CASSCF -3pd</td>
<td>6.90</td>
<td>4.63</td>
</tr>
<tr>
<td>$O_h$</td>
<td>CASSCF -3pd’</td>
<td>6.38</td>
<td>5.04</td>
</tr>
<tr>
<td>$O_h$</td>
<td>CASSCF -3pd’</td>
<td>6.12</td>
<td>4.48</td>
</tr>
</tbody>
</table>
Introducing lattice distortions in the system does not change the finding that the lower part of the valence spectra of LaMnO$_3$ is constituted of the \textit{d-d} excitations. The CT states constitute the higher part of the valence spectra. The energies of the lowest CT states are expected to become very close, even somewhat lower, to the energies of the highest quintet $d^4$ states of $T_{2g}$ symmetry in the \textit{[D]} cluster of the orthorhombic LaMnO$_3$. However the lowest gerade quintet CT states will remain still high above the highest $^5T_{2g}$ -like states in the $d^4$ manifold.

\section{Conclusions}

We performed a detailed investigation of the \textit{d-d} and CT excitations which constitute the valence electronic structure of LaMnO$_3$. This study provides an \textit{ab initio} evaluation of model parameters, such as JT, CF and exchange splitting parameters, which magnitudes appear to be a question of controversy in the theoretical and experimental literature. We studied separately the effects of the JT distortion and tilting of the [MnO$_6$] octahedra on the CF excitations. When the tilting is introduced in the system only moderate changes in the \textit{d-d} spectra occur compared to the \textit{d-d} spectra of the system with only JT distortions. Hence, we concluded that the main features of the $d^4$ manifold are already well described in an embedded cluster model which incorporates only the JT distortion. We find JT splitting parameter of about 1.3 eV in the tilted form compared to 1.2 eV in the JT distorted structure. Our value is close to some other theoretical results by Elfimov and co-workers \cite{20} and Ravindran \textit{et al}. \cite{15}. The peak at 1.9 eV in the optical conductivity spectra of Jung \textit{et al}. \cite{21} has been interpreted by these authors as determining the JT splitting parameter. However, the assignment of this peak turns out to be also controversial. The optical conductivity analyses of Quijada \textit{et al}. \cite{59} and Jung \textit{et al}. \cite{21} predict either a hopping CT between the JT split $e_g$ -like orbitals at adjacent Mn ions or an on-site $e_g \rightarrow e_g$ transition. We considered with attention the assignment of the peak at 1.9 eV by Quijada \textit{et al}. \cite{59} to an inter-site CT hopping transition. Our \textit{ab initio} estimate disregarded this alternative because of the large energy, required for CT hopping. The local \textit{d-d} excitation at 1.3 eV in the \textit{ab initio} CF spectra can not explain the origin of the controversial peak which imposes that this optical transition does not correspond directly to the JT splitting parameter, characterizing a localized excitation.

Our calculated CF parameter, 1.8 eV, in the orthorhombic LaMnO$_3$ compares well with the values obtained by Satpathy, Popovic and Vukajlovic \cite{14} within the LDA (+U) framework and by Lawler \textit{et al}. \cite{24} from optical transmission spectra. The Mn $3d$ exchange parameter is evaluated to be 1.8 eV. We considered the possibility the peak at 1.9 eV to originate from the $^5E_g \rightarrow ^5T_{2g}$ transition, which determines the CF parameter. We found however that this excitation is too high in energy to be associated with the transition at 1.9 eV.

The \textit{d-d} excitations showed only a modest change in the energies with the cluster size. The excitation energies converge fast with the expansion of the cluster and hence, even the smaller clusters provide a reasonable estimate of the CF spectra. These modest changes do lead to a decrease in 10 Dq by about 0.2 eV. This cluster
size dependence indicates that the $d$-$d$ excitations are rather localized. A $[\text{MnO}_6\text{Mn}_6]$ cluster already incorporates the most significant energetic effects and further cluster expansions do not introduce new insights in the CF spectra of the system.

Based on the analyses of the CT states, considered in this study, we conclude that the lowest CT excitation energies also converge relatively fast with the cluster size. For these lowest CT excitations, cluster $[\text{MnO}_6\text{Mn}_6\text{La}_8]$ is an adequate embedded cluster to incorporate the important electron correlation and relaxation effects. The effect of adding an $O_{24}$ shell of ions to the latter cluster on the change in the relaxation energy and external potential is minor for the low-lying CT states. The main contribution to the energy decrease of the CT excitations on increasing cluster size is due to a relaxation energy gain.

We found a small energy gap of 0.4 eV between the highest significant $d^4$ state, $^5T_{2g}$, considered in this study, and the lowest CT state, in cubic LaMnO$_3$. Hence, we expect that the lower part of the valence spectra of LaMnO$_3$ is constituted mainly of CF excitations. Introducing relevant distortions in the system does not lead to another interpretation of the valence electronic structure of LaMnO$_3$. Our analysis pointed out that the CT manifold is located at and above $\sim$3.0 eV in the cubic structure which is in agreement with the result obtained in previous $ab$ $initio$ embedded cluster calculations on the valence spectra of ideal and JT distorted LaMnO$_3$ [33].
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