Local excitations and magnetism in late transition metal oxides

de Graaf, Cornelis
Chapter 5

Core level ionization processes
Chapter 5: Core level ionization processes

5.1 INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a widely used technique for studying the electronic structure of ionic transition metal materials. Especially the shifts of core-level binding energies of an ion in different chemical environments (e.g. in the bulk or at the surface) can provide information about the electronic structure of the ground state of these materials. However, the interpretation of X-ray photoelectron spectra has been the subject of many discussions. The creation of a hole in one of the core orbitals of the TM ion causes a strong potential that lowers the excitation energy of the charge transfer states, in which an electron is transferred from the ligands to the TM ion. Hence, the hole potential may become screened depending on the electron affinity (EA) of the TM ion. For example, the lowest final state in the Cu-2p XPS (calculated EA is -20.3 eV) in cuprates can be interpreted in terms of mainly a 3d^{10}L^{-1} state, whereas the charge transfer contribution to the main peak in the Mn-3s XPS (calculated EA is -13.4 eV) of MnO is very small [1]. The interpretation of photoelectron spectra in NiO and other related nickel compounds is a delicate matter, since the electron affinity of Ni^{2+} (calculated EA of -18.0 eV) is in between those of Cu^{2+} and Mn^{2+}. Either the XPS of these compounds should be interpreted in a similar way as the Cu-2p XPS, i.e. the final state that screens the hole is lowest in energy [2-4], or should be interpreted as in MnO, where CT effects are not very important for the lowest final state. A third possibility is that neither of these two interpretations is correct and that the lowest final state does screen the hole, although not completely [1, 5]. This means that the lowest final state is best described as a strong mixture of d^8 and d^9L^{-1} configurations.

Figure 5.1 Ni-3s x-ray photoelectron spectrum of NiO taken from Ref. [5]
In this chapter we investigate the character of two final states appearing in the spectrum arising from the ionization of an electron from the Ni-3s orbital [5]. The spectrum shows a main line at ~113.7 eV (a), separated by ~2.2 (b), ~6.1 (c) and ~10.2 eV (d) from less intense features (a, b, c, d: see Figure 5.1). This spectrum was explained by Bagus et al. [5] on the basis of an MCSCF/CI study. The main peak and the feature at 6.1 eV higher binding energy were assigned to high-spin coupled 3s hole states and the features at 2.2 and 10.2 eV to low-spin coupled states. For the high-spin coupled states it was found that no large differential contributions arise from atomic correlation effects among the Ni-3s, 3p and 3d electrons, in contrast to the low-spin coupled states, for which the relative energies are strongly influenced by such electron correlation effects. In order to investigate the screening of the core hole by CT effects as clearly as possible, in the present study attention is focused on the high-spin coupled states.

In the previous chapters it has been shown that with ab initio methods on the basis of one set of orbitals for d8 and d9L-1 configurations rather involved calculations are needed to introduce CT effects in the wave function. To account for the different shape of the optimal orbitals in the different configurations, a large amount of additional configurations has to be added to the wave function. Because CT effects are expected to be important in the states at hand, we intend to include orbital relaxation effects in a more direct way.

To obtain a balanced description of d8 and d9L-1 configurations it is necessary to express both configurations in their own optimal orbitals and moreover, to lower the symmetry constraints to allow for the localization of the hole created in a CT process on one of the oxygens. The need for this is most easily seen by considering an NiO6 cluster with the Oh symmetry relations imposed on the wave functions. Clearly, the holes on the Ni centre in the origin of the cluster are completely localized and the full orbital relaxation is obtained, but a hole in the oxygens is always delocalized over symmetry equivalent centres and only part of the orbital relaxation is accounted for. Obviously, this leads to a rather unbalanced description of d8 and d9L-1 configurations.

The negative consequence of the separate optimization of the orbitals for the different configurations is that a CI has to be performed between configurations expressed in orbital sets that are mutually non-orthogonal. However, the evaluation of the non-orthogonal matrix elements can be evaluated efficiently with the GNOME routines developed in our laboratory [6]. The major advantage of this non-orthogonal CI (NOCI) approach is that with a very short wave function expansion all essential details, i.e. orbital relaxation and localization effects, are included in the description of the states of interest in a balanced way.
5.2 Computational Information

Cluster model, basis sets and wave functions

All calculations are performed on an NiO$_6$ cluster embedded in a set of 50 optimized point charges [7, 8] that represent the Madelung potential in a large number of grid points in the cluster region due to the ions outside the cluster. The basis sets are the same as were used by Bagus et al. [1, 5]. For nickel the (14s, 11p, 6d) set is contracted in a segmented way to [6s, 5p, 4d] and for oxygen (9s, 5p) to [4s, 3p]. As discussed in the introduction, a full treatment of the localization or orbital relaxation effects can often not be included in the description of the electronic structure when the complete point group symmetry of the cluster.

FIGURE 5.2 Graphical representation of the NiO$_6$ cluster embedded in point charges. The C$_{4v}$ symmetry equivalent centres are shown.

The thick lines link cluster atoms; large spheres represent from light to dark O$_{eq}$, O$_2^+$, O$_2^-$ and Ni, respectively. The small spheres represent positive (dark) and negative (light) point charges.
under consideration is imposed on the orbitals. The present cluster has an octahedral symmetry and therefore any charge transfer configuration involves a hole in an oxygen orbital which is delocalized over more than one centre. Instead, if C\textsubscript{4v} symmetry is imposed, CT configurations can be constructed in which the hole orbital is localized on a single oxygen centre. Figure 5.2 shows how the seven cluster ions are connected by the C\textsubscript{4v} symmetry relations; centres represented with the same grey scale are equivalent.

Before ionization, the ground state of an [NiO\textsubscript{6}]\textsuperscript{10-} cluster has \(3\text{A}\textsubscript{2g}\) symmetry in the cluster point group O\textsubscript{h}. The SCF solution corresponds to a \(4\text{a}_{\text{2g}}^2\text{3e}_{\text{g}}^4\text{4e}_{\text{g}}^2\text{2t}_{\text{2g}}^6\) configuration, where all other (closed) shells have been omitted. The \(4\text{a}_{\text{2g}}\) corresponds with the Ni-3s orbital. The \(4\text{e}_{\text{g}}\) and \(2\text{t}_{\text{2g}}\) MOs are mainly built from Ni-3d atomic orbitals and show a very small contribution from the ligand-2p orbitals. Detailed analysis showed that the configuration can be considered to a high extent as a pure \(3\text{s}^23\text{d}^8\) configuration \[9\], and is therefore labelled as NCT (non charge transfer) configuration. The 3s core hole has \(2\text{A}_{\text{2g}}\) symmetry and can be coupled to the valence holes \(3\text{A}_{\text{2g}}\) to form either a high-spin \(4\text{A}_{\text{2g}}\) state or a low-spin \(2\text{A}_{\text{2g}}\) state. As stated in the introduction, the calculations were limited to the high-spin couplings only in the present study.

Due to the strong potential arising from the core hole the CT effects are expected to be more important for the final ionized states. The NCT configuration can be written as \(4\text{a}_{\text{2g}}^1\text{3e}_{\text{g}}^4\text{4e}_{\text{g}}^2\). The \(\text{t}_{\text{2g}}\) orbital is omitted, because it remains completely filled in all configurations considered. The CT configurations with one hole in the Ni-3d type \(\text{e}_{\text{g}}\) orbital and one hole on the ligands can only have \(\text{A}_{\text{2g}}\) symmetry if the ligand hole is also in an orbital of \(\text{e}_{\text{g}}\) symmetry, leading to a \(4\text{a}_{\text{2g}}\text{3e}_{\text{g}}^3\text{4e}_{\text{g}}^3\) configuration. This means that the ligand hole is a \(\text{p}_\sigma\) hole composed of O-2p orbitals directed along the Ni - O bonds. Furthermore, it means that the CT configurations that have interaction with the NCT configuration are not the lowest CT configurations, since the latter have \(\text{T}_{\text{1g}}\) symmetry (see Chapter 2). The character of the \(3\text{e}_{\text{g}}\) and \(4\text{e}_{\text{g}}\) orbitals in the ionized state is not necessarily as localized as in the initial state and the character is investigated in the present study. Therefore, the labels used for the \(3\text{e}_{\text{g}}^4\text{4e}_{\text{g}}^2\) and \(3\text{e}_{\text{g}}^3\text{4e}_{\text{g}}^3\) configurations are somewhat arbitrary, since the MOs in these CT and NCT configurations may show a greater mixing of the Ni-3d and O-2p AOs.

On lowering the symmetry from O\textsubscript{h} to C\textsubscript{4v} the two components of the \(\text{e}_{\text{g}}\) orbitals turn into the \(\text{a}_1\) and \(\text{b}_1\) representations, respectively. The NCT configurations listed above become \(\text{a}_1^2\text{b}_1^2\text{a}_1^1\text{b}_1^1\), both for the initial and final states, in which the singly occupied \(\text{a}_1\) and \(\text{b}_1\) orbitals have mainly Ni-3d character. The O-2p orbital pointing along the Ni - O bond of the \(\text{O}_2^-\) and \(\text{O}_2^+\) centres transform
following the $a_1$ symmetry representation. For the CT configuration the same configuration as for the NCT applies, with the difference that the singly occupied $a_1$ orbital has mainly O-2p character and the singly occupied $b_1$ orbital is characterized as a Ni-3d orbital. The overall spatial symmetry of both the initial and final states is $B_1$.

Outline of the calculations

The full orbital relaxation accompanying the charge transfer is accounted for by determining the optimal wave function for the CT configurations with the hole localized on one of the ligands (e.g. $O_2^-$, see Figure 5.2). The increase in total energy caused by the localization of the hole is compensated by the gain in total energy due to the orbital relaxation effects. For O-2p holes these two effects are of comparable size [10] and need to be considered both. The second step generates the five other equivalent CT configurations with the holes localized on the other ligands. Note that this can be done without performing extra SCF calculations, simply by rotating the MOs obtained in the first SCF calculation. A wave function with the proper cluster symmetry is then constructed in a 6 x 6 non-orthogonal CI (see section 1.4) of the different localized CT configurations. Next, the NCT configuration is calculated in a separate SCF procedure. The final wave functions are obtained from a 2 x 2 NOCI between the CT and NCT configurations. These final wave functions are orthogonal to each other and can be used to interpret the experimental spectrum. Since the CT as well as the NCT configurations are expressed in their own optimal orbital set, both configurations are treated in a well-balanced way.

The relative intensities of the two final states are computed following the sudden approximation as applied by Åberg [11]. In this procedure an electron (here the 3s-electron) is removed from the initial state without any further change in the wave function. The overlap with the two final states is then calculated. The relative intensities are proportional to the square of these overlaps. In order to obtain a balanced description of the initial state and the final states, the CT effects were considered for the initial state in the same way as described above for the final states, i.e. accounting for the full orbital relaxation effects that accompany the charge transfer effects. The results of these calculations are also discussed later in this chapter.

To quantify the importance of the relaxation effects the calculations are also performed without releasing the symmetry restrictions. CT and NCT configu-
rations are constructed imposing the full $O_h$ cluster symmetry. The SCF solution for the NCT configuration is equivalent to the solution obtained with $C_{4v}$ symmetry, but the CT configuration is rather different, because the hole is created in a ligand orbital of $e_g$ symmetry which is a linear combination of AOs on all six ligands. Therefore only about one sixth of the total relaxation energy is obtained when the $O_h$ symmetry relations are imposed on the MOs [10].

5.3 Results

Final states under $O_h$ symmetry

First we discuss the results for the final states. A comparison is made between the calculations in which the orbital relaxation effects are fully accounted for and those in which this effect is only partially included. Figure 5.3 shows the relative energies of the wave functions at different stages in the calculation in which the MOs are restricted to transform following $O_h$ symmetry. The leftmost column shows the results of the separate SCF calculations on the NCT and CT configurations.

In $O_h$ symmetry the SCF solutions for the $^4A_{2g}$ (and the initial $^3A_{2g}$) state corresponding to the $3e_g^3 4e_g^3$ CT configuration cannot be found in the standard open-shell SCF methods because the energy expression not only contains the standard $J$- and $K$-integrals, but also so-called $R$-integrals over the open-shell orbitals. Therefore the orbitals are optimized for a weighted average of the $^4A_{1g}$, $^4A_{2g}$ and $^4E_g$ states. In the next column of Figure 5.3 the individual states are projected out of this average. This was done by performing a small CI with the four configurations that can be constructed with two electrons in the two components of the open shell $e_g$ orbitals. As the figure shows, the approximation of optimizing the orbitals for an average of states is not very severe, since the energies of the individual states are very close to the average energy; $^4A_{2g}$ at 4.55, $^4E_g$ at 4.69, $^4A_{1g}$ at 4.85 versus the average of states at 4.70 eV. The two $^4A_{2g}$ configurations have a rather large mutual overlap of 0.28, and therefore the energy difference between them is not very meaningful.
When a NOCI is applied for the two configurations, we obtain two states separated by 8.09 eV. In the NOCI results the effects of orthogonalization and the interaction of the two configurations can be separately considered. In a normal (orthogonal) CI the trace of the Hamilton matrix is conserved, in other words, the decrease in energy of the lowest state is equal to the increase in energy of the other state. In the NOCI the lower configuration lowered its energy by 0.48 eV, hence the orthogonal CT configuration increase by the same amount. The total energy effect on this configuration of the NOCI is +3.06 eV and the effect of orthogonalization is 3.06 - 0.48 = 2.58 eV, which results in a relative energy for the orthogonal CT configuration of 7.13 eV. The final separation between the two states of 8.09 eV is comparable to the separation of 7.7 eV obtained from CASSCF/CI calculations by Bagus et al. [5].
Final states under $C_{4v}$ symmetry

In the next series of calculations the imposed symmetry was lowered from $O_h$ to $C_{4v}$. As indicated above in the computational information this lowering of the symmetry opens the possibility of localization of the hole on the ligands in the CT configurations. In the leftmost column of Figure 5.4 the SCF energies are given of the two separate SCF calculations on the NCT and CT configurations. The total energy of the NCT configuration is exactly the same as when the $O_h$ symmetry relations are imposed, which indicates that for this configuration no symmetry breaking occurs. Table 5.1 summarizes the Mulliken population analysis of the open shell orbitals for the CT and NCT configurations. The table shows that the oxygen hole in the CT configuration is localized on the $O_2^-$ centre.

**FIGURE 5.4** Relative energies in eV for the final $3s^1$ states in the various steps of the calculations imposing $C_{4v}$ symmetry.
TABLE 5.1 Mulliken gross population of the open shell orbitals for the NCT and CT 3s\(^1\) configurations obtained by imposing C\(_{4v}\) symmetry.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Open orbital</th>
<th>Ni-3d</th>
<th>O(_{eq})</th>
<th>O(_{Z^+})</th>
<th>O(_{Z^-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCT</td>
<td>a(_1) / b(_1)</td>
<td>89</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>CT</td>
<td>b(_1)</td>
<td>96</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>a(_1)</td>
<td>8</td>
<td>1</td>
<td>–</td>
<td>88</td>
</tr>
</tbody>
</table>

When C\(_{4v}\) symmetry is imposed. Additional analysis of the degree of localization of the oxygen hole in the CT configuration is given by Bagus et al. [12]. The calculation of the dipole moment of the wave function along the z-axis shows that the hole on the oxygen is highly localized on the O\(_{Z^-}\) centre. This localization leads to a symmetry-broken CT configuration with a relative energy of 1.32 eV and an overlap of 0.48 with the NCT configuration. The relative energy of the orthogonalized CT configuration, 2.61 eV, with the hole localized on one oxygen is also indicated in the leftmost column of Figure 5.4.

Another matter of interest is the number of d-electrons in the different configurations. Table 5.2 presents the Ni(d) gross populations of the NCT and CT configurations imposing C\(_{4v}\) symmetry. The data in the table suggest that the NCT configuration has some charge transfer character incorporated via the closed shell orbitals. The number of electrons in Ni(d) orbitals for the NCT configuration is 8.49, whereas the formal ionic value equals 8. This shows that a significant transfer of electrons from oxygen to nickel occurs, which screens the potential arising from the hole in the Ni-3s orbital. The screening arises through an increase in the covalent bonding to Ni(3d) in the closed shell 3eg orbital, which (still) has dominantly O-2p character. The number of d-electrons in the CT configurations is calculated as 9.03, very close to the formal value. However, the increase of d-electrons compared to the NCT configuration is only 0.5, far from the expected value of 1. A detailed analysis of the number of d-electrons is presented in the recent work of Bagus et al. [12]. The d-count in the different configurations is determined on the basis of the projection operator method [13], which is less sensitive than MPA to the details of the basis set. Although the numbers are not exactly the same, this analysis confirms the conclusions derived from Table 5.2. For the NCT configuration a larger d-count is found than expected from a purely ionic picture and the increase of the numbers of d-electrons comparing the NCT to the CT configuration is clearly less than 1.
5.3 Results

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Symmetry</th>
<th>Closed shells</th>
<th>Open shells</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCT</td>
<td>(^4\text{A}_{2g}) (in (\text{O}_h))</td>
<td>6.71 (6)</td>
<td>1.78 (2)</td>
<td>8.47 (8)</td>
</tr>
<tr>
<td>CT</td>
<td>(^4\text{B}_1)</td>
<td>7.99 (8)</td>
<td>1.04 (1)</td>
<td>9.03 (9)</td>
</tr>
</tbody>
</table>

A CT configuration of the same symmetry \((^4\text{A}_{2g})\) as the NCT configuration can be constructed from a NOCI with the six different mutual non-orthogonal symmetry-broken CT configurations, each one with a hole on one of the ligands. The overlap of the CT configurations with the hole localized on oxygens on the same axis is 0.237 and with the hole on different axes, the overlap is 0.243. The second column of Figure 5.4 depicts the results of the projection. Note that this projection is not exactly the same as the projection applied in the calculations with \(\text{O}_h\) symmetry, in which the configurations are orthogonal. Three CT states of different symmetry are projected out in the NOCI; a \(^4\text{T}_{2g}\) at 2.0 eV, a \(^4\text{E}_g\) at 2.73 eV and the state of particular interest, the \(^4\text{A}_{2g}\) at -0.37 eV. At first sight, it might seem that this is in agreement with the interpretation that the main peak in the spectrum corresponds to the final state in which the hole is completely screened by CT effects. However, this projected CT configuration has a very large overlap, 0.80, with the NCT configuration and the symmetry projected CT configuration is strongly contaminated with the NCT configuration.

In the same way as discussed above for the calculations with \(\text{O}_h\) symmetry, we separated the effect of orthogonalization and interaction from the final NOCI results between the NCT and symmetry projected CT configurations. Removing the overlap between the two configurations has a very large effect, after orthogonalization the two configurations are separated by 4.19 eV. This energy difference can be compared with the previous calculation in which the \(\text{O}_h\) symmetry relations were imposed, since now we can compare energy differences between orthogonal configurations. The comparison shows that the CT configuration obtained in \(\text{O}_h\) symmetry is about 3 eV higher in energy than the CT configuration obtained when the orbital relaxation effects are fully accounted for. This difference is in good agreement with the findings of previous applications of the NOCI method to core-hole spectroscopy [14, 15]. The interaction between the two configurations lowers the energy of the NCT configuration by 0.77 eV and brings the energy separation between the two final states to 5.68 eV as indicated in the last column of Figure 5.4, which is more than
2 eV smaller than the energy calculated for the two final states when \( O_h \) symmetry is imposed.

Two observations remain to be made for these calculations. In the first place, the effect of orthogonalization depends on the choice of order of orthogonalization. Orthogonalizing the NCT to the symmetry projected CT configuration leads to an energy separation between the two orthogonal configurations of 4.9 eV. Nevertheless, the character and energy separation of the final states are of course not dependent of this. Secondly, a probably more elegant order of the different steps is first to orthogonalize the symmetry-broken CT to the NCT configuration and then perform the projection. In this way the extremely large overlap between NCT and symmetry projected CT configuration is avoided. Figure 5.4 also indicates the results of this order of performing the calculations.

Next, we interpret the character of the two final states. First, we note that the energy separation between the two states is in satisfactory agreement with the experimental value of 6.1 eV, considering the very simple structure of the wave functions which involve only two configurations. The two final NOCI wave functions, \( \Psi(1) \) and \( \Psi(2) \) are the following:

\[
\Psi(1) = 0.44 \Phi(\text{NCT}) + 0.61 \Phi(\text{symm. proj. CT}) \tag{5.1}
\]

\[
\Psi(2) = 1.60 \Phi(\text{NCT}) - 1.54 \Phi(\text{symm. proj. CT}) \tag{5.2}
\]

The reason for the somewhat unconventional size of the normalized coefficients is the non-orthogonality between the two configurations. This also prevents the interpretation of the final states through the size of the coefficients, which would lead to an interpretation that both final states are almost 1:1 mixtures of NCT and CT configurations. Alternatively, the overlap can be determined of the two NOCI wave functions with the two configurations from which the wave functions are constructed. However, as illustrated in Table 5.2, these configurations cannot be considered as pure non charge transfer or pure charge transfer configurations and therefore the overlap will not give the desired information. In order to determine the character of the two final states, we projected the two NOCI wave functions on the \( ^3A_{2g} \) ground state of the NiO\(_6\) cluster. This state can be considered as an almost pure \( d^8 \) configuration [9] and the size of the overlap between the NOCI wave functions and this \( d^8 \) configuration shows to what extent the final states can be considered to possess a screened or unscreened core hole. To compute the overlap a 3s electron is removed from the \( ^3A_{2g} \) state without changing the orbitals. The overlap with this frozen NCT is 0.81 and 0.47 for \( \Psi(1) \)
and $\Psi(2)$, respectively. This indicates that both final states have considerable charge transfer character and that the interpretation of the XPS-spectrum in terms of either screened or unscreened core hole states is not very appropriate due to the large overlap between the optimal NCT and CT configurations.

**Initial states under $O_h$ and $C_{4v}$ symmetry**

To estimate the relative intensities of the two final states it is necessary to describe the initial state at the same level as the two final states. Before turning to the relative intensities we first discuss the results of the NOCI calculations applied to the initial states. Again the results will be compared with and without accounting for the relaxation effects accompanying CT excitations. Figure 5.5 shows the relative energies of the $3s^2$ states under $O_h$ symmetry restrictions. Note that the energy axis has been cut. The CT configurations are again optimized for an average of states and the $^3A_{2g}$ is projected out in a small CI. This gives a splitting between the NCT and CT configurations of 11.30 eV. The orthogonalization of the two configurations increases the splitting between the NCT and CT.

**FIGURE 5.5** Relative energies in eV for the $3s^2$ states in the various steps of the calculations imposing $O_h$ symmetry.

![Figure 5.5](image)
configurations to 12.33 eV, which is 5.20 eV more than in the corresponding calculation on the final states. The reason for this is of course the presence of the strong potential due to the core hole in the final states. The inclusion of the interaction between the two configurations gives an energy separation of 12.47 eV for the two initial states.

The effect of relaxation is again studied by lowering the symmetry constraints to $C_{4v}$. Results are summarized in Figure 5.6 in the same way as in Figure 5.4. The non-orthogonal symmetry-broken CT configurations have an energy of 9.53 eV relative to the NCT configuration, which does not show any symmetry breaking although the symmetry restrictions are released. The overlap of the two configurations is 0.27 and the orthogonalized symmetry-broken CT configuration lies at 9.89 eV. This relative energy is 7.28 eV higher than the corresponding energy in the presence of the hole in the 3s orbital and 2.44 eV lower in energy than the delocalized CT configuration calculated under $O_h$ symmetry. In Table 5.3 and 5.4 we present the results of Mulliken population analysis of the two configurations. As in the final states, the MPA results show roughly the same trends as obtained with the projection operator method presented in Ref. [12].

**FIGURE 5.6** Relative energies in eV for the 3s² states in the various steps of the calculations imposing $C_{4v}$ symmetry.
TABLE 5.3 Mulliken gross population of the open shell orbitals for the NCT and CT 3s² configurations obtained by imposing C₄ᵥ symmetry.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Open orbital</th>
<th>Ni-3d</th>
<th>Oₑq</th>
<th>Oₓ⁺</th>
<th>Oₓ⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCT</td>
<td>a₁ / b₁</td>
<td>97</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CT</td>
<td>b₁</td>
<td>98</td>
<td>1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>a₁</td>
<td>15</td>
<td>–</td>
<td>–</td>
<td>83</td>
</tr>
</tbody>
</table>

The tables show that the hole in the 3s² CT configuration is rather localized on the Oₓ⁻ centre, although somewhat less than in the 3s¹ case. The dipole moments calculated in Ref. [12] confirm this observation; μₓ (3s¹) is 3.42 and μₓ(3s²) is 3.26. Furthermore, we conclude from Table 5.4 that the increase in the number of d-electrons comparing the CT to the NCT configuration does not follow the simple picture of a transfer of one electron from O-2p to Ni-3d.

The projection of the symmetry-broken CT configuration gives three CT states with relative energies of 9.40 eV (³T₂₈), 9.65 eV (³A₂₈) and 9.69 eV (³E₈). The mutual overlaps of the symmetry-broken CT configurations are 0.080 for holes on the same axis and 0.104 for holes on different axes. The ³A₂₈ CT configuration has an overlap with the NCT configuration of 0.58 and orthogonalization shifts the relative energy of the CT configuration up to 11.94 eV. The interaction between the two configurations slightly increases the energy separation to 12.50 eV. The normalized NOCI wave functions for the two initial states are as follows:

\[ \Psi(1) = 1.10 \Phi(\text{NCT}) - 0.18 \Phi(\text{symm. proj. CT}) \]  \hspace{1cm} (5.3)

\[ \Psi(2) = 0.56 \Phi(\text{NCT}) - 1.21 \Phi(\text{symm. proj. CT}) \]  \hspace{1cm} (5.4)

TABLE 5.4 Ni(d) gross populations of the NCT and CT 3s² configurations according to Mulliken population analysis.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Symmetry</th>
<th>Closed shells</th>
<th>Open shells</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCT</td>
<td>³A₂₈ (in O₅₈)</td>
<td>6.07 (6)</td>
<td>1.94 (2)</td>
<td>8.01 (8)</td>
</tr>
<tr>
<td>CT</td>
<td>³B₁</td>
<td>7.51 (8)</td>
<td>1.13 (1)</td>
<td>8.65 (9)</td>
</tr>
</tbody>
</table>
The character of the initial states was determined by calculating the overlap of \( \Phi(NCT) \) with the two NOCI wave functions. The overlap of the lowest initial state with this reference d\(^8\) configuration is very high (0.98), which indicates that this initial state can be thought of as an almost pure d\(^8\) state. On the other hand the overlap of the higher initial state is only 0.02 and carries much CT character.

The energy separations of the two initial states obtained under \( O_h \) and \( C_{4v} \) symmetry is effectively equal, whereas an important difference is found for the final states. At first sight, this is somewhat surprising, since the 3s\(^2\) CT configuration in \( C_{4v} \) symmetry is also rather localized. However, the energetic difference between the \( O_h \) and \( C_{4v} \) values for the CT configuration is smaller in the 3s\(^2\) case (11.65 - 9.65 = 2.00 eV) than in the 3s\(^1\) case (4.55 - (-0.37) = 4.92 eV). NOCI lowers this difference in the 3s\(^1\) case by 2.22 eV to 2.70 eV (7.61 - 4.91) and approximately the same decrease is found for the 3s\(^2\) states; a decrease of 1.82 eV in the difference of the energy of the CT configuration obtained in \( O_h \) and \( C_{4v} \) brings the total splitting of the initial states at 12.5 eV either obtained by imposing \( C_{4v} \) or \( O_h \) symmetry relations.

Relative intensities of the final states

As described in the computational information, the relative intensities of the two final states are calculated within the sudden approximation, i.e. by calculating the overlap of the NOCI wave functions (5.1) and (5.2) with the initial state wave function of equation (5.3). By normalizing the squared overlap of the lower final state with the initial state to 1, the intensity of the final state at 5.68 eV is calculated to be 0.17. Although the relative intensities are not determined experimentally, it is clear from the spectrum [5] (see also Figure 5.1) that the higher state (experimentally at 6.1 eV) carries much less intensity than the main peak. Furthermore, our result is rather similar to the theoretical estimate given in Ref. [5] of a relative intensity of the higher state of 0.20–0.25.

Ni-3s Ionization energy

The success of predicting ionization energies by Koopman's theorem [16] lies in the cancellation of orbital relaxation and electron correlation effects. In general this cancellation is more effective for the valence orbitals, since the two effects are comparable in size. The ionization energies for core levels are less accurately predicted by Koopman's theorem, because relaxation effects are larger than
5.3 Results

electron correlation effects. The Koopman's ionization energy for a Ni-3s electron is 133.08 eV. A more accurate estimate is obtained from the NOCI calculations; the calculated ionization energy of the lowest 3s-hole state ($\Psi(1)$ of equation (5.1)) is 122.51 eV, which is about 9 eV higher than the experimental value reported in Ref. [5]. However, the ionization energy is measured with respect to the Fermi level of Ag [17], whereas the computed value is determined with respect to vacuum. Taking an average value of the Ag work function of 4.5 eV [18], we estimate the experimental ionization energy with respect to vacuum at 118.2 eV. This value is still 4.3 eV smaller than the calculated value. Several reasons can be given for the discrepancy between calculated and experimental value. In the first place, we did not consider the long-range polarization effects of the crystal in response to the ionization process (see section 1.3). In previous work [19] these effects have been estimated to lower the ionization energies associated with Ni by 3–4 eV.

Another effect not included in the calculations is the short-range repulsion of the ions directly surrounding the NiO$_6$ cluster. At present these ions are represented by point charges, but calculations with different embedding schemes for alkali halides, MgO and CuCl [20] have shown that ionization energies are significantly lowered when the point charge approximation for the ions around the cluster is improved. The effect of the short-range repulsion is essentially a one-electron effect on the initial states, and therefore the effect can be determined by comparing orbital energies in the different embedding schemes. Although there are some differences in computational details, the calculations for the NiO$_6$ cluster and the NiO$_6$Ni$_{18}^{MP}$ cluster presented in Chapter 2 and the calculations on an NiO$_6$ cluster embedded in frozen Mg$^{2+}$ ions [21] can be used to estimate the effect of the short-range repulsion on the 3s-ionization energy. The energy of the 3s-orbital is increased by more than 4.5 eV when the point charges for the 18 Ni$^{2+}$ ions around the cluster are replaced by AIEMPs with (1s, 1p) functions. This effect is smaller when frozen Mg$^{2+}$ ions are used; ~4.0 eV. This reduction was also observed in the analysis of Sousa et al. [20]. The bare AIEMPs clearly overestimate the effect of the short-range repulsion; an increase of the 3s-orbital energy is observed of almost 7 eV.

Finally, the effect of the electron correlation is not included in the calculated value of the ionization energy. Since the number of electrons in the final state is one less than in the initial state, the inclusion of electron correlation stabilizes the final state more than the initial state and will cause an increase of the ionization energy. In summary, three effects are not included in the estimate of the ionization energy. Accounting for long-range polarization and short-range
repulsion will lower the ionization energy by 7–8 eV. This brings the theoretical estimate below the experimental value by about 3 to 4 eV. On the other hand the inclusion of electron correlation effects will increase the energy difference between initial and final state and is expected to bring the experimental and theoretical estimate of the Ni-3s ionization energy in rather good agreement.

The ionization of other core levels

The method described above is of course not restricted to the Ni-3s XPS, but can be equally well applied to final states arising from any other core level ionization process. Table 5.5 presents the splittings of the high-spin coupled final states for the ionization of a Ni-3s, 2p and 1s electron, both partially (O\textsubscript{h}) and fully (C\textsubscript{4v}) accounting for the orbital relaxation effects accompanying the CT excitations. The results show that the splittings are not very dependent on the specific level from which the electron has been removed. Evidently, the removal of a core electron on the TM centre causes a potential on the ligands which is largely independent of the spatial extent of the core hole.

To further illustrate this observation a computational experiment has been performed in which a positive point charge is placed at the same position as the nickel nucleus to simulate a core hole of infinitely small dimension. In computational practice this is most easily done by increasing the nuclear charge of nickel to Z=29, the so-called equivalent-core approximation. The splitting obtained in O\textsubscript{h} symmetry is practically equal to the splitting obtained for the Ni-1s and 2p core hole, and slightly smaller than for the 3s-hole.

From these results, we conclude that in first approximation the Ni-1s, Ni-2p and Ni-3s core holes can be considered as simple positive point charges, although for the Ni-3s hole a small deviation is observed due to the large spatial extent of

\begin{table}
\centering
\caption{Comparison of the splitting of the high spin coupled final states (in eV) for different ionized core levels.}
\begin{tabular}{lcc}
\hline

XPS & O\textsubscript{h} & C\textsubscript{4v} \\
\hline
Ni-3s & 8.09 & 5.68 \\
Ni-2p & 7.72 & 6.25 \\
Ni-1s & 7.62 & 6.15 \\
Z=29 & 7.58 & \\
\hline
\end{tabular}
\end{table}
the hole. The application of this hypothesis predicts a lowering of the CT states due to the presence of a core hole on the TM ion by approximately the inverse of the Ni - O distance: \( \Delta E \approx \frac{Q}{r} = \frac{1}{3.9343} \text{ au} = 6.9 \text{ eV} \). In the calculations listed above for the initial and final states for the Ni-3s XPS a decrease in the relative energy of the CT configurations is observed of 7.28 eV for the localized orthogonal CT configuration and of 7.03 eV for the symmetry projected orthogonal CT configuration, which is in qualitative agreement with the values predicted from the point charge model for the core hole.

5.4 CONCLUSIONS AND SUMMARY

In this chapter we have applied \textit{ab initio} cluster calculations to investigate to what extent the high-spin coupled final states of the Ni-3s ionization process in NiO screen the core-hole potential. This screening effect appears as an increase of the importance of the CT configurations in the wave functions of the final states. We have demonstrated that these CT effects can be accounted for within the conceptually very attractive NOCI approach. Because both the \( d^8 \) and the \( d^9L^{-1} \) configurations are expressed in their own optimal orbital set, a balanced description of the different configurations can be obtained.

In the conventional octahedral TMO\(_6\) cluster the orbital relaxation due to the presence of holes on the central TM is fully accounted for, whereas the holes created on the ligands are always delocalized over more than one oxygen centre and therefore only part of the orbital relaxation is accounted for. To remedy this imbalance between NCT and CT configurations, we lowered the symmetry restrictions to C\(_{4v}\). An SCF wave function has been constructed in which the hole on the ligands is localized on one ligand only. Thereafter, a CT configuration of the correct cluster symmetry has been constructed by projection. This CT configuration is not only expressed in its own optimal orbitals but also includes the full orbital relaxation effects due to the presence of a hole on the oxygens.

The character of the two configurations, NCT and CT, has been analyzed by MPA. It was shown that the open shell orbitals have an almost atomic character, either localized on the Ni or on one of the oxygens. The total d-count for the NCT, 8.5, is far from the ionic formal number of 8 d-electrons. This indicates that the NCT configuration in the final states cannot be considered as a pure \( d^8 \) configuration. The two configurations have a very large overlap of 0.80 and are
Chapter 5: Core level ionization processes

almost degenerate; the CT configuration is 0.37 eV lower than the NCT configuration. When this overlap is removed and the interaction between the two configurations is accounted for, two final states result separated in energy by 5.68 eV in satisfactory agreement with the experimental splitting of ~6.1 eV.

The character of the two final states has been determined by calculating the overlap with the initial NCT configuration, which, in contrast to the NCT in the presence of a 3s-hole, can be considered as a d8 configuration. It has been found that both final states have a significant overlap with this reference configuration; 0.81 for the lower final state and 0.47 for the higher one. This shows that both final states do screen the potential arising from the core-hole, although not completely as assumed in many other interpretations of XPS spectra. The main reason for the breakdown of the simple picture of states with either one or no electron transferred from the ligands to the TM ion is that these CT and NCT configurations have a very large mutual overlap, which needs to be removed to obtain wave functions that can be interpreted in terms of observed final states.

The calculated relative intensities of the final states (1 : 0.17) are similar to what is found in experiment. Furthermore, we have given some arguments for the difference in absolute value of the experimental (118.2 eV with respect to vacuum) and theoretical (122.5 eV) estimate of the ionization energy. Three effects are not included in the calculations, which are: the long-range polarization of the cluster due to the ionization process (-3–4 eV); the short-range repulsion of the ions in the direct surrounding of the cluster (-3–4 eV); and the electron correlation effects on initial and final states. Adding up all these corrections brings theory and experiment in rather good agreement.

Finally, we have shown that the spectra arising from the ionization of other core levels on the TM ion are expected to be very similar to the Ni-3s XPS. It has been argued that the core potential can be considered as a positive point charge and that the spatial extent of the hole hardly influences the splitting of the two final states. Recent experiments for the Ni-2p XPS [22] showed that there is indeed a large similarity to the Ni-3s XPS.
5.5 References