Delocalized and correlated wave functions for excited states in extended systems

Stoyanova, Alexandrina

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Delocalization of excited, hole and added-electron states in NiO

ABSTRACT — A new theoretical approach was formulated in Chapter 3 for the generation of delocalized and correlated many-electron wave functions for excited states in extended systems. Using this method, we study the dispersion of the energy of excitations in NiO which are considered to be predominantly localized. The excited state associated with the crystal field splitting of the system is discussed in some detail. Furthermore, the lowest hole and added-electron states are addressed in relation with the top of the valence and the bottom of the conduction band.

7.1 Introduction

We introduced in Chapter 3 a new wave function based method for describing excited states in extended systems with strong electron correlation effects. One aspect of this approach is the computation of the Hamiltonian matrix elements and overlap integrals between localized states in extended systems. This was addressed in Chapter 4 where we studied the double exchange parameters in lightly hole- and electron-doped manganites.

In this chapter, we probe the energy $\epsilon(K)$ dispersion of hole and added-electron states in NiO by means of the new method, designed to take into consideration explicitly the electron correlation and relaxation effects. The lowest hole and added-electron states are associated with the top of the valence and the bottom of the conduction bands and hence, the method allows for obtaining an estimate of the fundamental band gap of the compound. Before addressing these states we direct our attention towards the $K$-dependence of the lowest excited state, which is associated with the crystal field splitting of the Ni 3$d$ orbitals in NiO.

NiO has a cubic face-centered (FCC) NaCl (rock salt) crystal structure with a
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crystal space group $Fm\bar{3}m$ above its Néel temperature, $T_N=523$ K. In this T regime the crystal is paramagnetic [51]. Below the Néel temperature, NiO is a type-II FCC antiferromagnetic compound ($AF2$) [51] with a ferromagnetic alignment of the magnetic moments of Ni ions on every $(111)$ plane and an antiferromagnetic alignment for adjacent planes (see Figure 7.1). The transition from the paramagnetic state to the antiferromagnetic state is accompanied by a slight rhombohedral distortion from the original cubic unit cell along one of the \{111\} directions, ($R\bar{3}m$). The lattice constant is 4.17 Å below $T_N$ and increases slightly up to 4.20 Å between 7 and 700 K [52]. In a simple ionic ansatz NiO is thought to be built from Ni$^{2+}$ (\ldots3d$^8$) and O$^{2-}$ (\ldots2p$^6$) ions.

Embedded-cluster models have been routinely applied in the calculation of the d-d excitations in NiO (see for example [32,33]). These excitations have been referred to as predominantly localized and hence, the local cluster approach has been considered as an adequate model. A relevant question is whether indeed the cluster approach is justified for the d-d excitations. This question has been addressed by Fink [34] by means of the periodic CI method, which allows the author to describe transitions which belong to different $K$-vectors. See also Chapter 3 for somewhat more detail on the periodic CI method.

The conventional band structure calculations based on the effective one-electron picture have provided valuable information for compounds with weakly correlated electrons. Most often the effective potentials employed in this one-electron picture are derived within the LDA or LSDA to DFT [1]. The theoretical foundations of ground state- DFT do not provide a justification to relate the eigenvalues of the Kohn-Sham equations to the one-electron excitation energies of a system. Nevertheless, the band structures obtained within this approximation, are often in a quantitative agreement with results obtained in the angle-resolved photoemission spectroscopy [6]. In Time-Dependent DFT however the differences between the eigenvalues of occupied and unoccupied one-electron orbitals are considered to be approximations to the one-electron excitation energies.

It is well known that in some classes of solids the LDA or LSDA-DFT fails to describe correctly the band gaps of the compounds. The transition metal compounds (TMO) with partially filled $d$- and $f$- shells with strong electron Coulomb interactions are representative for those classes of solids. These solids are referred to as strongly correlated materials.

NiO belongs to the family of the strongly correlated materials. The LSDA band structure calculations predict a value for the band gap of only a fraction of an eV [2]. NiO is known experimentally as an antiferromagnetic insulator with a band gap of 4.3 eV [3].

Although LSDA-DFT performs usually well for the ground state properties of the compounds, the excitations related to the band gaps can not be derived correctly from the Kohn-Sham eigenvalues obtained from a ground state calculation. The effective potentials, felt by the valence and conduction states are different, but within the Kohn-Sham theory the same potential is employed in both cases. We mention in this context the unoccupied-states potential correction within the LSDA formalism.
proposed by Anisimov et al [9] which is based on using different potentials for the electrons in the valence and conduction bands. The method produces a band gap of the compound of 3.9 eV.

Norman and Freeman [5] have shown, that if the band gap can be expressed as the difference of the total energies of the ground state and excited states (the latter are considered to be the states with Ni $d^7$ and Ni $d^9$ configurations) instead of being read off from the LSDA band structure, it is indeed possible to obtain a reasonable agreement within the framework of the LD super-cell impurity approach with angle-resolved-photoemission spectra (PES) [6], x-ray-PES [3] and Bremsstrahlung isochromat spectroscopy (BIS) [3].

A general explanation for the discrepancy is the strong Coulomb interaction between the electrons in the Ni-3d shell. Due to these interactions, the differential electron correlation effects between $d^n$ configurations with a different $n$ are rather substantial and hence, lead also to a substantial contribution to the energy splitting between $d^n$ configurations with different $n$. The $d^n$ configurations of the initial and final states, involved in transitions across the band gap, are characterized usually by different $n$. The complex $d^n$ multiplet structure of the TM compounds is hard to describe starting from the Kohn-Sham equations. The valence band PES [12] spectra as well as x-ray absorption spectra (XAS) [13] of various TMO are well reproduced by configuration interaction (CI) calculations on small clusters, that contain one TM ion and the neighbouring shell of ligands.

Within an ab initio cluster study, the intra-shell Coulomb and exchange interactions are treated explicitly. The advantages with respect to the LD approaches are that an extension beyond the effective one-electron models is straightforward and the $d^n$ multiplet structure can be described with a high level of accuracy [11]. The $d^n$ multiplet structure of the d-shell, modified by the crystal field splitting, is proved by valence band PES [12, 21] as well as valence band XAS [13] to persist in TM solids. While the cluster CI studies of Fujimori et al [12] on the valence band PES employ a semi-empirical determination of parameters, other cluster studies are based on a fully ab initio treatment of the cluster. The localized $d$-$d$ excitations observed in the optical spectra of NiO have been studied in detail using cluster models [32]. Early ab initio embedded cluster calculations on the [NiO$_6$]$^{10-}$ cluster have been performed using SCF and limited CI expansions by Bagus and Wahlgren [69] who have demonstrated also that the localized approach is appropriate as a starting point for the description of the 3d states. Most recently, Satitkovitchai et al [14] have performed ab initio embedded cluster calculations on the ground and low-lying exited states of the bulk and of the (001) surface of NiO in relation with the second-harmonic and optical absorption spectra of the compound.

In this context, we also mention the CI approach with model Hamiltonians applied to Anderson impurities and clusters [27, 28]. These models provide many-electron solutions for the system by taking into account the multiplet splitting of the single $d$-shell [31].

When one discusses the valence hole (ionization) spectra and the electron addition spectra in transition metal oxides one must consider the effect of the $d$-$d$ correlation
and, in addition, also the TM 3d -O 2p interactions on the ionization and electron-addition processes. Those effects can be incorporated in the quantum mechanical treatment in a straightforward manner if the systems are modeled within the embedded cluster approach. We discussed in the previous chapters applications of this approach in the calculation of localized excited states, ionized and added-electron states as well as magnetic couplings in transition metal compounds. In this Chapter we consider the \textit{ab initio} embedded cluster study of the band gap in NiO performed by Janssen and Nieuwpoort [11].

The nature of the fundamental absorption edge, charge transfer or Mott-Hubbard type, has been a question of controversy for a long time. Initially NiO was considered as a representative Mott insulator in which the insulating gap arises from the strong on-site Coulomb d-d repulsion [20]. This point of view however was not supported by PES and Bremsstrahlung-isochromat-spectroscopy measurements [3]. Sawatzky et al [3] proposed that NiO should be classified as CT insulator with a fundamental band gap resulting from the energy difference between an ionized state of oxygen character and an added-electron state of Ni d⁹ character. However the oxygen hole state in their interpretation of the valence band structure lies inside the large correlation gap in the Ni 3d band and is thus considered to be a 3d hole strongly screened by an oxygen electron.

Recent X-ray emission and absorption spectroscopy studies accompanied by X-ray photoelectron spectroscopy measurements of the valence and conduction band states of NiO by Schuler et al [4] indicated that the valence and conduction states immediately below and above the Fermi energy are primarily of Ni 3d -character hybridized with a small amount of O 2p -character states. These authors suggested that the character of the fundamental band gap of NiO may be better considered as a mixture of CT and Mott-Hubbard type.

The optical band gap in NiO is usually assumed to be of CT type. The photoelectron spectroscopy measurements [3] have estimated the conductivity band gap to be 4.3 eV which is slightly larger than the optical absorption edge at 3.8 eV [22]. The optical band gap is regarded by Hüfner et al. [23] as the energy difference between the onset of the O 2p ionization considered to be near the Fermi level and the first d⁹ state, and its magnitude is almost the same as that of the fundamental band gap. On the other hand some revised experimental results obtained by Hüfner [24] re-invoked the possibility that the optical band gap in NiO corresponds to a transition between lower and higher Ni 3d bands.

Despite the fact that NiO is now widely accepted to be best characterized as CT insulator, the character of the fundamental band gap is still somewhat questionable. While the bottom of the conduction band regarded as arising mainly from the lowest Ni d⁹ added-electron state is not questionable, the top of the valence band appears to be a subject of debate.

Along with the experimental results some theoretical model Hamiltonian calculations on impurities Ni ions in an O 2p band [27,28] have predicted the lowest ionized state to be predominantly of d⁸O⁻ character. Fujimori et al [12] performed a model CI study on an embedded \([\text{NiO}]_{6}^{9−}\) cluster and proposed the interatomic 3d-3d charge
transfer transitions to be the origin of the NiO fundamental absorption edge. However they also considered the possibility that the 3d hole state associated with the lowest ionization energy is accompanied by an oxygen to metal 3d charge transfer.

Janssen and Nieuwoort have addressed as well this controversial subject using the cluster approach [11]. Cluster models have been employed in a combination with the LDA-DFT formalism [25], but they reproduce to some extent the problems existing in the conventional LDA band structure calculations, the band gaps are found to be less than an 1 eV.

Janssen and Nieuwoort obtained an estimate for the Mott-Hubbard gap $U$ and the CT gap $\Delta$ of NiO using a model $[\text{NiO}_6]^{10-}$ cluster in an electrostatic field of optimized point charges. They performed HF and first-order CI (FOCI) [11] calculations to investigate the ionization and electron-addition spectra of $[\text{NiO}_6]^{10-}$ which allowed them to obtain an insight in the character of the states involved in the band gap transition. The authors also adopt the widely accepted point of view concerning the Ni-Ni interactions in the bulk solid as being negligible. They justify their choice with the resemblance of the low-energy optical spectrum of MgO:Ni and that of NiO [47]. The values obtained for $U$ and $\Delta$ within the cluster model are rather similar and no definite answer could be given as to which quantity $\Delta$ or $U$ determines the band gap. This was due to the large uncertainty in the relative positions of the first ionization energies obtained from the cluster study. Nevertheless the authors have shown the importance of the inclusion of the local electron correlation and relaxation effects as well as the extra-cluster bulk polarization corrections for the accurate determination of $U$ and $\Delta$. Janssen and Nieuwoort comment on the inclusion of the Ni-Ni interactions but they do not expect a large effect on the energies.

The purely localized approach explains the experimental observations in the X-ray PES and Bremsstrahlung-isochromat -spectroscopy [3]. Band calculations based on the self-interaction-corrected DFT [27] and the LDA+U method [7,8] were performed to compute the energy gaps. Indeed the energy gaps improved compared to the LDA and LSDA results however, the usual implementation of LDA+U [8] introduces two semi-empirical parameters and the strong on-site electron correlation effects, which are of importance for the Ni 3d states, are parametrized.

Another post-LDA approach which handles the self-energy error, is the many-body GW approximation [35]. The self-consistent GW approximation has been found able by Massidda et al [37] to obtain a magnitude of the band gap in reasonable agreement with experiment, $\sim 3.7$ eV. Non-self-consistent GW calculations, carried out by Aryasetiawan and Gunnarsson [36], have yielded a band gap significantly larger ($\sim 5.5$) than the experimental band gap. Recent self-consistent GW calculations within the all-electron full potential linear muffin-tin orbital method [38], carried out by Faleev et al, have led to a band gap of 4.8 eV in a very good agreement with the experimental gap of 4.3 eV [3].

A detailed study of the electronic structure of NiO performed by Moreira et al [39] using three different periodic approaches, UHF, LDA and exploiting several hybrid DFT functionals, such as the B3LYP functional, has revealed the potentials and drawbacks of the three approaches for the description of the band gap, magnetic
coupling, lattice constant and other properties. DOS obtained within UHF, LDA, B3LYP and other hybrid functionals with 35% and 50% Fock exchange, predicts an insulating character with a large band gap while, LDA predicts NiO to be a metal. They show that the band gap is rather sensitive to the amount of the Fock exchange and varies from 15.1 eV to almost 0.0 eV. The B3LYP method predicts a band gap in excellent agreement with the experiment. The authors point out that increasing the fraction of the Fock exchange leads to an increase in the O (2p) density at the Fermi energy and a decrease in the Ni 3d density, thus resulting into a charge transfer type band gap. Dovesi et al [43] performed also periodic UHF and L(S)DA calculations on the electronic structure of NiO and their findings are essentially the same.

Within the framework of the UHF, UHF+LYP, B3LYP, Perdew-Wang GGA DFT approaches to periodic calculations, Bredow and Gerson [40] discussed the nature of the upper part of the valence band in NiO. These authors also found that the most important difference between the methods based on the pure HF exchange and those based on a hybrid DFT approach is that in the DFT approaches the contribution of the Ni 3d orbitals in the upper part of the valence band is increased [40]. We mention also the analogous periodic HF study performed earlier by Towler et al [42].

Takahashi et al [41] carried out UHF calculations within the local cluster approach employing a [NiO$_6$] cluster embedded in a point charge representation of the ions surrounding the cluster. They noted that the main discrepancy between the band gap obtained from their study, 9.9 eV, and that reported by Zaanen et al [30], 4.3 eV, is due to the fact that electron correlation has not been taken into account within their analysis and that the point charge representation of the ions, surrounding the cluster, is only a rough approximation of the Coulomb short-range interactions between cluster and surrounding crystal. The latter results into not sufficiently accurate ionization energy and electron affinity. As we see later in the section 7.4 the ionization energies and electron-addition energies are indeed very sensitive to the model representation of the nearest embedding ions around the cluster. Furthermore, compared to Janssen and Nieuwpoort [11], Takahashi et al [41] obtained distinguishable values of the Mott-Hubbard gap, $U$, and the CT gap, $\Delta$, from which they concluded that the band gap of the compound is a CT type. However, Janssen and Nieuwpoort [11] carried out ab initio calculations of a higher accuracy accounting in a rigorous manner for the electron correlation and relaxation effects (see above).

As discussed above, angle-resolved photo-emission studies on NiO by Shen et al [6] have revealed that neither the conventional one-electron band structure theory nor the purely localized (cluster) approaches can yield complete and accurate picture of the lowest holes states. A semi-empirical model of Bala et al [15], which includes the multiplet structure of the electronic excitations in NiO and the interaction of the O 2p holes in the O bands with the spins localized on Ni ions, agrees well with the experimental data of Shen et al [6]. Bala et al have found that the low-energy hole states in NiO are O 2p hole states and they show a considerable $k$ -dependence.

Despite the success of the cluster approach to reproduce accurately angle-integrated quantities in different photoemission and photoabsorption spectroscopies and to allow for a proper account for the electron correlation and relaxation effects, its local
character makes it impossible to obtain $k$-resolved electron ionizations and additions. It disregards the periodicity of the correlated sites and the dispersion of the bands in the solid.

The necessity of a new ab initio approach which incorporates both the local many-electron and band-like effects in one becomes evident from the discussion above. In Chapter 3, we mentioned a number of such approaches that make use of the so-called incremental scheme [48] which allows for incorporating the electron correlation effects in the band structure calculations [49, 50]. We introduced as well the method developed in this thesis to allow for combining the advantages of the local methods with those of the band approaches. The study of the top of the valence band and the bands at the bottom of the conduction band is based on this new method and demonstrates its advantages above the conventional local and one-electron band approaches.

The rest of the chapter is organized in the following manner. We outline in a concise form the formalism of the method, that was introduced in Chapter 3. Next we consider the $K$-dependence of the excitation related to the 10 Dq parameter. Then, we report our results for the dispersion of the energy $\epsilon(K)$ with the momentum $K$ of hole and added-electron states in NiO. The role of the magnitude of the Hamiltonian matrix elements and overlap integrals, related to this process is analyzed.

### 7.2 Theory

As described in Chapter 3, one can express the crystal wave functions $\Psi_{nK}$ of excited, ionized or added-electron states in an extended system in terms of linear combinations of Bloch sums of local many-electron (ME) basis functions $\{\Phi_a(r_1, r_2, ..., r_{N+M})\}$. The Bloch-type ME basis functions are given as:

$$\Theta_{aK}(r_1, r_2, ..., r_{N+M}) = \frac{1}{\sqrt{N_1N_2N_3}} \sum_R e^{iK \cdot R} \Phi_a(r_1 - R, r_2 - R, ..., r_{N+M} - R), (7.1)$$

where $\Phi_a(r_1, r_2, ..., r_{N+M})$ describes a localized excited, ionized or added-electron state $a$ and $N_1$, $N_2$ and $N_3$ are the number of unit cells in each of the three crystal dimensions, respectively. The summation runs over all lattice vectors $R$. Using these Bloch-type ME basis functions, one needs to apply the variational procedure to obtain the best approximations to the crystal wave functions $\Psi_{nK}$,

$$\Psi_{nK}(r_1, r_2, ..., r_{N+M}) = \sum_a \kappa_{na}(K) \Theta_{aK}(r_1, r_2, ..., r_{N+M}) (7.2)$$

The $\Psi_{nK}$ can be derived by solving a generalized eigenvalue problem. Furthermore, the matrix elements of $H(K)$ and $S(K)$ between the Bloch-type ME basis functions are expressed in terms of the matrix elements between the localized ME basis functions from the basis set $\{\Phi_a(r_1, r_2, ..., r_{N+M})\}$.

Next the localized ME basis functions are chosen to be antisymmetrized product wave functions, constructed from a correlated MCSCF wave function for a relevant N-electron super-cluster and an M-electron embedding wave function, where the latter
represents a frozen electron distribution for the environment. This approximation to the local ME basis functions allows one to approximate the $H(R)$ and $S(R)$ matrix elements between the localized ME basis functions by the matrix elements of the super-cluster.

The Hamiltonian matrix elements and overlap integrals obtained within the embedded super-cluster calculations are employed to obtain the eigenvalues $\epsilon_{n\mathbf{K}}$ associated with the eigenfunctions $\Psi_{n\mathbf{K}}$. We referred in Chapter 3 to the distribution of the $\epsilon_{n\mathbf{K}}$ for a given $n$ with respect to $\mathbf{K}$ as to a ”many-body” energy band.

We employ this approach below to study the $\mathbf{K}$- dependence of hole and added-electron states in NiO associated with the top of the valence and the bottom of the conduction bands. The localized orbital sets in which the CASCI wave functions of the super-clusters, representing the localized ME basis functions, are expressed, are derived from CASSCF calculations on fragments. The study of different overlapping fragment schemes applied to hole and electron states in hole- and electron-doped manganites (Chapter 4) has shown, that the optimal scheme for those states is OF1. This OF1 scheme is employed throughout this study to obtain the localized orbital sets of the super-clusters.

Before addressing in detail the hole and added-electron states in NiO, we study the $\mathbf{K}$- dependence of d-d excitations, regarded usually as localized excitations. We consider in particular the excitation which determines the 10 $D_q$ parameter in the compound. While for the hole and added-electron states the OF1 scheme was established to be optimal, this may not be true for localized excitations. We discuss this issue in section 7.4.1.

### 7.3 Material model and Computational information

To obtain the dispersion of the bands at the top of the valence band and at the bottom of the conduction band, the $AF2$ state of NiO without the small rhombohedral distortion is considered and the bands are calculated along selected symmetry directions and at high symmetry points within the first Brillouin zone corresponding to the cubic AF compound. The Ni-O distances are fixed to the experimental values of 2.085 Å or 3.9343 bohr [53]. In the rock salts structures, each ion is surrounded by its six nearest neighbour counterions so the NiO$_6$ units form regular octahedra and have a local symmetry, characterized by the $O_h$ symmetry point group. The formal ionic charges are +2 for Ni and -2 for O which leads, omitting the inner shell orbitals, to the Ni$^{2+}$ (... $3d^8$) O$^{2-}$ (... $2p^6$) valence shell configuration for the ground state. The ground state of Ni$^{2+}$ in NiO is a $^3A_{2g}$ state in terms of the $O_h$ symmetry point group.

Making use of the concept of a super-cluster built from fragments, we designed [NiO$_6$] fragments and various super-clusters along the (100) direction of the cube, [Ni$_2$O$_{11}$] and [Ni$_2$O$_{11}$O$_{12}$] and within the (110) plane, [Ni$_2$O$_{10}$] and [Ni$_2$O$_{10}$O$_{12}$]. These super-clusters allow us to access the Hamiltonian and overlap matrix elements between CASCI wave functions representing Ni hole or added-electron states localized around two distinct Ni lattice sites.
Furthermore a super-cluster \([\text{Ni}_6\text{O}_6]\) was designed to allow for a balanced treatment the two different hole states at the Ni or O ions. The treatment is not balanced if one employs the \([\text{NiO}_6]\) cluster for both Ni and O hole states, because of the non-equivalent nearest environment of the Ni and O ions. Finally, to obtain an estimate for the matrix elements between the localized O hole states, a linear super-cluster \([\text{O}_2\text{Ni}_3]\), built along the \((100)\) direction, is employed which is constructed from two overlapping \([\text{ONi}_2]\) fragments, built also along the \((100)\) direction of the cube. The model super-cluster \([\text{O}_2\text{Ni}_3]\) provides an access to O-O \(\sigma\sigma\)-type interactions along the \((100)\) direction. In order to access also the O-O \(\pi\pi\)- and \(\sigma\pi\)-type interactions along the \((100)\) direction and within the \((110)\) plane, respectively, three other super-clusters were designed, namely \([\text{O}_2\text{Ni}_5]\) with the O-Ni-O bonds along \((100)\), and \([\text{O}_2\text{Ni}_3]\) and \([\text{O}_2\text{Ni}_4]\) within the \((110)\) plane. The four super-clusters can be viewed as constructed from two overlapping \([\text{ONi}_2]\) or \([\text{ONi}_3]\) fragments with one shared Ni ion for \([\text{O}_2\text{Ni}_3]\), \([\text{O}_2\text{Ni}_3]\) and \([\text{O}_2\text{Ni}_5]\), and two shared Ni ions for \([\text{O}_2\text{Ni}_4]\), respectively.

The fragments and super-clusters are embedded in effective model potentials \([54]\). The short-range Coulomb interactions are accounted for by representing the nearest neighbour ions by either bare ab initio model potentials \([54]\) or AIMPs augmented with 1s1p basis functions (for the case of super-cluster \([\text{Ni}_6\text{O}_6]\)). The latter functions are used to maintain the strong orthogonality condition between the cluster and the ions in the direct environment \([55,56]\).

The long range electrostatic interactions are described by an array of optimized point charges placed at lattice positions to reproduce the external Madelung potential on a fine grid within the fragment/super-cluster region. The orbitals are expanded in atom centered ANO-type basis functions \([65]\): for Ni a primitive set of \([21s, 15p,\)
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Figure 7.2: Super-cluster [Ni₆O₆]. The ions in the super-cluster are depicted as white (O) and black (Ni) balls. The hollow equatorial balls represent embedding Ni ions (AIMPs-1s1p) while the hollow striped balls represent the embedding O ions (AIMPs-1s1p).

10d] Gaussians is contracted to (6s, 5p, 4d) and for O a [14s, 9p]/(4s, 3p) Gauss type basis set is used.

The specification of the active spaces, employed for fragments and super-clusters in the construction of the CASCI and CASSCF wave functions for the hole and added-electron states, is provided in the sections, where those states are discussed.

7.4 Results and Discussion

7.4.1 Delocalization of d-d excitations

Employing the new method we studied the delocalization of an excited state in NiO associated with the crystal field splitting 10 $D_q$ of the compound. Earlier investigations have been performed within the conventional cluster models (see e. g. [32,33,55]) and have shown that the excitations involved in the determination of the crystal field splitting (10 $D_q$) have a rather local character. Moreover, de Graaf et. al. [55] have established that the details of the embedding influence the 10 $D_q$ by a small amount of +0.15 eV when replacing the nearest point charges for Ni and O ions around a [NiO₆] cluster by AIMPs augmented with 1s1p basis functions.

In a simple crystal-field model the five Ni 3d levels split into three $t_{2g}$ and two $e_g$ levels. The $^3A_{2g}$ ground state has a ....$t_{2g}^6e_g^2$ configuration; the first excited state, $^3T_{2g}$, has one electron promoted from $t_{2g}$ to $e_g$: ....$t_{2g}^5e_g^3$. The energy difference between the two states is to first approximation equal to the $t_{2g}$-$e_g$ energy splitting. This energy difference is traditionally called 10 $D_q$. For the 10 $D_q$ excitation, a value
of 1.13 eV was deduced experimentally [19]. Furthermore, de Graaf et al. [32, 55] have found that an accurate account for the static and dynamic electron correlation effects via the CASSCF/CASPT2 method is necessary for obtaining a quantitative agreement with experiment. Their best estimate of 10 $D_g$ of ~ 1.15 eV is obtained within the CASSCF-pdd/CASPT2 method and an embedding representation of the nearest 18 Ni ions around the basic [NiO$_6$] cluster by either AIMPs+1s1p or by a frozen charge distribution [55].

The delocalization effects on the excitation have been probed explicitly by Fink [34], using a newly designed periodic CI method which combines wave function based approaches for excited states with accounting for the translational symmetry of the crystal. The method allows Fink to calculate energy bands associated with the excitations, i.e. $K$-dependent excitation energies. The periodic CI approach incorporates a large amount of static electron correlation effects but it gives only limited account of orbital relaxation and dynamic correlation. The latter can be obtained in a straightforward manner within the cluster and within the method, presented in this thesis.

To obtain an insight into the delocalization effects on the excitation involved in the 10 $D_g$ transition, we calculated the effective hopping matrix elements associated with the hopping of the exciton between two neighbouring Ni lattice sites along the $\langle 100 \rangle$, $\langle 001 \rangle$ and $\langle 110 \rangle$ directions. For this purpose, we employed two-Ni-center super-clusters, [Ni$_2^3$O$_{11}$], [Ni$_2^3$O$_{11}$] and [Ni$_2^{xy}$O$_{10}$], built along $\langle 100 \rangle$, $\langle 001 \rangle$ and $\langle 110 \rangle$, respectively from two overlapping [NiO$_6$] fragments. The [NiO$_6$] fragments, as well as the super-clusters, are embedded in bare AIMPs, representing the nearest Ni ions around the basic clusters, and a set of optimized point charges describing the distant Ni and O ions. Compared to the ionized and added-electron states which energies are very sensitive to the details of the embedding, the localized excitations are affected little by the presence of orthogonalizing 1s1p basis functions on the bare AIMPs. Using a [NiO$_6$] cluster, de Graaf et al. [55] have found a decrease of 0.1 eV in the excitation energy when the bare AIMPs are augmented with 1s1p basis functions.

CASSCF calculations are carried out for the ground state, $^3A_{2g}$, and excited state, $^3T_{2g}$, of the [NiO$_6$] fragment within an active space of 8 electrons in 5 Ni 3$d$ orbitals (CASSCF-d). Within this active space, the configurational composition of the wave function of $^3A_{2g}$ is 100 $\%$ ($t_{2g}^2$) ($t_{2g}^2$) ($t_{2g}^2$) ($e_g^2$) ($e_g^2$) ($e_g^2$) from the conventional notation [70]. In this notation $t_{2g}^2$, $t_{2g}^2$ and $t_{2g}^2$ are the three components, $yz$, $xz$ and $xy$, of $T_{2g}$, and $e_g^2$, $e_g^2$ and $e_g^2$ are the two components, $2z^2$ - $x^2$ - $y^2$ and $(x^2 - y^2)$, of $E_g$ in the point group $O_h$. The CASSCF energy of $^3T_{2g}$ within CASSCF-d is at 1.07 eV above the ground state. In the present study we concentrate attention on the component of the $^3T_{2g}$ excited state which is represented by a single Slater determinant within the formalism of the crystal-field theory. Using conventional notation [70] we write the dominant electronic configuration associated with this component $^3T_{2g}^3\xi$ of the $^3T_{2g}$ excited state as $^3T_{2g}^3\xi$ ($t_{2g}^2$) ($t_{2g}^2$) ($t_{2g}^2$) ($e_g^2$) ($e_g^2$) ($e_g^2$) ($e_g^2$) ($e_g^2$) ($e_g^2$) ($e_g^2$). The contribution of this configuration in the wave function of the $^3T_{2g}$ excited state is practically 100 $\%$. We compute $t$ of this component, $^3T_{2g}^3\xi$, with the same excited state, but now translated to neighbouring Ni ions in the $\langle 100 \rangle$, $\langle 001 \rangle$ and $\langle 110 \rangle$ directions. Interactions of $^3T_{2g}^3\xi$ with other $^3T_{2g}$ components at these neighbouring
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Table 7.1: Comparison of OF1 and OF2 for the description of the localized excited state, $^5E_z$, of the $[\text{Ni}_2\text{O}_{11}]^{38-}$ super-cluster and the localized excited state, $^5B_2$, of the $[\text{Ni}_{2y}\text{O}_{10}]^{16-}$ super-cluster; CASCI energies, $H_{11}=H_{22}$, in hartrees; Effective hopping integrals $t_x$ (along $\langle 100 \rangle$) and $t_{xy}$ (along $\langle 110 \rangle$) are listed in meV.

<table>
<thead>
<tr>
<th></th>
<th>OF1</th>
<th>OF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-t_x$</td>
<td>1.35</td>
<td>2.86</td>
</tr>
<tr>
<td>$H_{11}^{5E_z}$</td>
<td>-3959.927628</td>
<td>-3959.904043</td>
</tr>
<tr>
<td>$-t_{xy}$</td>
<td>1.30</td>
<td>0.81</td>
</tr>
<tr>
<td>$H_{11}^{5B_2}$</td>
<td>-3687.328499</td>
<td>-3687.267739</td>
</tr>
</tbody>
</table>

Ni ions as well as interactions with other sites are zero by symmetry or negligible. The composition of the singly occupied $e_g\theta$, or $2z^2-x^2-y^2$ orbital for this state according to Mulliken population analysis constitutes of 91% Ni $3d$ character. The singly occupied $t_2g\zeta$ or $xy$ orbital is rather localized: 99% Ni $3d$.

In constructing the localized orbital basis for the CASCI wave functions of the super-clusters, representing the same excited state, but now localized around one or the other Ni ions in the super-clusters, we compared both OF1 and OF2 schemes. In the OF1 scheme the doubly occupied orbitals for the O ion, shared between the fragment with the excitation, $[\text{NiO}_6]^*$, and the fragment in the ground state configuration, $[\text{NiO}_6]$, are constructed as linear combinations, with equal coefficients, of the unitary transformed doubly occupied orbitals of that O ion, derived for the fragments $[\text{NiO}_6]^*$ and $[\text{NiO}_6]$. In the OF2 scheme, the doubly occupied orbitals for the shared O ion are chosen to be those derived for the excited $[\text{NiO}_6]^*$ fragment.

The $[\text{Ni}_2\text{O}_{11}]^{38-}$ super-cluster has $D_{4h}$ symmetry with the $C_4$ axis along the $\langle 100 \rangle$ direction, but the localized CASCI wave functions have only $C_{4v}$ symmetry. They transform as $E_z$, $E_y$ and $A_2$. The localized CASCI excited state, that we concentrate on has symmetry $^5E_z$. Analogously, the symmetry of this state in the $[\text{Ni}_{2y}\text{O}_{10}]^{16-}$ super-cluster is $^5B_2$.

The symmetry of the $[\text{Ni}_{2y}\text{O}_{10}]^{16-}$ super-cluster is $D_{2h}$ with the $C_2$ axis along the $\langle 110 \rangle$ direction. The localized CASCI excited state transforms according to $^5B_2$ in $C_{2v}$. In Table 7.1 we summarize for both OF1 and OF2 schemes the CASCI energies of the localized excited states as well as the effective hopping integrals associated with the hopping of the exciton between two neighbouring Ni ions. As expected, the effective hopping integrals are small. An inspection of the values of $t_x$ and $t_{xy}$, the hopping integrals along $\langle 100 \rangle$ and along $\langle 110 \rangle$, respectively, shows that they are affected by the chosen overlapping scheme. The $t_z$ integrals are not listed in the Table because they were found to be negligible in agreement with the mutual $\delta$-type orientation of the singly occupied $t_2g\zeta$ orbitals in the two localized excited states.

Comparing the total CASCI energies of the localized excited states of the super-clusters, obtained within OF1 and OF2 (in Table 7.1) reveals that the OF1 scheme yields lower total energies. These energies are at about 1.0 eV above the super-clusters
ground state in both $OF1$ and $OF2$, which is essentially the same as the excitation energy for the $[\text{NiO}_6]$ fragment. Although $OF1$ and $OF2$ yield different magnitudes for the effective hopping integrals, in both schemes these effective matrix elements are very small. The $OF1$ scheme appears to be the best scheme for this study of the excited states because it produces lower CASCI energies.

The small hopping integrals lead to very narrow energy bands associated with the localized excited states. The band stabilization energy $\Delta E$ related to the delocalization of, for example, the localized excited CASCI state which has the $e_{2g}\theta$ and $t_{2g}\zeta$ orbitals singly occupied, is obtained using the simple relation, $\Delta E \sim 4t_{xy}+2t_x+2t_y+2t_z \approx -0.01 \text{ eV}$. Clearly, the excitation energy bands will have a width of at most 0.02 eV. This finding is in reasonable agreement with the results of Fink [34] who obtained the energy of the localized d-d excitation to differ from the excitation energy at the $\Gamma$ point by about 0.05 eV. The explicit derivation of the many-body excitation energy bands, associated with the localized excited states, $^5E_z$, does not bring new insights and thus, it is not presented.

7.4.2 Delocalized hole and added-electron states

Key ingredients to the correct description of valence hole states and added-electron states in these strongly correlated TM oxides are an accurate account for the electron correlation and relaxation effects as well as the polarization effects that occur in the crystal upon ionization or electron addition. A delocalized one-electron approach does not allow for incorporating these effects. The local effects stabilize the localized electron or hole state and in case their contribution is dominant, the localized states provide a better description. For extensive studies on localized states in molecules and solids see [60–62] and [57–59], respectively. Wave functions which describe hole states localized at a particular lattice site are not in general adequate approximations to the electronic wave functions of the crystal because of the relaxed symmetry restrictions. The localized wave functions do not transform according to the irreducible representations of the space group of the crystalline system. Therefore, they have to be re-symmetrized. While in the case of core hole states the on-site effects are predominant [60,61] and the energy associated with the localized wave function may be (almost) the same as the energy associated with the resymmetrized wave function, it has been shown by Janssen [57–59] et al. and Broer [60,62] that the delocalizing and localizing effects are of equal importance in the case of valence hole states of TM oxides and thus, they must be treated on an equal footing. It is clear that the effective one-electron model, on which the conventional band theory is based, is not sufficient for the proper treatment of those states. The delocalized description must incorporate relaxation and polarization contributions, which is not feasible within the one-electron approach. The (band) stabilization energy for the lowest (translational) symmetry-adapted states may be comparable to the relaxation energy for the localized states. In that case, as pointed out by Janssen [57], resymmetrization of the localized states is necessary.

The discussion above concerns the hole states but similar considerations hold for
the added-electron states for which the delocalization effects are expected to have also a contribution comparable to that of the localization effects. Within the new approach both the localization and delocalization effects can be included.

7.4.3 Localized valence hole states

In order to incorporate the relevant electronic relaxation effects at the same level of approximation for both Ni and O hole states, one must design fragments and super-clusters for which the nearest neighbour environment is equivalent. The relative energy difference between localized hole states at Ni and O ions respectively, is obtained employing a neutral super-cluster \([\text{Ni}_6\text{O}_6]\), that treats the electronic relaxation effects for the two different types of holes on an equal footing. The super-cluster’s topology is illustrated in Figure 7.2. The local symmetry of the super-cluster is \(D_{4h}\), the symmetry of the localized hole states is \(C_{4v}\). The central Ni ions is denoted \(\text{Ni}^c\), the central oxygen ion \(\text{O}^c\).

In analogy with the studies in Chapter 4 we can choose the starting fragments to be \([\text{ONi}_6]\) and \([\text{NiO}_6]\) embedded clusters. In that case the procedure for constructing the localized orbital sets for the wave functions of the hole states in the super-cluster \([\text{Ni}_6\text{O}_6]\) would involve corresponding orbital analysis between the inactive or doubly occupied orbitals of the two fragments as well as between the inactive and active or singly occupied orbitals. The general approach was already discussed in Chapter 3 and applied in Chapter 4 only between the inactive orbitals of two or more \([\text{MnO}_6]\) fragments. The corresponding orbital analysis between the inactive and active occupied orbitals is straightforward but we choose in this case to obtain the relative energies of the Ni and O hole states by performing CASSCF calculations directly for the \(\text{Ni}_6\text{O}_6\) super-cluster, because it is simpler.

The dependence of the Ni 3\(s\) ionization energies in NiO on different embedding schemes has been established by de Graaf et al [55]. The authors have shown that the description of the Pauli repulsion between the ions in the basic cluster and the ions in its nearest surrounding is of a significant importance for the ionization energies. In particular the use of bare AIMPs leads to an overestimation of the effect of the Pauli repulsion and a consequent underestimation of the ionization energies. The AIMPs augmented with 1s1p basis functions, used here, produce results close to those, obtained by representing the ions in the nearest cluster environment by frozen charge distributions [55].

For the sake of interest we computed the first Ni 3\(d\) ionization energy for a \([\text{NiO}_6]\) fragment, using three different embeddings, using CASSCF results with an active space of 5 Ni 3\(d\) orbitals. The first Ni 3\(d\) ionization energy is taken as the relative energy of the lowest state of the \([\text{NiO}_6]\)^{9-} fragment, with symmetry \(4T_{1g}\), with respect to the ground state \(^3A_{2g}\) energy of \([\text{NiO}_6]\)^{10-}. This means that the hole is predominantly in Ni 3\(d\) (t\(_{2g}\)). The configurational composition of the CASSCF wave function of \(^4T_{1g}\) shows 92 % t\(_{2g}\)^5\(e_g^2\) and 8% t\(_{2g}\)^3\(e_g^3\) character. The CASSCF energy of \(^3A_{2g}\) is obtained within an active space containing 8 electrons in 5 Ni 3\(d\) orbitals. The CASSCF wave function of the ground state is 100 % t\(_{2g}\)^6\(e_g^2\). As expected, the
three different embedding schemes, optimized point charges, bare AIMPs and AIMPs augmented with 1s1p basis functions for the nearest Ni embedding ions of [NiO₆], produced diverse ionization energies. The ionization energy was largely overestimated using point charges (11.16 eV) and largely underestimated using bare AIMPs (3.09 eV). The AIMPs+1s1p1d yielded for the ionization energy 6.14 eV.

It is clear that in order to obtain the relative energy difference for the Ni and O hole states, one needs to choose the optimal description of the embedding ions. Preliminary CASSCF calculations on the [ONi₆] fragment, within an active space containing 17 electrons in 12 Ni -3d (e₉) -like and 3 O -2p orbitals, have indicated that the ionization energy of the lowest high-spin coupled O ionized state, ¹⁴T₁₃, of the [ONi₆] fragment decreases by only about 0.1 eV when the point charges description of the nearest embedding O ions is replaced by bare AIMPs.

The O ionization energy, associated with the creation of an O hole, is much less sensitive to the representation of the closest environment of the [ONi₆] fragment than the ionization energy for the Ni hole to the nearest embedding of the [NiO₆] fragment.

The ground state of [ONi₆] is denoted as ¹A₂ in the symmetry species of the Oₜ symmetry point group. The magnetic structure of NiO (see Figure 7.1) indicates low spin couplings between the high-spin coupled spins at each of the distinct Ni ions in the [ONi₆] fragment. Note however that at this level of approximation (CASSCF) we estimated the exchange coupling constant J between two neighbouring Ni ions along each of the three directions x, y, z to be -3.1 meV.

Because of the pronounced dependence of the Ni ionization energy on the embedding, the nearest Ni and O ions around [Ni₆O₆] have to be described by AIMPs+1s1p. This requirement leads to the following symmetrical configuration [Ni₆O₆]Ni₁₂MP O₁₂MP Ni₅MP O₅MP. Constructing this super-cluster from two overlapping [ONi₆] and [NiO₆] fragments would imply the use of embeddings for the fragments analogous to that of the super-cluster, [NiO₆]Ni₁₂MP O₈MP Ni₆MP and [ONi₆]O₁₂MP Ni₈MP O₆MP.

Using AIMPs+1s1p fragment embeddings for ions that are present in the super-cluster leads to some technical problems. To circumvent this technical difficulty, in this particular case, we performed the CASSCF calculations directly for the super-cluster.

CASSCF calculations within an active space containing 24 electrons in 12 Ni -3d (e₉) -like orbitals, 3 Ni° -t₂g-like orbitals, and 3 O° -2p are performed for the lowest high-spin coupled state ¹³A₁₉ of [Ni₆O₆]. This active space is denoted as CASSCF-pd. The absolute CASSCF energy of ¹³A₁₉ changes by about 1 meV when an active space consisting of only twelve Ni 3d (e₉) orbitals and 12 electrons is employed (minimum active space: CASSCF-d). ¹³A₁₉ lies above the ground state ¹A₁₉ of [Ni₆O₆] by about 0.02 eV. It differs from ¹A₁₉ by the high-spin coupling between the spins at distinct Ni ions. To a very good approximation this state may be regarded as a relative zero energy when evaluating the relative energies of the lowest O° and Ni° hole states with respect to the ground state of [Ni₆O₆].

An estimate of the effect of the different representation of the embedding on the ionization energies of the high-spin coupled Ni and O holes is obtained by comparing their relative energies yielded within the frozen orbital approximation for three
different embeddings of $[\text{Ni}_6\text{O}_6]$, optimized point charges, bare AIMPs and AIMPs augmented with 1s1p basis functions. Although the energies obtained within the frozen orbital approximation are not reliable in a quantitative sense, the change in the relative energies of the Ni$^c$ and O$^c$ hole states with the embedding is instructive for the embedding effect. The relative energies of the Ni$^c$ and O$^c$ hole states obtained from the energy of the $^{13}A_{1g}$ state of $[\text{Ni}_6\text{O}_6]$ within the three embeddings and within CASSCF -d, are depicted in Figure 7.3. The Ni$^c$ hole states, $^{14}B_2$ and $^{14}E$, in $C_4v$ notation have the hole in a Ni$^c$-3$d$ ($t_{2g}$) -like orbital. Within the three embeddings, the hole states associated with the central O$^c$ ion, $^{14}A_1$ and $^{14}E$ in $C_4v$ notation, are found below those associated with the central Ni$^c$ ion. The threefold degeneracy of the hole states is lifted because the site symmetry of Ni$^c$ and O$^c$ in the [Ni$_6$O$_6$] cluster is not strictly O$_h$. The relative energy difference between the Ni and O hole states changes significantly from PC ($\sim 5.17$ eV) to bare AIMPs ($\sim 1.97$ eV) and AIMPs+1s1p ($\sim 3.74$ eV).

Figure 7.3: $[\text{Ni}_6\text{O}_6]$ cluster. Relative energies (in eV) of Ni and O hole states obtained within the frozen orbital approximation for three embeddings: point charges (PC), bare AIMPs and AIMPs+1s1p.

Clearly, there is an initial state effect of the embedding on the relative energy difference between the Ni and O hole states. This is due to a compression of the electron distribution when AIMPs are used. While the point charges description largely overestimates the FO ionization energies, the bare AIMPs overestimate the Pauli repulsion and consequently underestimate the FO ionization energies. The AIMPs augmented with 1s1p functions yield ionization potentials which are close to those obtained within the frozen electron distribution approximation for the nearest embedding ions. Figure 7.3 shows clearly that the embedding effect is more pronounced.
Table 7.2: Super-cluster ([Ni₆O₆]) relative energies (in eV) of some low lying hole states, associated with an ionization from the central Ni and O ions; The relative energies are given with respect to the lowest Ni-Ni-high-spin coupled state \(^{13}A_1\).

<table>
<thead>
<tr>
<th>Hole character</th>
<th>State</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-3d ((e_g))</td>
<td>(^{12}A_1), (^{12}B_1)</td>
<td>8.60, 8.67</td>
</tr>
<tr>
<td>Ni-3d ((t_{2g}))</td>
<td>(^{14}B_2), (^{14}E)</td>
<td>7.02, 7.05</td>
</tr>
<tr>
<td>O-2p</td>
<td>(^{14}A_1), (^{14}E)</td>
<td>8.36, 8.39</td>
</tr>
<tr>
<td></td>
<td>(^{12}A_1)</td>
<td>7.47</td>
</tr>
<tr>
<td></td>
<td>(^2A_1)</td>
<td>7.43</td>
</tr>
</tbody>
</table>

for the Ni hole states than for the O hole states.

This simple analysis confirms our initial statement that the relative energy difference between the Ni and O hole states must be obtained using [Ni₆O₆], embedded in AIMP for the nearest embedding Ni and O ions, augmented with 1s1p basis functions. This cluster model was employed in the next set of CASSCF calculations, the results are listed in Table 7.2.

Next, CASSCF calculations were carried out for the Ni\(^c\) and O\(^c\) hole states, with an active space containing the Ni 3d \((e_g)\) -like orbitals plus, depending on the hole state considered, one Ni\(^c\)- 3d \((t_{2g})\) and one O\(^c\)- \((2p \cdot t_{1u})\). The results in Table 7.2 show that at this level of approximation (no dynamical correlation effects and only intra- cluster relaxation included), the Ni-Ni high-spin coupled hole states localized at the central Ni\(^c\) ion are about 1.3 eV lower in energy than the lowest Ni-Ni high-spin coupled hole states localized at the central O\(^c\) ion. The nearly degenerate \(^{14}B_2\) and \(^{14}E\) Ni\(^c\) hole states have the additional hole in a Ni\(^c\)-3d \((t_{2g})\) -like orbital. They can be related to the three \(^4T_{1g}\) states in the [NiO₆] fragment. The nearly degenerate localized Ni\(^c\) hole states \(^{12}A_1\) and \(^{12}B_1\) have the additional hole in Ni\(^c\)-3d \((e_g)\). They are associated with the \(^2E_g\) states in [NiO₆] and are found at about 1.6 eV higher energies. The lowest energies of the Ni-Ni-high-spin coupled Ni and O hole states and the corresponding Ni-Ni -low-spin coupled Ni and O hole states with total spin \(S=\frac{3}{2}\) are anticipated to differ by about 0.02 eV in [Ni₆O₆].

Furthermore we constructed the CASSCF-pd wave function of an O hole in [Ni₆O₆] with a total spin \(S=\frac{11}{2}\). The composition of this \(^{12}A_1\) wave function is rather complex but using Mulliken Population Analysis in combination with Mulliken Spin Population Analysis we identified that the main electronic configuration has a hole at O. This electronic configuration is analogous to that of \(^{14}A_1\), except for the low-spin coupling between the unpaired electron at the central O\(^c\) and the 3d \((e_g)\) -type electrons at Ni\(^c\). The total energy gain for \(^{12}A_1\) is about 0.9 eV compared to the relative energy of the Ni-Ni-high-spin-coupled O hole state \(^{14}A_1\).

To complete the analysis we constructed the CASSCF wave function of the lowest O hole state with total spin \(S=\frac{1}{2}\). The composition of this wave function shows contributions of different CSFs and in order to determine the leading electronic configurations we made use of Mulliken (spin) population analysis. This analysis showed that the spin couplings between the spins residing at different Ni ions are antiferro-
magnetic. The energy gain for $^2A_1$ compared to $^{12}A_1$ is about 0.04 eV.

The energy of the O hole states is lowest for low-spin Ni-O couplings. To estimate the energy difference between high- and low-spin coupling between an O hole and one Ni$^{2+}$ ion, we computed the energies of O hole states of a Ni-O cluster with total spin $S=\frac{3}{2}$ and $S=\frac{1}{2}$. The Ni-O cluster was embedded in AIMP$^s$ augmented with 1s1p basis functions. CASSCF wave functions were constructed for $^4\Pi$ and $^2\Pi$ states (in C$_{\infty v}$ point symmetry group) within an active space of 2 Ni- 3d ($e_g$) and 1 O- 2p orbitals. We find the lowest O hole state $^2\Pi$ to be below the high-spin coupled O hole state $^4\Pi$ by about 0.44 eV. The energy difference between high and low spin coupling of the O hole with the Ni ions in [Ni$_6$O$_6$] is 0.9 eV, i.e. twice as large as in [NiO], because there are now two relevant Ni-O spin couplings instead of one. The $^2\Pi$ state which has a low spin coupling between the electrons within the Ni 3d shell is $\sim 3.0$ eV higher. The relative energy of the high-spin coupled O hole state $^4\Pi$ with respect to the ground state $^3\Pi$ is 8.53 eV which is approximately the same as the relative energy of the lowest Ni-Ni-high-spin coupled O hole state $^{14}A_1$ found in [Ni$_6$O$_6$] (see Table 7.2).

An important question to be addressed is also the interaction between localized O 2p hole states and localized Ni 3d hole states. To obtain an estimate of the effective hopping integral parametrizing such an interaction, we allowed for the two localized hole states of the [Ni$_6$O$_6$] super-cluster, which have the hole localized at either a Ni$^c$ 3d $e_g$-like orbital or the O$^c$ 2p$_x$ orbital, to interact. The O$^c$ 2p hole state with symmetry $^{12}A_1$ has the hole localized at the O$^c$ 2p$_x$ orbital. The Ni$^c$ hole state $^{12}A_1$ has the hole localized mainly at $3d_{2x^2-y^2-z^2}$, taking the $x$ axis along the $\langle 100 \rangle$ direction. The energy difference between these two localized hole states is 1.2 eV. When the two localized hole states are allowed to interact the resulting eigenstates differ by 3.87 eV. The wave function of the lower eigenstate is a linear combination of the localized hole wave functions with a largest coefficient for the localized O hole wave function. The energy of this eigenstate is about 0.3 eV below the energy of the localized O hole state. After constructing also the proper normalized linear combination of the Ni$^c$ 3d holes localized at the nearest neighbour Ni ions along $\langle 100 \rangle$ of the O ion with the hole, we obtain an energy gain of 0.42 eV with respect to the energy of the localized O hole state. The effective hopping integral associated with the hopping of the hole between the nearest neighbour Ni and O lattice sites is evaluated to be 1.8 eV. If in addition we take into consideration also the correction to the energies of the localized Ni and O hole states due to the dynamical electron-correlation effects, the energy difference between the two localized hole states becomes $\sim 3.0$ eV. The correlation energy correction for the Ni$^c$ 3d ($e_g$) -like hole is estimated to be $+2.1$ eV using the method by Janssen et al. [11], described below. Even if we assume that the effective hopping matrix element between the nearest neighbouring Ni$^c$ and O$^c$ lattice sites, is not affected by dynamical electron correlation, the overall energy gain upon the formation of the mixed states is expected to decrease. We do not consider the interactions between the Ni$^c$ 3d ($e_g$) -like hole states and O$^c$ 2p hole states at this level of approximation. Including those interactions will lead to an additional lowering in the energies of the states at the top of the valence band (a shift to lower binding
Delocalization of hole and added-electron states 221

energies), but the character of the top of the valence band will remain predominantly O.

The extra-cluster polarization effects related to the polarization of bands and ions outside the [Ni₆O₆] cluster, discussed by Janssen and Nieuwpoort [11], will be of the same magnitude for both Ni and O hole states obtained employing the [Ni₆O₆] super-cluster and therefore, accounting for them is not expected to change the relative energy difference between the lowest Ni and O hole states. Another important contribution to the relative energies of the hole states, however, is due to the dynamical correlation effects. In this study we used estimates of the dynamical correlation effects analogous to those, made by Janssen and Nieuwpoort [11], of the change in the electronic correlation energy due to the removal or addition of an electron in the system. The estimates concerning the Ni hole and added-electron states have been deduced by those authors by comparing the atomic experimental ionization energies and electron affinities with those obtained from numerical Hartree-Fock calculations. Including the dynamical correlation effects leads, to higher ionization energies and lower electron affinities: +2.4 eV for the ionization of a 3d electron from a free Ni²⁺ ion and -3.0 eV for the addition of a 3d electron to Ni²⁺. These estimates include not only the dynamical correlation effects but also relativistic effects, though the latter constitute a smaller fraction of the total energy correction. The electron correlation effect for the ionization of an O 2p electron from O²⁻ ion is estimated to be 0.4 eV based on HF and CI calculations on O ions surrounded by a set of point charges to mimic the NiO electrostatic field, and using a large basis set [11]. Accounting for the dynamical electron correlation effects by using similar estimates leads to an increase in the lowest Ni ionization energy to about 9.4 eV and brings the lowest O ionization energy to about 7.8 eV.

7.4.4 Added-electron states

Finally, the lowest added-electron state of the [Ni₆O₆] super-cluster was considered. CASSCF calculations for a [NiO₆] fragment within an active space of 5 Ni -3d orbitals were carried out using three embeddings, point charges, AIMPs and AIMPs+1s1p1d. The configuration of the lowest 2E_g states within the given active space is t_6^2e_g^3. While the point charges embedding provides a low value of the lowest Ni -3d electron affinity (-2.3 eV), the bare AIMPs gives -11.2 eV. The AIMPs+1s1p embedding yields a value of -7.8 eV. Thus the difference between the ionization potential I and electron affinity A, I-A, depends on the embedding. This simple analysis illustrates the importance of model potentials augmented with orthogonalizing basis functions.

Next, CASSCF wave functions for the Ni⁶ 3d (t_2g^3e_g^2) states ¹²A₁ and ¹²B₁ of the [Ni₆O₆] super-cluster were constructed within an active space of all Ni 3d (e_g) orbitals. The lowest added-electron states, ¹²A₁ and ¹²B₁, which have the extra electron on the central Ni⁶ ion are found at 7.05 and 7.08 eV above the ground state. Introducing low-spin couplings between the spins at the distinct Ni ions leads to an energy gain of 0.02 eV. Accounting for the dynamical electron correlation effects, by using the estimates made by Janssen and Nieuwpoort [11], leads to a decrease in energy, to
7.4.5 Effective hopping matrix elements for hole states

At this level of approximation the lowest ionization potential is associated with the O hole states. The question which of them will mainly constitute the top of the valence band can be addressed with a higher certainty after a consideration of the band-like effects for the different hole states. The relevant quantities are the band stabilization energies associated with the lowest O and Ni hole states. Since those quantities are directly related to the effective hopping matrix elements for Ni holes and O holes, respectively, the next study is concerned with obtaining those effective hopping integrals. The effective hopping matrix elements associated with the hopping of a hole between two neighbouring lattice Ni sites are calculated in four super-cluster models. Here, we analyze the hopping matrix elements related to the two lowest Ni hole states of the two (Ni)-center super-clusters. The super-clusters, used to access the unique hopping matrix elements for the Ni hole states are the [Ni\textsubscript{2}O\textsubscript{11}] and [Ni\textsubscript{2}O\textsubscript{11}O\textsubscript{12}] super-clusters, built along the ⟨100⟩ crystal direction and the [Ni\textsubscript{2}O\textsubscript{10}] and [Ni\textsubscript{2}O\textsubscript{10}O\textsubscript{12}], built along ⟨110⟩. The overlapping fragments are [NiO\textsubscript{6}] and [NiO\textsubscript{6}O\textsubscript{8}] embedded clusters.

The localized orbital sets, in which the wave functions of those hole states are expressed, are derived from CASSCF calculations on the fragments. The embedding of fragments and super-clusters in this set of calculations consists of bare AIMPs for the nearest embedding Ni ions. Since the hopping matrix elements concern two localized hole states of the same type, i.e. Ni holes, we do not anticipate that the AIMPs augmented with basis functions will have an impact on the magnitude of the hopping integrals. It has been demonstrated in Chapter 5 that the hopping integrals for Mn–Mn holes change by only few meV when the bare AIMPs are replaced by AIMPs augmented with 1s1p basis functions. The use of bare AIMPs will lead to an underestimation of the energies, E\textsubscript{1} and E\textsubscript{2}, for the two hole states localized at either one of the two Ni ions in the super-clusters. However, the hopping integrals will not be significantly affected by the introduction of the 1s1p basis functions.

We consider first the hopping integrals obtained using the model [Ni\textsubscript{2}O\textsubscript{11}] super-cluster built along the ⟨100⟩ direction. The super-cluster is viewed as constructed from two overlapping [NiO\textsubscript{6}] fragments. It has a D\textsubscript{4h} symmetry but the localized CASCI wave functions of the hole states have only C\textsubscript{4v} symmetry. The orbitals of the fragments are optimized within a CASSCF active space containing either 8 or 7 electrons in 5 Ni 3d orbitals, for either the \textsuperscript{3}A\textsubscript{2g} ground state of the [NiO\textsubscript{6}]\textsuperscript{10−} fragment, or for one of the two lowest states, \textsuperscript{4}T\textsubscript{1g} and \textsuperscript{2}E\textsubscript{g} of [NiO\textsubscript{6}]\textsuperscript{9−}. The orbitals of the [NiO\textsubscript{6}]\textsuperscript{10−} fragment are optimized accounting for the presence of the neighbouring hole. This is done by increasing the effective nuclear charge at the neighbouring Ni ion by one, just as in the case of the doped manganites. The configurational composition of the \textsuperscript{4}T\textsubscript{1g} states is 92% t\textsubscript{2g}e\textsubscript{g}\textsuperscript{2} and 8% t\textsubscript{2g}e\textsubscript{g}\textsuperscript{3}. The CASSCF wave functions of the \textsuperscript{2}E\textsubscript{g} states consist of 95% t\textsuperscript{2g}e\textsubscript{g}\textsuperscript{1}, 4% t\textsuperscript{4g}e\textsubscript{g}\textsuperscript{3} and about 1% t\textsuperscript{3g}e\textsubscript{g}\textsuperscript{4}.

A corresponding orbital analysis on the fragments [NiO\textsubscript{6}]\textsuperscript{10−} and [NiO\textsubscript{6}]\textsuperscript{9−} orbitals...
Table 7.3: Hopping matrix elements \( t_{\text{Ni-Ni}} \) for a hole state of symmetry \(^6E\) and \(^6B_2\). The hole is localized mostly in a \( t_{2g} \) orbital; CASCI 5d+5d; The presence of the neighboring hole is accounted for in the calculations for the [NiO\(_6\)] fragment in a ground state configuration; First row: \( t^h_{\text{Ni-Ni}} \) for a high-spin coupling between the Ni ions; Second row: \( t^h_{\text{Ni-Ni}} \) for a low spin Ni-Ni coupling.

<table>
<thead>
<tr>
<th>Cluster ( t_{2g} ) hole</th>
<th>( \text{Ni}<em>2\text{O}</em>{11} ) ( d_{xy} ) ( d_{xz} ) ( d_{yz} )</th>
<th>( \text{Ni}<em>2\text{O}</em>{10} ) ( d_{xy} ) ( d_{xz} ) ( d_{yz} )</th>
<th>( \text{Ni}<em>2\text{O}</em>{11}\text{O}<em>{12} ) ( d</em>{xy} ) ( d_{xz} ) ( d_{yz} )</th>
<th>( \text{Ni}<em>2\text{O}</em>{10}\text{O}<em>{12} ) ( d</em>{xy} ) ( d_{xz} ) ( d_{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>- ( t^a_{\text{Ni-Ni}} ) (meV)</td>
<td>63, 62, &lt; 1</td>
<td>72, 24, 24</td>
<td>95, 95, 1</td>
<td>117, 27, 19</td>
</tr>
<tr>
<td>- ( t^b_{\text{Ni-Ni}} ) (meV)</td>
<td>22, 21, &lt; 1</td>
<td>24, 7, 7</td>
<td>32, 32, &lt; 1</td>
<td>39, 9, 6</td>
</tr>
</tbody>
</table>
The interaction between those states is considerable, while the interaction between $2\pi\pi$ corresponds to a negligible small. In a simple model, this hopping parameter 1 have the hole at the $a$-orbital corresponding to the Ni 3$d$ orbital $3d_{2x^2-y^2-z^2}$, which is smaller than 1 meV and it will not be considered in the following analysis. In a simple model, this hopping parameter corresponds to a $\pi\pi$ interaction between the $b_2$ $(yz)$ - type orbitals in the hole states $2B_2$, localized around either one or the other Ni ions in [Ni$^2$O$_{11}$]. The interactions between localized hole states with a different singly occupied orbital, for example $b_2$ $(yz)$ for $2B_2$ and $e$ $(xy)$ for $2E$, are not considered because we expect them to be negligibly small.

The first column in Table 7.4 lists $t^h_{Ni-Ni}$ associated with the localized $4A_1$ and $4B_1$ states of [Ni$_2$O$_{11}$]. The Table lists only the interaction between the $4A_1$ states which have the hole at the $a_{1}$ -orbital corresponding to the Ni 3$d$ $(e_g)$ orbital $3d_{2x^2-y^2-z^2}$. The interaction between those states is considerable, while the interaction between the $4B_1$ states, which have the hole at the other $b_{1}$ -orbital corresponding to the Ni 3$d$ $(e_g)$ orbital $3d_{\sqrt{3}(y^2-z^2)}$, is smaller than 1 meV. The interaction between a $4A_1$ state localized at one of the Ni ions and a $4B_1$ state localized at the other Ni ion is also less than 1 meV and it will not be considered in the following studies. The degeneracy of the states $4A_1$ and $4B_1$, localized at the same Ni ion, is lifted ($\Delta E(4A_1-4B_1)=0.19$ eV) due to the different super-cluster environment experienced by the hole at $3d_{\sqrt{3}(y^2-z^2)}$ or $3d_{2x^2-y^2-z^2}$. The value of $t^h_{Ni-Ni}$ in the first row of Table 7.4 is for the high-spin coupling between the adjacent Ni ions along $\langle 100 \rangle$. The value of $t^h_{Ni-Ni}$ for the low-spin coupling is the relevant parameter for NiO. As expected from the simple Anderson-Hasegawa spin dependence, this value is 182 meV, half the magnitude of $t^h_{Ni-Ni}$ for the high-spin coupling. Clearly this interaction will contribute considerably to the delocalization of the hole along the $\langle 100 \rangle$ direction.

It is well known, that when an extra charge is introduced at a lattice site in the crystalline system the surrounding medium polarizes [57]. In NiO, one may expect both O$^{2-}$ and Ni$^{2+}$ ions to polarize, but the polarization effects on the O$^{2-}$ ions are found to be largest when the extra polarizing charge is set at a Ni lattice site [57]. The polarization energy is also found to be proportional to $r^{-4}$ with $r$ the distance between the polarizing charge at the Ni site and the O$^{2-}$ ions at the other lattice sites.

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Table 7.4: Hopping matrix elements $t^h_{Ni-Ni}$ for an hole state of symmetry $4A_1$ and $4B_1$. The hole is mostly in a $e_g$ orbital; CASCI 5$d$+5$d$; The presence of the neighbouring hole is accounted for in the calculations for the $[NiO_8]$ fragment in a ground state configuration; First row: $t^h_{Ni-Ni}$ for a high-spin coupling between the Ni ions; Second row: $t^h_{Ni-Ni}$ for a low spin Ni-Ni coupling.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Ni$^4$O$_{11}$</th>
<th>Ni$^{2g}$O$_{10}$</th>
<th>Ni$^2$O$<em>{11}$O$</em>{12}$</th>
<th>Ni$^2g$O$<em>{10}$O$</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_g$ hole</td>
<td>$d_{2x^2-y^2-z^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
</tr>
<tr>
<td>- $t^h_{Ni-Ni}$ (meV)</td>
<td>362, &lt;1</td>
<td>1, 1</td>
<td>367, &lt;1</td>
<td>22, 5</td>
</tr>
<tr>
<td>- $t^h_{Ni-Ni}$ (meV)</td>
<td>182, &lt;1</td>
<td>&lt;1, &lt;1</td>
<td>184, &lt;1</td>
<td>11, 3</td>
</tr>
</tbody>
</table>

$^a$x and y axes are chosen along $\langle 100 \rangle$ and $\langle 010 \rangle$, respectively.
The polarization effects have been found to be of a significant importance for the first ionization energies of the Ni and O ionized states as well as for the first electron addition energy of the lowest added-electron state with Ni d⁹ electron configuration and finally, for the magnitude and character of the fundamental band gap [11].

Within our approach, we study the effect of the polarization, induced by a hole within the super-cluster on the surrounding O ions and the effective hopping matrix elements. Assuming that the effect is most significant only for the first layer of O ions around the [NiO₆] fragments and [Ni₂⁵O₁₁] super-cluster, respectively we extended the fragments and super-cluster by including those 8 and 12 O ions, respectively in the quantum mechanical treatment. This results into the super-cluster [Ni₂⁵O₁₁O₁₂] built from two overlapping extended fragments [NiO₆O₈]. These 8 and 12 O ions are represented with the same O [14s, 9p]/(4s, 3p) Gaussian type basis set used for the initial fragments and super-cluster O ions.

The results for the effective hopping integrals obtained using the model super-cluster [Ni₂⁵O₁₁O₁₂] are listed in the third columns of Tables 7.3 and 7.4 for the ⁶₂E and ⁶₂B₂ states and the ⁴₂A₁ and ⁴₂B₁ states, respectively. The hopping integrals associated with the ⁴A₁ and ⁴B₁ hole states are slightly affected by the presence of the additional O ions in [Ni₂⁵O₁₁O₁₂] partly, because of the orientation of the relevant a₁ or a₂ orbital, where the hole resides, with respect to those polarizable O ions. A slightly larger increase in t of at most 0.03 eV is observed for the ⁶₂E states.

Next, analogous to the super-clusters built along the (100) crystal direction, two other super-clusters, [Ni₂⁹yO₁₀] and [Ni₂⁹yO₁₀O₁₂], within the xy plane are considered. Localized hole states in these super-clusters have lower symmetry than C₄v, namely C₂v, with the C₂ axis along the (110) direction. The ⁶₂E, ⁶₂B₂ and ⁴₂A₁, ⁴₂B₁ states belong to different irreducible representations in C₂v. To avoid new notations for the same states but denoted according to the symmetry species of C₂v, we preserved the C₄v, symmetry notations for the states.

In the [Ni₂⁹yO₁₀O₁₂] super-cluster, the hopping integral within the xy plane associated with the ⁴A₁ hole state is comparable to the hopping integrals associated with the ⁶B₂ and ⁶E₂ states. The presence of the polarizable O ions around the super-clusters affects at most the magnitudes of those hopping integrals t between localized states for which the orbitals φ₁ and φ₂, where the holes reside, are oriented within the xy plane. Moreover the overlap integral ⟨Φ₁relax|Φ₂relax⟩ becomes smaller due to the opposite direction of the orbital polarization effects in Φ₁relax and Φ₂relax. The Hamiltonian matrix elements ⟨Φ₁relax|H|Φ₂relax⟩ also decrease and thus t becomes smaller. Despite the fact that the two orbitals φ₁ and φ₂, where the holes reside in Φ₁relax and Φ₂relax, are also allowed to relax and delocalize, in this case the delocalization is limited, and it does not compensate the reduction of t. The latter is due to relaxation of the other super-cluster orbitals. The delocalization of the relaxed φ₁relax=3dy and φ₂relax =3dxₙy is limited because they are oriented between the axes x and y, i.e. they are not directed along any Ni-O-Ni bond. The overall effect is a decrease in t compared to the t that was obtained in the same super-cluster [Ni₂⁹yO₁₀O₁₂] but without accounting for the presence of the extra charge at the neighbouring Ni ion while deriving the orbitals of the fragment in the ground state configuration (these results
are not discussed explicitly here). The interactions between the nearest neighbour Ni ions within the \(xy\), or \(xz\) or \(yz\) planes are either ferromagnetic or antiferromagnetic depending on whether both ions lay in the \((111)\) plane or one of them lays in a plane parallel to the \((111)\) plane (see Figure 7.1). Therefore the effective hopping matrix elements for high- and low- spin coupling between the neighbouring Ni ions are both relevant parameters.

Finally, the effective hopping matrix elements associated with the O hole states were considered. As explained in the section 7.3, to access the different type of interactions between hole states, localized at neighbouring O ions along the \(\langle 100\rangle\) and \(\langle 110\rangle\) directions, various super-clusters are designed, [O\(_2^y\)Ni\(_3\)], [O\(_2^x\)Ni\(_3\)], [O\(_2^z\)Ni\(_5\)] and [O\(_2^x\)Ni\(_4\)]. The corresponding fragments are [ONi\(_2\)] and [ONi\(_3\)] embedded clusters. The [ONi\(_2\)] fragments are built along the \(\langle 100\rangle\) or \(\langle 010\rangle\) direction with an angle Ni-O-Ni of 180°. The [ONi\(_3\)] fragments are constructed in such a manner that the two Ni ions which have an angle Ni-O-Ni of 180° with the O ion are along the \(\langle 100\rangle\) direction while the third Ni ion lays on the \(\langle 110\rangle\) or \(\langle 1-10\rangle\) direction. The different super-clusters have different point symmetry groups. For all super-clusters we consider the same type O hole states and for simplicity we adopt symmetry notations for these states corresponding to the point symmetry group \(C_1\).

The CASSCF wave functions of O hole states of symmetry \(^6A_1\) (in the \(C_1\)) in the [ONi\(_2\)] fragments are constructed within an active space containing 9 electrons in 4 Ni- 3\(d\) (\(e_g\) -like) orbitals and 3 O- 2\(p\) orbitals. For the [ONi\(_3\)] fragments, the CASSCF wave functions are constructed for the \(^8A_1\) O hole states within an active space of 11 electrons in 6 Ni- 3\(d\) (\(e_g\) -like) orbitals and 3 O- 2\(p\) orbitals. The CASSCF wave functions of the fragments [ONi\(_2\)] and [ONi\(_3\)] in the ground state configurations, described by the \(^5A_1\) and \(^7A_1\) states, are defined within an active space of 10 or 12 electron in 4 or 6 Ni- 3\(d\) (\(e_g\) -like) orbitals, respectively, and 3 O- 2\(p\) orbitals. The orbitals in which these wave functions are expressed incorporate information about the presence of the nearby hole, localized at one or the other O ions.

The localized orbital sets for the CASCI wave functions of the super-clusters, representing localized hole states, are derived within the \(OF1\) scheme. In this particular case any two fragments share a Ni ion and hence, the corresponding orbital analysis involves not only the doubly occupied orbitals of the two fragments, associated with the shared Ni ion, but also the singly occupied Ni- 3\(d\) (\(e_g\) -like) orbitals, localized at this ion. The shared Ni ion contributes with \(e_g\) -like orbitals to the active spaces of the fragments and thus, to eliminate the double counted electrons, associated with those double counted \(e_g\) -like orbitals, the active\(_{Ni,1}\)-active\(_{Ni,2}\) block of the orbital overlap matrix between the fragments orbitals is also transformed via a bi-orthogonalization. The double counted active or inactive orbitals are eliminated according to the \(OF1\) scheme. The corresponding orbital analysis is done separately for the inactive and active orbitals.

In Table 7.5 are listed the effective hopping matrix elements associated with the hopping of the O hole between two nearest neighbourg O ions along the \((100)\) and \((110)\) directions. Note that for the hopping integrals for the O holes as well as for the Ni holes, we have provided only the symmetry unique parameters in two
Table 7.5: Hopping matrix elements $t_{\text{O-O}}$ for an O hole state of symmetry $^{2}A_{1}$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$O_{2}^{x} \text{Ni}_{3}$</th>
<th>$O_{2}^{xy} \text{Ni}_{3}$</th>
<th>$O_{2}^{xy} \text{Ni}_{4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{12}$</td>
<td>0.0577</td>
<td>0.0643</td>
<td>0.0110</td>
</tr>
<tr>
<td>$H_{22}-H_{11}$ (meV)</td>
<td>0</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>$- t_{\text{O-O}}^h$ (meV)</td>
<td>107</td>
<td>193</td>
<td>31</td>
</tr>
</tbody>
</table>

crystal directions $\langle 100 \rangle$ and $\langle 110 \rangle$, chosen arbitrary. All other parameters in the other directions of the crystal can be derived by symmetry. Table 7.5 lists only the hopping matrix elements associated with the Ni-Ni low-spin coupled O hole states, which are the relevant hopping integrals for total spin of the hole states wave functions $S=\frac{1}{2}$.

In the first column are reported the hopping integrals associated with O hole states of $[O_{2}^{x} \text{Ni}_{3}]$, which have the hole at O orbitals, $a_{1}$, oriented along the $\langle 100 \rangle$ direction. These $a_{1}$ orbitals correspond to O $2p_x$ orbitals. The mutual orientation of those O $2p$ orbitals in the two localized CASCI oxygen hole states is denoted as $\sigma\sigma$.

In the second column are summarized the relevant effective hopping integrals associated with O hole states of $[O_{2}^{xy} \text{Ni}_{3}]$. In this super-cluster, the CASCI hole state, localized around the O ion, lying along $\langle 100 \rangle$, has the hole at O $2p_x$ orbital, whereas the other CASCI hole state, localized around the O ion, lying along $\langle 010 \rangle$, has the hole at O $2p_y$ orbital. This mutual orientation of the O $2p$ orbitals is denoted as $\sigma\pi$-type.

Finally the last two columns report the interactions between two O hole states localized at nearest neighbouring O ions along $\langle 100 \rangle$ and $\langle 110 \rangle$, respectively, for which the O $2p$ orbitals, where the hole resides have a mutual orientation of $\pi\pi$-type. In $[O_{2}^{x} \text{Ni}_{5}]$, the two localized CASCI hole states have the hole at O $2p_y$ orbitals, whereas in $[O_{2}^{xy} \text{Ni}_{4}]$, the holes for both localized CASCI states reside at O $2p_x$ orbitals.

An inspection of the effective hopping integrals between two localized CASCI states, reveals that the interactions, denoted above as $\sigma\pi$-type interactions contribute at most to the delocalization of the O hole. The relevant Ni-Ni low-spin coupled O hole states involved in the $\pi\pi$-type interactions along $\langle 100 \rangle$ and $\langle 110 \rangle$, respectively are an order of magnitude smaller than the $\sigma\pi$ and $\sigma\sigma$-type interactions. The effective hopping integrals for the low spin couplings are not related via a simple Anderson-Hasegawa model to those for the highest spin couplings (not shown in the Table).

The effective hopping matrix elements obtained in this study determine clearly a larger width of the bands associated with the O holes than the band width for the Ni holes.

Effective hopping matrix elements for added-electron states

Next, we analyzed the effective hopping matrix elements associated with the hopping of an added electron between two neighbouring Ni lattice sites. The super-clusters are the same as those used in the study of the Ni hole states. CASSCF wave functions are constructed for the lowest $^{2}E_g$-like states of the $[\text{NiO}_{6}]^{11-}$ or $[\text{NiO}_{6}\text{O}_{8}]^{27-}$ fragment within an active space containing 9 electrons in 5 $\text{Ni}$ $3d$ orbitals. The CASSCF
Chapter 7, Delocalization of excited, hole and added-electron states in NiO

Table 7.6: Hopping matrix elements $t_{\text{Ni}-\text{Ni}}^e$ for an added-electron state of symmetry $^4A_1$ and $^4B_1$. The electron is localized mostly in a $e_g$ orbital; CASCI 5d+5d; The presence of the neighbouring added-electron is accounted for in the calculations for the $[\text{NiO}_6]$ fragment in a ground state configuration; First row: $t_{\text{Ni}-\text{Ni}}^e$ for a high-spin coupling between the Ni ions; Last row: $t_{\text{Ni}-\text{Ni}}^e$ for a low spin Ni-Ni coupling.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$\text{Ni}<em>2^3\text{O}</em>{11}$</th>
<th>$\text{Ni}<em>2^2\text{yO}</em>{10}$</th>
<th>$\text{Ni}<em>2^5\text{O}</em>{11}\text{O}_{12}$</th>
<th>$\text{Ni}<em>2^2\text{yO}</em>{10}\text{O}_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>added $e_g$ electron</td>
<td>$d_{2x^2-y^2-z^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
</tr>
<tr>
<td>$t_{\text{Ni}-\text{Ni}}^e$ (meV)</td>
<td>240, &lt; 1</td>
<td>53, 18</td>
<td>233, &lt; 2</td>
<td>64, 11</td>
</tr>
<tr>
<td>$t_{\text{Ni}-\text{Ni}}^e$ (meV)</td>
<td>121, &lt; 1</td>
<td>37, 10</td>
<td>117, &lt; 1</td>
<td>42, 7</td>
</tr>
</tbody>
</table>

Calculations for the $[\text{NiO}_6]^{10-}$ or $[\text{NiO}_6\text{O}_8]^{26-}$ fragments, i.e. the fragments in the ground state configuration, are carried out within the same active space as that used for the hole states, namely, 8 electrons in 5 Ni-3d orbitals. Analogous to the hole states the orbitals of the $[\text{NiO}_6]^{10-}$ or $[\text{NiO}_6\text{O}_8]^{26-}$ fragments are optimized accounting for the presence of the nearby added-electron by decreasing the effective nuclear charge of the relevant Ni ion by one. A corresponding orbital analysis between the doubly occupied orbitals of two fragments, $[\text{NiO}_6]^{10-}$ and $[\text{NiO}_6]^{11-}$ or $[\text{NiO}_6\text{O}_8]^{26-}$ and $[\text{NiO}_6\text{O}_8]^{27-}$ is performed in order to determine the localized orbital bases for the localized CASCI wave functions of the super-clusters. The configurational composition of the CASCI wave functions of the $^4A_1$ and $^4B_1$ states of, for example, the $[\text{Ni}_2^2\text{O}_{11}\text{O}_{12}]$ super-cluster is 100 % $t_{2g}^6e_g^3$, $t_{2g}^6e_g^2$ (for the Ni 3d-Ni 3d shell).

In Table 7.6 we have listed the effective hopping integrals associated with the hopping of an extra electron between two neighbouring Ni lattice sites. As expected, the hopping integrals between the Ni ions along the $\langle 100 \rangle$ cube direction are an order of magnitude larger compared to those between the Ni ions in the $\langle 110 \rangle$ direction. This is due to the fact that the lobes of the orbitals involved in the interaction, between the Ni ions aligned at $\langle 100 \rangle$, are oriented along the $x$ and $y$ axes and hence, the interaction along $\langle 100 \rangle$ is a $\sigma\sigma$-type. Along the $\langle 110 \rangle$ direction, the interaction involves the same type of orbitals but now their mutual orientation is a $\delta\delta$-type. The magnitudes of the hopping integrals, obtained from the $[\text{Ni}_2^2\text{O}_{11}]$ and $[\text{Ni}_2^5\text{O}_{11}\text{O}_{12}]$ super-clusters, are considerable only between those CASCI states, localized at either one or the other Ni ions, which have the $e_g$-like orbitals $3d_{3z^2-r^2}$ doubly occupied. The other two CASCI states with the $3d_{2y^2-x^2-y^2}$-like orbitals doubly occupied contribute negligibly to the delocalization of the added electron along the $\langle 100 \rangle$ direction. The contribution of those localized CASCI states to the delocalization of the extra electron along the $\langle 110 \rangle$ direction is smaller. Note that while the hopping integrals for high- and low-spin couplings along $\langle 100 \rangle$ are in agreement with the Anderson-Hasegawa model, this is not the case for the hopping integrals along $\langle 110 \rangle$. The magnitudes of the effective matrix elements in all directions are not affected by the presence of the electron clouds on the nearest polarizable O ions.
7.4.6 Many-body hole and electron bands

The many-body O 2p and Ni 3d hole bands are derived within the framework of the method described in Chapter 3. We construct only the energy bands derived from the lowest localized hole states because they may contribute to the top of the valence band which character appears to be controversial in the literature.

In Figures 7.4 and 7.5, we have plotted the bands along the high symmetry directions, $\Gamma \to X$ and $\Gamma \to L$ in the first Brillouin zone. We have used 50 $k$ points in each symmetry direction. The energies are given with respect to the ground state energy, approximated by the energy of the ground state of the [Ni$_6$O$_6$] super-cluster. These many-body hole bands reflect the dispersion of the energy of the many-electron $N-1$ ionized states in the different symmetry directions. The ionized states are associated with the localized Ni and O hole states, considered in the previous section. We have considered explicitly the bands derived from the localized CASSCF Ni hole states with symmetry $12A_1$, and $14E$ in the [Ni$_6$O$_6$] super-cluster. The many-body Ni hole band derived from the localized hole state with symmetry $14B_2$ is degenerate with the $14E$ band by symmetry. The band associated with the Ni hole state with symmetry $12B_1$ is degenerate with the $12A_1$ band. In constructing the Ni hole bands we have employed the Hamiltonian matrix elements and overlap integrals, computed from the $ab$ initio embedded super-cluster calculations. Since these matrix elements were derived from different super-clusters, they were transformed to the corresponding matrix elements between localized states, obtained from the super-cluster [Ni$_6$O$_6$] and localized states, obtained by translating the former on the nearest and next-nearest neighbouring Ni lattice sites. The ferro- and antiferromagnetic couplings in different crystal planes are taken into consideration.

The construction of the many-body hole bands associated with the O holes requires some further attention. In Figure 7.6 the O ions in the reference unit cell are illustrated as black balls and the Ni ions are represented schematically by grey equatorial balls. The reference coordinate system is positioned at the O ion which lays along the $\langle 100 \rangle$ direction. This O ion is denoted as O1. The ions O2, O3 and O4 lay along the $\langle 110 \rangle$, $\langle 101 \rangle$ and $\langle 011 \rangle$ directions, respectively. For each O lattice site in the unit cell, we have considered three degenerate localized ME basis functions, corresponding to the three localized O 2p hole states with symmetries $^2A_1$, $^2Ey$ and $^2Ez$ in [Ni$_6$O$_6$]. These states have the hole residing on O 2px, O 2py and O 2pz orbital, respectively. In the [Ni$_6$O$_6$] super-cluster these three localized hole states were only nearly degenerate because of the slightly different cluster environment in the three crystal directions. We considered them degenerate in the band calculation. The ferro- and antiferromagnetic couplings between the Ni ions in the lattice are also taken into consideration by employing the Hamiltonian matrix elements and overlap integrals between the Ni-Ni low spin coupled localized O hole states.

The $ab$ initio many-body bands in Figures 7.4 and 7.5 show that the bands associated with the O 2p hole states have the lowest electron binding energies, or lowest ionization energies. The band stabilization energy, $E_d$, obtained as the difference in the energy of the localized O hole CASSCF states and the lowest band energy, $\epsilon(K)$ which is at the $\Gamma$ point, is 1.4 eV. The width $W$ of the O bands is the difference in
Figure 7.4: Energy bands associated with the lowest Ni and O hole states in AF2 cubic NiO, along the symmetry direction $\Gamma \rightarrow X$. Solid lines: O 2p bands; Dashed thick lines: Ni 3d ($t_{2g}$) bands; Dashed thin lines: Ni 3d ($e_g$) bands.
Figure 7.5: Energy bands associated with the lowest Ni and O hole states in AF2 cubic NiO along the symmetry direction $\Gamma \to L$. Solid lines: O 2p bands; Dashed thick lines: Ni 3d ($t_{2g}$) bands; Dashed thin lines: Ni 3d ($e_g$) bands.
the energy of the top and bottom bands at the Γ point and is 3.1 eV. In this case the estimates of those quantities, obtained using effective hopping matrix elements, are not accurate enough because of the more significant overlap integrals between the localized O hole states. This is reflected also in the low symmetry of the O bands. Our computed band width corresponds well to the band width of 3.8 ± 0.2 eV derived from photoemission measurements, performed by McKay and Henrich [71]. Janssen and Nieuwpoort [11] have also obtained a theoretical band width of the O 2p ionized states equal to 3.5 eV by setting it equal to the range of O 2p orbital energies of their [NiO$_6$]$^{10-}$ cluster.

The t$_{2g}$ type Ni hole bands, derived from the $^{14}E$ localized Ni hole states, have a width of 0.79 eV at the Γ point and the band stabilization energy, associated with the formation of the bands is 0.31 eV, computed again at the Γ point. Although the overlap integrals between those localized hole states are smaller than those between the localized O hole states, their magnitude is sufficient to introduce asymmetry in the bands. In this case an estimate based on the effective hopping matrix elements yields about 0.38 eV for $E_d$ and about 0.76 eV for $W$.

The e$_g$ type Ni hole bands, derived from the $^{12}A_1$ localized Ni hole states have a width of 0.6 eV which is the difference in the energy of the lowest band at the Γ point and the highest band at the L point. The band stabilization energy is about 0.5 eV. Using effective hopping matrix elements we estimated about 0.42 eV for $E_d$ and about 0.84 eV for $W$. Clearly also in this case the overlap integrals between the localized ME basis functions, approximated by the super-cluster localized CASSCF wave functions, can not be neglected.

We have not considered explicitly the interaction between the localized Ni and O hole states. This interaction will lead to O -hole wave functions with Ni-hole character mixed in which will give rise to modified O hopping matrix elements and consequently,
to modified O bands. However due to the large energy difference between the localized Ni and O hole states, the additional energy gain for the lowest mixed hole states is expected to be smaller. The character of the top of the valence band, formed by those mixed hole states, will have still predominantly O character. Because those interactions are not explicitly included, Figures 7.4 and 7.5 represent a super-position of the Ni and O many-body hole bands. Introducing the interactions between the Ni and O hole states in the non-orthogonal tight-binding calculation will lead to a change in the bands at the higher electron binding energies, however the states at the lowest binding energies, i.e. at the top of the valence band, will remain mostly the many-body O hole states with some Ni $3d$ character mixed in. Thus our \textit{ab initio} many-body hole bands indicate that NiO is a CT type insulator. This finding is analogous to the result, obtained in the HF band structure calculations [39, 42]. However our many-body hole bands incorporate electron correlation and relaxation effects which are not accounted for in the HF band calculations.

In principle, if we are concerned with the lowest ionization energy of the crystal, then using a very large embedded cluster combined with a MC wave function description of the that ionized state, will provide an ionization energy very close to the lowest ionization energy which would be obtained if we would consider also the additional stabilization energy from the formation of the corresponding band states. As long as one is concerned only with the magnitude of this lowest ionization energy, such an embedded cluster calculation provides a reasonable estimate, particularly when the width of the band is very small, i.e. when the ionization is rather localized. In the case when the band stabilization energy is more substantial one can still obtain a reasonable lowest ionization energy within the local approach, however a very large cluster is needed. In any case, the check of the convergence in the energy with the cluster size is compulsory.

Instead, we considered using a smaller cluster with an accurate MC wave function description of the lowest ionized state. Then we obtained the additional stabilization energy contribution to the lowest ionization energy by calculating explicitly the Hamiltonian matrix elements and overlap integrals between such ionized wave functions, centered around different lattice sites. Thus we started with Wannier-like functions and then we re-symmetrized them in order to obtain Bloch-like many-body functions. Hence, we obtained a continuous spectra of many-body hole states. The same considerations hold for the added-electron states. Because we optimized the localized wave functions for the hole- or added-electron states, we also incorporated electronic relaxation. The important non-dynamical energy contributions connected with the presence of CT configurations in the wave function CI expansion of the Ni hole states can be accounted for by considering the hopping of the hole between the Ni and O lattice sites. In this case we have not explicitly included the corresponding hopping matrix elements.

An important effect, left out of the present study, are the bulk polarization effects. These effects arise from the change in the electron density in the crystal upon the creation of the hole or added electron state. The bulk polarization effects associated with the removal or the addition of an electron to a \([\text{NiO}_6]\) cluster were evaluated by
Janssen and Nieuwpoort, using classical methods [11]. They have found that the polarization energies arising from introducing the hole and added-electron in the [NiO$_6$] cluster are about 3-5 eV. We did not consider explicitly these effects. Accounting for them will only lead to a shift in the many-body bands to even lower binding energies and we expect that the lowering for both Ni and O hole states will be of the same magnitude.

The many-body electron-bands are not explicitly derived because, taking into consideration the hopping integrals associated with the localized added-electron states, they will be similar to the Ni 3$d$ hole bands.

### 7.5 Summary and Conclusions

We performed a detailed investigation of the lowest hole and added-electron states in NiO which form the top of the valence and the bottom of the conduction bands in NiO. To do so, we considered all unique interactions between Ni or O hole states localized at nearest and next-nearest Ni or O lattice sites. In addition, the interactions between the hole states, localized at nearest neighbour Ni and O lattice sites were also investigated but they were found to be of less importance for deducing the character of the states with the lowest electron binding energies. The latter form the top of the valence band.

To compute the ionization energies associated with the Ni and O hole states, we employed a large embedded cluster, [Ni$_6$O$_6$], which allows for treating of the Ni and O hole states on the same footing. We found that the energy difference between the lowest localized O and Ni hole states is only 0.4 eV and in the lowest hole state the hole resides at Ni $t_{2g}$-like orbital. Applying corrections, which include atomic dynamical electron correlation and relativistic effects, to the ionization energies, we deduced for the lowest Ni hole state a relative energy of 9.5 eV and for the lowest O hole state a relative energy of 7.8 eV. Thus after accounting for the relevant electron correlation effects, the lowest localized hole state is an O hole state, i.e. a state in which the leading configuration has a singly occupied orbital, which is mainly localized on one oxygen ion. Next, we computed the interactions between the hole states localized at nearest and next-nearest lattice sites, using smaller two-center (Ni-Ni) or (O-O) super-clusters of different shape and size in order to access all unique interactions. Using the computed Hamiltonian matrix elements and overlap integrals, modified so to correspond to the hole states obtained in the [Ni$_6$O$_6$] cluster, we carried out a non-orthogonal tight-binding calculation to construct the many-body hole bands. These bands include explicitly the electron correlation and relaxation effects which accompany the ionization processes. We obtained that the band states which form the top of the valence band originate mainly from the localized O hole states. The bottom of the conduction band is formed by Ni 3$d^9$ added electron states. Hence, we conclude that NiO is a CT insulator. The O hole bands showed a significant dispersion along relevant symmetry directions and a large band stabilization energy of about 1.4 eV and a band width of 3.1 eV. The bands derived from the localized Ni hole states are characterized with a band width of less than 1.0 eV and a band
stabilization energy of at most 0.5 eV.

Furthermore we considered the lowest localized added-electron states with Ni $3d^9$ character, the states $^{12}A_1$ and $^{12}B_1$ in the $[\text{Ni}_6\text{O}_6]$ cluster. Analogous to the Ni and O hole states, we computed all unique interactions between such added electron states, localized at nearest and next-nearest Ni lattice sites. To do so, we made use of the same two-center Ni-Ni clusters as for the Ni hole states. We found the effective matrix elements associated with the hopping of the added-electron for these lowest localized states to be of about the same magnitude as those for the localized Ni hole states of $^{12}A_1$ and $^{12}B_1$ symmetries. These effective hopping matrix elements lead to an estimate of the band stabilization energy of about 0.5 eV which is the same as the band stabilization energy for the Ni hole states of symmetry $^{12}A_1$. We did not derive explicitly the bands originating from the added-electron states because they are expected to be similar to the bands derived from the Ni hole states, $^{12}A_1$.

Finally, we also considered the $\mathbf{K}$-dependence of one of the lowest excited states in NiO, denoted as $^{3}T_{1g}$ in the octahedral Ni$^{2+}$ site symmetry, which determines the 10 Dq of NiO. We found the effective matrix elements, associated with the hopping of the exciton between two nearest or next-nearest neighbouring Ni lattice sites to be less than 2 meV. Thus, we concluded that indeed those excited states are very localized and their treatment within the embedded cluster approach is fully justified.
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Bibliography

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