Chapter 1

General introduction and theoretical framework
1.1 INTRODUCTION AND OUTLINE OF THE DISSERTATION

A very fundamental and successful concept in both physics and chemistry is the ordering of the chemical elements in the periodic table; virtually any textbook on elementary physics or chemistry contains a periodic table. In the 1860s the concept was developed independently by Mendeleyev and Meyer. The known elements were ordered by increasing atomic weight in such a way that elements with similar properties were placed in the same column. The power of this concept is illustrated by the prediction by Mendeleyev of the properties of scandium (Sc; Z=21) and germanium (Ge; Z=32); at that time these elements had never been observed in an isolated form, but Mendeleyev was able to predict correctly many of their properties by simply looking at the properties of the other elements in the corresponding column. The idea of ordering the elements has not changed very much since then, but the number of elements in the table has increased considerably, including even some artificially made elements. One group of elements in the periodic table comprises the so-called transition metals. These elements share the feature of a progressive filling of shells of d-orbitals. Three such series of transition metals can be distinguished, depending on the d-shell being filled. In this dissertation attention is focused on the electronic properties of some solid-state compounds containing elements from the first series of transition metals, which runs from scandium (Sc; Z=21) to zinc (Zn; Z=30). In addition, the compounds studied in this dissertation contain one or more other elements from the periodic table, e.g. a halogen (F, Cl, ....) or a chalcogen (O, S, ...). This kind of compounds —here referred to as transition metal materials— shows a wide range of properties depending on the composition. Some transition metal (TM) materials show a very intense colour, due to a strong absorption of visible light of certain wavelengths, some behave as strong magnets. Furthermore, the TM materials show extremes in the conduction of electric current, from true insulators to metals. Some of the TM materials even possess the very intriguing property of superconductivity below a certain temperature, i.e. their resistance drops to zero.

This dissertation deals with the description of the electronic structure of TM materials, because many of the properties characteristic to TM materials are mainly connected to the behaviour of the electrons. TM materials often can be considered as ionic compounds. This means that in a first approximation they can be thought of as constructed from ions with an integral number of electrons.
Notwithstanding its simplicity, the ionic model provides a basis for many useful predictions about the electronic structure of TM materials.

In this first chapter a framework is given for the theoretical investigation of the electronic structure. The local cluster approach is introduced as an improvement on the simple ionic model. Furthermore, the concept of electron correlation is described and it is briefly sketched how electron correlation can be accounted for in TM materials. In Chapter 2 all concepts and methods introduced in Chapter 1 will be investigated and tested for the model system nickel oxide (NiO), as this material has been studied very extensively both experimentally and theoretically for a long time. Therefore, many properties of the electronic structure are well known, although some controversial points still remain (for a review of the properties of TM oxides see [1]). The findings for bulk NiO will be compared to those for the NiO (100) surface, about which much less is known, although interest has recently been growing. Chapter 3 is devoted to the study of TM materials other than NiO, namely CoO, La$_2$CuO$_4$ and La$_2$NiO$_4$. Questions are addressed concerning the interpretation and assignment of so-called d-d transitions. In Chapter 4 magnetic properties are investigated. Again bulk NiO serves as a model system for testing the quantum chemical approaches outlined in Chapter 4. An estimate for the size of the magnetic coupling is given and the mechanisms determining the magnetic interaction are discussed. A prediction is presented for the magnetic coupling in a (100) surface layer of NiO, for which no experimental data exist yet. Finally, in the last chapter we investigate the Ni-3s photoelectron spectra of NiO.

1.2 MOTIVATION FOR A LOCAL APPROACH

A crystal is a macroscopic object built from a very large number of atoms. Neglecting impurities, defects and other irregularities, a crystal can be thought of as constructed from a unique building block, which is repeated many times in all three directions. This building block is known as the unit cell. Properties of interest in solid-state physics and chemistry are not only ground state properties, such as equilibrium geometries and cohesive energies, but also the electronic spectra arising from excited or ionized states. Because the immense number of atoms in a crystal makes an exact theoretical or computational treatment of the electronic structure of the crystal as a whole impossible, it is inevitable to
introduce simplifications. To a very good approximation all symmetry equivalent atoms in the bulk of the crystal experience the same influence of their surroundings. Therefore a very natural simplification is the introduction of translational symmetry by imposing periodic boundary conditions, thus leading to the band theory of electrons moving in a periodic potential. A different approach is to model the crystal by a small number of atoms at positions as they occur in the real crystal and to embed this collection of atoms in a potential that accounts for the part of the crystal not explicitly treated. This way of representing the crystal is generally known as the embedded cluster approach and will be applied in this dissertation to study local excitations and magnetic interactions in TM materials.

The most straightforward way of treating the electronic structure is the one-electron model. In the periodic approach this leads to band theory (see standard textbooks on solid-state physics or chemistry, e.g. [2-4]) and within the local approach to the molecular orbital method. For the electronic ground state of ionic materials built from closed-shell ions, e.g. NaF or CuCl, it is known that the two approaches lead to identical results in the one-electron model. The wave functions obtained from a sufficiently large (embedded) cluster calculation are equivalent to so-called Wannier functions, i.e. crystal wave functions that are peaked at the lattice positions. These Wannier functions can be transformed into delocalized Bloch functions by a unitary transformation, hence connecting the embedded cluster approach and the band theory [5]. Therefore, ground state properties can often be described satisfactorily with approaches based on band theory, computationally implemented either on the basis of density functional theory (DFT) [6, 7] or the Hartree-Fock scheme [8, 9]. The situation changes for open-shell systems, both for the electronic ground state, and for excited states.

The dissimilarity between band theory and the cluster approach can be illustrated for the ionisation from a Cu-3d level in CuCl [5]. As argued above for the un-ionized system the band approach and the cluster approach are equivalent in the limit of large clusters. In the delocalized band description an electron is removed from a Bloch state at the top of the filled band with mainly Cu-3d character. Because this state is delocalized over all copper sites, the change in the electronic density at each site is infinitely small and no relaxation effects occur. On the other hand, in the local description an electron is removed from any of the Cu-3d Wannier states, which are strongly peaked around the Cu sites. Hence, locally a large change in the density occurs and the electronic wave function responds to this. The relaxation is rather similar to the relaxation effect when an isolated Cu\(^+\)(3d\(^{10}\)) ion is ionized, i.e. a decrease in energy of about 6 eV. In
general, when local relaxation effects are large compared to delocalization interactions, which lead to the band width: a wide band indicating large delocalization effects and a narrow band highly localized electrons, the lowest energy is obtained by first accounting for the local relaxation and after that restoring the translational symmetry. This is particularly the case in the study of properties connected with the 3d states of the TM atoms in TM materials, hence the local approach is the more natural basis for describing these properties.

Another important advantage of the cluster model approach is the ability to extend the description of the electronic structure beyond the one-electron model in a systematic and controlled manner. An \textit{ab initio} many-body description of the electronic wave function can be obtained with the use of standard quantum chemical techniques (see section 1.4), which are also applied in molecular quantum mechanics for correlated wave functions. There also exists an \textit{ab initio} implementation to treat electron correlation in band calculations on the basis of the Hartree-Fock scheme [10, 11], however, this approach is limited to ground state properties only. In the density functional approach many-body effects are incorporated without losing the appealing picture of the one-electron model. Several functionals exist nowadays that improve the simple local density approximation considerably, but a systematically converging scheme does not exist and the functionals tend to become rather complex. Furthermore, in general DFT is limited to describe ground state properties. Only recently has it become possible to calculate excitation energies and oscillator strengths through time dependent DFT [12].

In semi-empirical cluster approaches on the basis of model Hamiltonians as proposed by Anderson [13] and Hubbard [14] the competitive delocalization and electron interaction effects are incorporated in parameters with values obtained by fitting to experiment. This leads to a simple physical picture that provides a powerful approach to rationalize the electronic excitations occurring in, for example, TM materials. Nevertheless, problems can arise when parameters are needed for new materials or situations for which experimental data are lacking. An example of this will be given in Chapter 4, in which the contradicting \textit{ab initio} and semi-empirical predictions for the magnetic interaction in NiO (100) are discussed.
1.3 THE EMBEDDED CLUSTER MODEL APPROACH

The static interaction of the cluster with the surroundings can be divided into a long-range electrostatic part and a short-range repulsion. The latter is primarily due to the Born or Pauli repulsion supplemented by Coulomb and exchange effects brought about by the charge distributions of the neighbouring centres. The first interaction is easily incorporated into the material model by calculating the Madelung field of the ions not included in the cluster and adding the potential to the cluster Hamiltonian. To this purpose first the exact Madelung field is calculated by an Ewald summation [15] with formal point charges at the experimentally determined lattice positions. From this total potential the contribution of the cluster ions is subtracted. The choice of using formal charges is consistent with the assignment of an integer number of electrons to the cluster. For additional information on this subject the reader is referred to [16].

To include this external potential essentially three methods can be applied. The first one is not very appropriate and consists of just putting formal charges at all lattice positions and summing their contributions to the potential. It is well known that the convergence of the Madelung potential with distance is very slow. Hence, a very extensive array of point charges is needed to obtain sufficient accuracy. Better is the Evjen method [17], which ensures a much faster convergence with the number of point charges by requiring overall charge neutrality. This is achieved by putting formal charges at all lattice positions except for the charges in the outermost shell: half of the formal charge is used for the faces; a quarter for the edges; and one eighth for the vertices. The third method is fitting a small set of point charges at lattice positions within a certain radius of the cluster to the exact value of the potential at a large number of grid points in the cluster region.

Because of its quantum mechanical nature, the short-range electrostatic repulsion cannot be accounted for by simple schemes based on classical mechanics. There are different approaches to account for these interactions [18-35], two of these methods will be discussed here. The first approach is a method based on the Adams-Gilbert equations, which transform the extended Hartree-Fock orbitals for the complete crystal into localized orbitals modified to incorporate the effect of the environment of this local region. The second method is discussed somewhat more extensively, since it is applied in this dissertation. It is based on the theory of electron separability and differs from the Adams-Gilbert
approach in the requirement that the orbitals belonging to different subsystems are orthogonal.

**Adams-Gilbert approach**

One method to include the short-range interactions of a quantum mechanically treated region with its surroundings is based on the building block approach formulated by Adams [36-38] and, in more general terms, by Gilbert [39-41]. In this approach the Hartree-Fock equations for a large system, for example a complete crystal, are transformed to a smaller set of self-consistent equations by localizing the orbitals into different subsystems. The Adams-Gilbert equations are defined as follows:

\[
\left( \hat{F} - \hat{\rho} \hat{L} \hat{\rho} \right) \left| \phi_{i}^{\text{occ}} \right\rangle = \beta_{i} \left| \phi_{i}^{\text{occ}} \right\rangle
\]

(1.1)

where \( \left| \phi_{i}^{\text{occ}} \right\rangle \) are the modified HF orbitals, related to the standard HF orbitals, \( \left| \psi_{i}^{\text{occ}} \right\rangle \), by a linear transformation and \( \hat{\rho} \) is the one electron density operator:

\[
\hat{\rho} = \sum_{i=1}^{n} \left| \psi_{i}^{\text{occ}} \right\rangle \left\langle \psi_{i}^{\text{occ}} \right|
\]

(1.2)

Choosing an appropriate form of the operator \( \hat{L} \), which is added to the standard Fock operator \( \hat{F} \), the delocalized HF orbitals for the complete crystal transform into localized orbitals mainly centred in smaller subsystems. Orbitals belonging to different subsystems are not necessarily orthogonal to each other.

Kunz and Klein incorporated the interaction of a cluster A with its surroundings by choosing the following form of the Adams-Gilbert equations [18]:

\[
\left[ \hat{F}_{A} + \hat{V}_{L}^{A} + \hat{V}_{S}^{A} - \rho^{A} \hat{V}_{S}^{A} \rho^{A} \right] \left| \phi_{i}^{A} \right\rangle = \beta_{i} \left| \phi_{i}^{A} \right\rangle
\]

(1.3)

where \( \hat{F}_{A} \) is the cluster Fock operator, and \( \hat{V}_{L}^{A} \) and \( \hat{V}_{S}^{A} \) account for the long and short-range interaction of A with its environment, respectively. In the limit of self-consistency \( \hat{V}_{S}^{A} \) and \( \rho^{A} \hat{V}_{S}^{A} \rho^{A} \) cancel, which leads to

\[
\left[ \hat{F}_{A} + \hat{V}_{L}^{A} \right] \left| \phi_{i}^{A} \right\rangle = \beta_{i} \left| \phi_{i}^{A} \right\rangle
\]

(1.4)
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-\( p^A \hat{V}_S^A p^A \) is called the Kunz-Klein localizing potential, it selects a set of occupied cluster orbitals, \( |\phi_i^A\rangle \), having incorporated the effect of the rest of the crystal as a weak perturbation.

Theory of electron separability

An alternative approach to include the short-range interaction of a cluster with its environment is based on the theory of electron separability (TES) [42-46]. This results in a method that is very appropriate to combine with the standard quantum chemical approaches developed for isolated systems. The crystal is divided in groups \( \{A, B, ..., R, ...\} \) each with \( \{N_A, N_B, ..., N_R, ...\} \) electrons. Each group is described by an antisymmetrized wave function \( \Phi_R(x_1, x_R) \) built from orthogonal orbitals. The total wave function for the crystal is written as a properly antisymmetrized product of group functions:

\[
\Phi(x_1, x_N) = M \hat{O}^a \{ \Phi^A(x_1, x_{N^A}) \Phi^B(x_{N^A+1}, x_{N^B}), ..., \}
\]

where \( M \) denotes the normalization factor and \( \hat{O}^a \) the antisymmetry operator. TES assumes the condition of strong orthogonality [42] between the different group functions

\[
\int \Phi^A \Phi^B_{\text{ex}} d\tau_{\text{ex}} = 0
\]

in which \( \Phi^B_{\text{ex}} \) represents what is obtained from \( \Phi^B \) by exchanging one or more of its electrons with electrons of \( \Phi^A \). The integration is over the coordinates of the exchanged electrons [42]. Under the condition of strong orthogonality the total energy of the system can be written as a sum of the internal energies of all groups plus the interaction energies between the different groups

\[
E = \sum_R H^R + \frac{1}{2} \sum_{R \neq S} \left[ J^{RS} - K^{RS} \right]
\]

with

\[
H^R = \langle \Phi^R | \sum_{i \in R} \hat{h}(i) |\Phi^R\rangle + \frac{1}{2} \sum_{i \neq j \in R} \hat{g}(i,j) |\Phi^R\rangle
\]
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\[ J^{RS} = \langle \Phi^R \Phi^S | \sum_{i \in R} \sum_{j \in S} \frac{1}{r_{ij}} \Phi^R \Phi^S \rangle \]  

(1.9)

and

\[ K^{RS} = \langle \Phi^R \Phi^S | \sum_{i \in R} \sum_{j \in S} \frac{\hat{P}(i, j)}{r_{ij}} \Phi^R \Phi^S \rangle \]  

(1.10)

\( \hat{P}(i, j) \) interchanges electron i in \( \Phi^R \) with electron j in \( \Phi^S \) and \( r_{ij} \) is the distance between electron i and electron j. Equation (1.7) implies that the total wave function can be optimized by optimizing the wave function of each group sequentially. Instead of solving one N-electron problem a set of smaller equations have to be solved repeatedly until self-consistency is obtained. By introducing the Coulomb and exchange group operators \( J_S(i) \) and \( K_S(i) \)

\[ J_S(i) = \langle \Phi^S | 1_{R} \Phi^S \rangle \]  

and

\[ K_S(i) = \langle \Phi^S | \hat{P}(i, j) \frac{1}{r_{ij}} \Phi^S \rangle \]  

(1.11)

the total energy for a group R in the presence of all other groups can be written as

\[ E^R = \langle \Phi^R | \sum_{i \in R} \hat{h}(i) + \sum_{i \in R} \sum_{S \neq R} [J^S(i) - K^S(i)] \Phi^R \rangle + \frac{1}{2} \langle \Phi^R | \sum_{i \neq j \in R} \hat{g}(i, j) \Phi^R \rangle \]  

(1.12)

and the optimization of the wave function for group R is now reduced to an essentially \( N^R \)-electron problem with the influence of the electrons of the other groups absorbed into the one-electron Hamiltonian. In other words, the static interaction of a quantum mechanical cluster (group R) with its surroundings can be accounted for by adding specific one-electron matrix elements to the standard energy expression of the total cluster energy. Notice that \( \Phi_\kappa \) does not need to be a single determinant (Hartree-Fock) wave function; electron correlation within the groups can be included by means of different methods which will be commented on later in this chapter.

The total wave function \( \Psi \) is further improved by accounting for the mixing of different products of group functions. In analogy with configuration interaction, this is known as group state interaction.

\[ \Psi = \sum_{\kappa} c_\kappa \Phi_\kappa \]  

(1.13)
where $\kappa$ selects for all groups a particular state. Up to first order, only matrix elements need to be considered that differ in at most two group functions.

$k$ and $k'$ differ in group $R$ only: $k$ selects $MO \Phi_a^A \Phi_b^B ... \Phi_r^R$ $\Phi_k^*$ selects $MO \Phi_a^A \Phi_b^B ... \Phi_r^R$ $k'$

\[ \langle \Phi_k | \hat{H} | \Phi_{k'}^* \rangle = H(rr') + \sum_{S \neq R} [J_{RS}(rr',ss) - K_{RS}(rr',ss)] \]  
\[ (1.14) \]

$k$ and $k''$ differ in group $R$ and $S$: $k$ selects $MO \Phi_a^A \Phi_b^B ... \Phi_r^R \Phi_s^S$ $\Phi_k''$ selects $MO \Phi_a^A \Phi_b^B ... \Phi_r^R \Phi_s^S$ $k''$

\[ \langle \Phi_k | \hat{H} | \Phi_{k''}^* \rangle = J_{RS}(rr',ss') - K_{RS}(rr',ss') \]  
\[ (1.15) \]

The energy expression, which can be derived from variation theory with the use of these matrix elements, has an important implication in the form of the group function analogue of the Brillouin theorem:

$H_{eff}^R(rr') = \langle \Phi_{R}^r | \hat{H}_{eff}^R | \Phi_{R}^r \rangle = 0$  
\[ (1.16) \]

$\hat{H}_{eff}^R$ is the effective Hamilton operator for group $R$ in the field of the other groups as used in equation (1.12). This implies that in the limit of self-consistency the contribution of terms in (1.13) connected to single replacements in group functions vanishes. Since the admixture of single excitations polarizes the group function owing to changes in the charge distribution of other groups, the conclusion can be drawn that the polarization of each group by the presence of other groups has been fully accounted for by optimizing the one-group state approximation of equation (1.5).

**TES applied to a cluster interacting with a lattice**

The above considerations are completely general and can be applied to any system that can be considered to consist of well-separated groups of electrons. The theory can be used to treat intermolecular forces by dividing the system into electrons belonging to molecule $A$ and to molecule $B$, or more generally to
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handle the effects of a solvent on a solute [47-50]. It can also be applied to derive model potentials for atoms to represent the core electrons, as they are well separated from the valence electrons [51-57]. Furthermore, the theory of electron separability was used to derive the energy expression of a cluster interacting with the rest of the crystal [22, 26]. The crystal is divided into groups \{A, B, ..., R, ....\}, each with \{N^A, N^B, ......, N^R, ....\} electrons and \{v^A, v^B, ...., v^R, ...\} nuclei. Group R is the cluster described with either a Hartree-Fock wave function or any type of wave function which accounts for electron correlation. For the moment, all other groups are represented by frozen charge clouds. In analogy to equation (1.12) the total energy of the cluster in the field of the other groups can be written as a sum of the internal cluster energy \(E^R\) plus the interaction energy with the other groups \(E^{RS}\).

\[
E^R = \left\langle \Phi^R \right| \sum_{i \in R} \hat{T}_i - \sum_{\alpha \in R} \sum_{i \in R} \frac{Z^R_{\alpha i} R^{\alpha i}}{R^{\alpha i}} + \sum_{\alpha \beta \in R} \frac{1}{R^{\alpha i}} \left| \Phi^R \right\rangle + \sum_{\alpha \beta \in R} \frac{Z^R_{\alpha} Z^R_{\beta}}{R^{\alpha \beta}} \tag{1.17}
\]

\[
E^{RS} = \left\langle \Phi^R \right| \sum_{i \in R} \sum_{\beta \in S} \frac{Z^S_{\beta R}}{R^{i \beta}} \left| \Phi^R \right\rangle + \left\langle \Phi^S \right| \sum_{i \in R} \left[ \hat{J}^S(i) - \hat{K}^S(i) \right] \left| \Phi^R \right\rangle + \sum_{\alpha \in R} \sum_{\beta \in S} \frac{Z^R_{\alpha} Z^S_{\beta}}{R^{\alpha \beta}} + \left\langle \Phi^S \right| \sum_{i \in S} \sum_{\alpha \in R} \frac{Z^S_{\alpha R}}{R^{i \alpha}} \left| \Phi^S \right\rangle \tag{1.18}
\]

In these expressions \(\hat{T}(i)\) is the kinetic energy operator, \(Z\) is the nuclear charge, and \(\hat{J}^S\) and \(\hat{K}^S\) are the Coulomb and exchange operators as defined in equation (1.11). All indices in Greek characters refer to nuclei. After some reordering of the terms the effective total cluster energy can be written as:

\[
E^{R}_{\text{eff}} = \left\langle \Phi^R \right| \hat{H}^{R}_{\text{eff}} \left| \Phi^R \right\rangle + \sum_{S \neq R} \left[ \left\langle \Phi^S \right| - \sum_{\alpha \in R} \sum_{j \in S} \frac{Z^S_{\alpha j} R^{j \alpha}}{R^{j \alpha}} \left| \Phi^S \right\rangle + \sum_{\alpha \in R} \sum_{\beta \in S} \frac{Z^R_{\alpha} Z^S_{\beta}}{R^{\alpha \beta}} \right] \tag{1.19}
\]

\[
\hat{H}^{R}_{\text{eff}} = \sum_{i \in R} \left\{ \hat{T}(i) - \sum_{\alpha \in R} \frac{Z^R_{\alpha i} R^{\alpha i}}{R^{\alpha i}} + \sum_{S \neq R} \left[ \hat{V}^S_{\text{eff}}(i) + \hat{P}^S(i) \right] \right\} + \sum_{i \neq j \in R} \frac{1}{R^{ij}} + \sum_{\alpha \beta \in R} \frac{Z^R_{\alpha} Z^R_{\beta}}{R^{\alpha \beta}} \tag{1.20}
\]

The first term in (1.19) shows that the interaction of the cluster electrons with the other electrons in the crystal is absorbed into an effective 1-electron Hamiltonian for the cluster group only. The operator \(\hat{V}^S_{\text{eff}}\) in (1.20) is the
potential energy operator that takes into account the interaction of electron i of group R with the frozen group S. This operator can be replaced by fixed contributions to the 1-electron integrals, provided sufficient knowledge exists of the frozen group S, as will be discussed further in the next section. \( \hat{P}_S^i \) is a shift operator and is added to the expression to ensure that the wave function of group R remains strongly orthogonal to the other group functions during the optimization process by shifting upwards all occupied orbitals of group S.

\[
\hat{P}_S^i (i) = \sum_{g \in S} \left| \phi_g^S \right| - x_g^S \epsilon_g^S \left| \phi_g^S \right|
\]

(1.21)

\( x_g^S \) is a projection factor and \( \epsilon_g^S \) is the orbital energy of orbital g in group S. The value of the projection factor \( x_g^S \) has been subject of discussion [58-61]. It has been shown by Francisco et al. [59] that for the case of closed-shell groups described at the HF level a rigorous derivation of the energy expression leads to a value of 2. However, in some applications deviating values were used to correct for the lack of orthogonality between the cluster and the rest of the crystal when no functions are present at the groups around the cluster [61].

The second term in (1.19) contains the interaction of the nuclei of the cluster with the nuclei and electrons of the environment. It contains Coulomb and nuclear interactions only, which are constant as long as the groups are kept frozen and the positions of the nuclei remain unchanged.

Practical implementations

The only approximations to the electronic structure of the crystal made so far are the usual Born-Oppenheimer approximation, which separates the movement of the nuclei and the electrons, and the approximation that the crystal can be considered to consist of groups of electrons with negligible mutual overlap. The latter is only true in systems where no excitations from one group to another occur. Therefore, charge transfer effects between different groups cannot be included in the expansion of the total wave function of equation (1.13), because they violate the strong orthogonality condition. For this reason the method is only applicable to rather ionic systems and cannot be used to study electronic transport properties. It is very suitable, however, to improve on the point charge approximation for the embedded cluster model approach to study local electronic
excitations. Furthermore, it can be used to study structural properties of ionic systems.

Two slightly different implementations of the ideas of the theory of electron separability for solid-state problems exist. The first method, the \textit{ab initio} embedding model potential (AIEMP) method [22] is an extension of the model potential method developed by Huzinaga and co-workers [51-57] to represent core electrons. The influence of the environment on a particular group of electrons is accounted for by an adaptation of equation (1.19), in which the Coulomb operator $J^S(i)$ is approximated by an analytical function and the non-local exchange operator $K^S(i)$ by its spectral representation in the function space used for the ions in the determination of the model potential.

\begin{equation}
V_C^S(i) = \sum_j A_j^S r_{ij}^S \exp\left[-\alpha_j^S r_{ij}^2\right]
\end{equation}

\begin{equation}
V_{Ex}^S(i) = \sum_{a,b} |a\rangle A^S(a,b) |b\rangle
\end{equation}

with:

$A^S(a,b) = -S^{-1} K S^{-1}$, where $S_{pq} = \langle p | q \rangle$ and $K_{pq} = \langle p | \sum_{i \in S} \hat{K}^S(i) | q \rangle$

The AIEMPs are obtained by optimizing the wave function for each type of atom of the crystal in the field of the other ions until self-consistency is obtained. In the case of open-shell atoms, e.g. Ni$^{2+}$ ions, a spherical charge distribution is assumed. Once the model potentials are obtained a cluster can be constructed that typically consists of a central ion with the first shell of neighbours. The short-range interaction of the cluster with the crystal is then included by placing the appropriate AIEMP at the lattice positions; usually about three or four layers around the cluster are used. After also incorporating the long-range Coulomb interaction, the cluster wave function can be optimized with any quantum chemical method available. In the applications discussed in subsequent chapters this AIEMP method will be applied to improve on the point charge approximation for embedding the cluster.

The second approach, the \textit{ab initio} perturbed ion (AIPI) approach [25, 27], is aimed at structural and other global crystal properties. The same scheme is followed as in the construction of the AIEMPs. Each ion is optimized in the field of the other ions in an iterative process until self-consistency is obtained. After that no cluster is constructed, but global properties of the crystal are extracted.
from the results. The main difference with the AIEMP implementation is that the AIPI method is not a molecular orbital method and therefore it is not the most appropriate method to study localized electronic excitations for which charge transfer effects of neighbouring ions are expected to be of importance. On the other hand, the method goes beyond static embedding; because the wave functions of all groups are determined variationally, the polarization of each group due to change in the other groups is fully accounted for. Another advantage is that very large clusters (a collection of individually optimized ions) can be used. For example, in the study of the local geometry distortion due to a Cu\textsuperscript{+} impurity in NaF the complete relaxation of the position and the electronic wave function was considered of the first 179 ions surrounding the impurity [62].

*Long-range polarization*

Although the methods described above do have the possibility to include some polarization effects of the rest of the crystal due to changes in the electron distribution in the cluster region [23], it is almost impossible to account for the long-range polarization accompanying ionization processes such as occur for example in core level spectroscopy. An immense set of group functions needs to be optimized in order to obtain a reasonable estimate for the long-range polarization effects, creating a demand on computer resources which is clearly out of proportion. To estimate the long-range polarization one needs to employ more approximate methods. One way to include the effect is to embed the cluster in a set of point polarizabilities, and solving the complete system self-consistently by means of the (Direct) Reaction Field method [63-65]. This approach gives very satisfying results for the interaction of solute and solvent molecules [47-50], and was also successfully applied to describe large biomolecules [66]. One problem in applying this method to embed clusters representing semi-conducting compounds is to uniquely define a value for the polarizability of the ions in the crystal. An estimation of the long-range polarization effects was given by Janssen and Nieuwoort in their study of the band gap in NiO [16, 67]. The polarization energy was calculated by using the classical Mott-Littleton method and by the DRF approach, both yielding essentially the same result. For an NiO\textsubscript{6} cluster the correction to the ionization or electron addition process on a Ni\textsuperscript{2+} site was estimated to be 3-4 eV. The effect on a local charge transfer process was estimated to be smaller (about 1 eV) which can be rationalized by the fact that the overall
charge in the cluster is not changed so that at larger distances from the cluster the electrons do not experience a different potential.

A somewhat different approach to incorporate the long-range polarization effects is the so-called shell model [68-70]. The embedding ions are represented by a core of charge $X$ and a shell of charge $Y$, with $X + Y$ equal the formal charge. The shell and the core are elastically coupled with an empirical force constant $k$. The long-range Coulomb interaction is fully accounted for and the short-range repulsion between ions and the remaining dispersion interaction are modelled by the Buckingham potential

$$V(r) = B \exp(-r/\rho) - C/r^6 \quad (1.24)$$

where $r$ is the ion-ion distance and $B$, $\rho$, and $C$ are constants to be optimized for the system under investigation. Because this method is often combined with the methods formulated on the basis of the Adams-Gilbert approach [36-41] this classical approximation of the short-range interaction is not as severe as it seems because in that approach the cluster orbitals already incorporate part of the effect of the environment. Pascual and Seijo coupled this shell model to the AIEMP method [71] as an alternative for the very elaborate way described in Ref. [23, 24] of accounting for polarization effects via group state interaction.

1.4 THE N-ELECTRON WAVE FUNCTION

Once the material model is chosen, it remains to find approximate solutions of the Schrödinger equation for the $N$ electrons in the system under investigation. A common approach is to expand the $N$-electron wave function in antisymmetrized products $\Phi_k$ of one-electron functions, $\varphi_i$.

$$\Psi = \sum_k C_k \Phi_k \quad (1.25)$$

$$\Phi_k = \hat{O}^{a} (\varphi_p(1)\varphi_q(2)......\varphi_s(N)) \quad (1.26)$$

$\Phi_k$ are normally referred to as Slater determinants. The spinorbitals $\varphi_i$ depend on four coordinates, the three space coordinates and one spin coordinate. Since spin-orbit interaction is neglected, the $\varphi_i$ can be written as the product of an orbital (the
spatial part) and a spin function $\alpha$ or $\beta$. In principle the exact wave function is given as a complete (i.e. infinite) expansion of all Slater determinants that can be generated from a complete one-electron space. This is (of course) not possible, and therefore approximations have to be made in all practical applications. A few methods will be briefly summarized here; for a more complete description of the wide range of quantum chemical methods to approximate the N-electron wave function the reader is referred to for example [44, 72-74].

**Hartree-Fock**

The simplest approximation is to limit the N-particle space to just one Slater determinant. The best wave function of this type can be found by applying variation theory to minimize the expectation value of the Hamiltonian. This leads to the Hartree-Fock (HF) or Self-Consistent Field (SCF) equations:

$$\hat{F}\phi_i = \sum_j^{\text{occ}} \phi_j \epsilon_{ij}$$

$$\hat{F} = \hat{h}(1) + \hat{j}(1) + \hat{K}(1)$$

$$= \hat{h}(1) + \sum_j^{\text{occ}} \langle \phi_j(2) | \hat{g}(1,2) | \phi_j(2) \rangle + \sum_j^{\text{occ}} \langle \phi_j(2) | \hat{g}(1,2) \hat{P}_{12} | \phi_j(2) \rangle$$

The Coulomb operator $\hat{J}$ and the exchange operator $\hat{K}$ depend on the set of one-electron functions $\phi_i$ and hence the equations need to be solved in an iterative scheme until self-consistency is obtained. In the Unrestricted Hartree-Fock (UHF) approach no additional restrictions on the one-electron functions are imposed. As a consequence in the case of open-shell systems, the wave function is not an eigenfunction of the $S^2$ operator. This problem is remedied in the Restricted Hartree-Fock (RHF) approach, formulated by Roothaan [75, 76]. In RHF the sets of orbitals for $\alpha$ and $\beta$ spin are restricted to be identical. For open-shell systems a single Slater determinant is not always sufficient for obtaining eigenfunctions of $S^2$ and it is necessary to use linear combinations of Slater determinants. Moreover, it is customary that the wave functions are constructed so as to transform following one of the irreducible representations of the point group of the cluster model, thus leading to the spatial and spin Restricted Hartree-Fock approach. The linear combinations of Slater determinants that fulfil the spin and
spatial symmetry requirements are usually referred to as configuration state functions (CSF).

In principle, the one-particle space can consist of numerical functions obtained by numerical integration of equation (1.27). Since in practice this can only be applied for atoms, the one-particle space is almost always spanned by analytical functions that are expressed as expansions in a set of basis functions [75].

$$\varphi_i = \sum_p \chi_p c_{pi}$$  \hspace{1cm} (1.29)

This expansion of the one-electron functions into a discrete set of basis functions turns the Hartree-Fock equations into a matrix equation, the so-called Roothaan equation [75, 76].

$$FC = SC \Sigma$$  \hspace{1cm} (1.30)

Here $F$ is the Fock-matrix, $C$ the collection of column vectors $c_i$, $S$ the overlap matrix of the basis functions $\chi$ and $E$ the eigenvalue matrix, which can be diagonalized by a unitary transformation of the orbitals to yield the orbital energies.

**Multiconfigurational SCF**

For many systems in the electronic ground state and not too far from their equilibrium geometry the RHF method gives a rather good description of the electronic structure and often useful information can be extracted from the results. However, the method is known to have some drawbacks. For example it is unable to correctly describe dissociation or bond breaking processes in molecules. Furthermore, in many cases it is not possible to approximate the electronic wave function by a single configuration because some configurations are (almost) degenerate and need to be included in the wave function from the beginning. In the Multiconfigurational SCF (MCSCF) method the N-electron wave function is approximated by a linear combination of CSFs.

$$\Psi = C_1 \Phi_1 + C_2 \Phi_2 + ... C_i \Phi_i + ... C_m \Phi_m$$ \hspace{1cm} (1.31)
The variational parameters are both the orbital expansion parameters of equation (1.29) and the CSF expansion parameters $C_i$. One method to determine the best set of parameters is based on a Taylor expansion of the energy expression.

$$E(p) = E(0) + \sum_i \left( \frac{\partial E}{\partial p_i} \right) p_i + \frac{1}{2} \sum_{ij} p_i \left( \frac{\partial E}{\partial p_i \partial p_j} \right) p_j$$

(1.32)

Here, $p_k$ are both kinds of expansion coefficients. The best parameters at the expansion point can be found with a Newton Raphson algorithm. These new parameters define a new expansion point, leading to an iterative scheme in which the optimization of the orbital and CSF expansion parameters is done at the same time. Among various other alternatives, the method can be simplified somewhat by leaving out the mixed second-order terms in equation (1.32) in which $p_i$ refers to orbital expansion coefficients and $p_j$ to the CSF coefficients. In this way a two-step formalism is obtained in which the parameters are optimized in turn. Another method, the so-called super-CI approach [77], also performs the optimization of the parameters in a two-step formalism, but has a different strategy to find the optimal parameters. First the CI problem is solved, i.e. for the present set of orbitals the best CSF coefficients are calculated. The optimization of the orbitals is performed by the construction of a super-CI wave function of the form:

$$\Phi = \Psi + \sum_{i,a} C_i^a \Psi_i^a$$

(1.33)

in which $\Psi_i^a$ denotes the configurations connected to single excitations with respect to the present MCSCF wave function. Now the super-CI problem is solved and the resulting CI coefficients are used to express a new set of orbitals $\tilde{\Phi}_p$.

$$\tilde{\Phi}_p = \sum_q c_{pq} \Phi_q$$

(1.34)

This cycle is repeated until self-consistency is obtained.

Both methods have advantages and disadvantages. The Newton-Raphson methods usually converge faster given a reasonable start; the super-CI is computationally more complicated but more stable and will always converge to a minimum, whereas in the Newton-Raphson methods special precautions must be taken to avoid convergence to saddle points or maxima. For a more complete discussion see Ref. [78, 79] and references therein.
Within the MCSCF formalism different kinds of wave functions can be constructed. The most common one is based on the Complete Active Space SCF (CASSCF) method [77, 78]. The orbital space is divided in three subspaces: in the inactive space the orbitals remain doubly occupied in all configurations in the wave function expansion; in the secondary or virtual space the orbitals remain unoccupied; and within the active space a fixed number of electrons is distributed over the active orbitals in all spin and symmetry allowed ways. Performing a complete CI in the active space has the advantage that the orbital rotations among active orbitals are redundant and do not need to be considered. A more general MCSCF method is the Restricted Active Space SCF (RASSCF) method [80]. In this approach the active orbital space is divided in three subspaces, normally referred to as RAS1, RAS2 and RAS3. Restrictions are imposed on the number of electrons or holes in the different subspaces. In RAS1 a maximum number of holes is allowed, in RAS3 a maximum on the number of electrons is imposed and in RAS2 a complete CI expansion is constructed. This has the advantage above the CASSCF method that in general more active orbitals can be considered; the disadvantage is that the active - active orbital rotations between the three active spaces are no longer redundant and need to be included.

**Configuration Interaction**

In the Hartree-Fock wave function the electron-electron repulsion is accounted for in a mean-field way. The most straightforward way to improve on this approximation is to include more terms in the configuration expansion and to variationally optimize the configuration expansion coefficients without changing the orbitals as is done in the MCSCF method. For systems where the Hartree-Fock wave function is a good starting point, the inclusion of configurations connected to single and double excitations usually recovers a large part of the electron correlation effects. This method is referred to as the singles doubles CI (SDCI):

$$\Psi^{SDCI} = C_0 \Phi^{HF} + \sum_{i,a} C^a_i \Phi^a_i + \sum_{ij,ab} C_{ij}^{ab} \Phi_{ij}^{ab}$$  \hspace{1cm} (1.35)$$

The first sum in equation (1.35) depicts all configurations connected to the Hartree-Fock reference state by single excitations and the second sum those connected by double excitations (i and j are used as indices for orbitals which are
occupied and a and b for orbitals which are unoccupied in the HF wave function. The optimal set of coefficients is obtained from the secular equations:

$$
\sum_q \left( H_{pq} - E_{pq} \right) C_q = 0
$$

where p and q run over all configurations in equation (1.35). Normally, the overlap matrix S is diagonal (the non-orthogonal CI discussed in the following section is an exception to this rule). Because of the Brillouin theorem, the initial Hamilton matrix H contains zeros for all matrix elements between the HF configuration and singly excited configurations. The matrix elements between the latter and the doubly excited configurations are non-zero, however, and therefore singly excited configurations can have significant contributions to the SDCI wave function as well.

In cases where the HF wave function gives a poor description of the N-electron wave function, SDCI is not the most appropriate method to include electron correlation. Then an MCSCF wave function which contains all near-degenerate configurations is a much better reference wave function. The resulting multireference CI (MRCI) wave function is most easily written by ordering the external configurations by their number of external electrons:

$$
\Psi^{\text{MRCI}} = \sum_m C_m \Phi_m + \sum_{m,a} C^a_m \Phi^a_m + \sum_{m,ab} C^{ab}_m \Phi^{ab}_m
$$

where m indexes all configurations in the reference wave function. This method provides a very potent scheme to include both non-dynamical (molecular) and dynamical (atomic) electron correlation in the N-electron wave function. A wide variety of very efficient implementations exists nowadays and very large CI expansions can be handled. Approximations are made in some schemes to reduce the number of parameters in the calculation under the restriction that the accuracy is not significantly affected. This can be done either by selecting (with perturbation theory) those configurations that are expected to have the largest contribution to the wave function, or by imposing additional restrictions on the configuration expansion coefficients. In the internally contracted multireference CI (ICMRCI) scheme [81, 82] the configurations are generated by applying excitation operators to the reference wave function as a whole. This results in a configuration space that has non-orthogonal and even linear dependent contributions which need to be removed. The evaluation of the matrix elements
is rather complicated but the advantage is that the number of parameters is greatly reduced without any significant loss of accuracy.

Non-Orthogonal CI

Non-Orthogonal CI (NOCI) [83, 84] is a somewhat different approach to describe the N-electron wave function. The central idea is that the number of configurations in the CI expansion can be greatly reduced when each configuration in the expansion is expressed in its own optimal orbital set instead of one common orbital set. This leads to a wave function expansion consisting of mutually non-orthogonal configurations and therefore the secular equations cannot be solved with the standard schemes as applied in the conventional CI calculations. Based on the factorized cofactor method [85] an approach was developed [83, 84] and implemented in the computer code GNOME [86] that enables the routine evaluation of the matrix elements between configurations expressed in mutually non-orthogonal orbitals.

The method is well suited to study systems for which a much lower energy is obtained with a symmetry-broken Hartree-Fock wave function, i.e. a function that does not transform in accordance with the full symmetry group of the Hamiltonian of the system. This symmetry breaking occurs, for example, in the description of core level ionization processes in molecules with N symmetry-equivalent atoms. The HF wave function with a hole localized on only one of the symmetry-equivalent atoms has a much lower total energy than the HF wave function in which the hole is delocalized over all N equivalent atoms. Similarly, for valence hole states symmetry breaking can occur. The N HF wave functions —each with a valence hole localized on one of the N symmetry-equivalent centres— are obtained in separate SCF calculations. In contrast to the core hole states, these wave functions have large mutual overlap and interaction matrix elements. Therefore, a symmetry projection followed by NOCI is necessary to account for the overlap and interaction. Note that valence hole states not only occur in valence ionization processes but also in charge transfer configurations.

Complete Active Space second-order Perturbation Theory

The possibility of improving on the Hartree Fock wave function by perturbation theory is not yet discussed. For closed-shell systems with a dominant
HF wave function a division of the Hamiltonian was proposed by Møller and Plesset [87]. In \( \hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \) the zeroth-order Hamiltonian \( \hat{H}^{(0)} \) is defined as the sum of the one-electron Fock operators:

\[
\hat{H}^{(0)} = \sum_{I} \hat{F}(I), \quad \hat{F}(I) = \varphi_{I}(I) = \varepsilon_{I} \varphi_{I}(I)
\]

(1.38a)

\[
\hat{H}^{(0)} \Phi_{HF} = E^{(0)} \Phi_{HF}, \quad \left\langle \Phi_{HF} | \hat{H} | \Phi_{HF} \right\rangle = E^{(0)} + E^{(1)}
\]

(1.38b)

where \( I \) runs over all electrons. The zeroth-order energy is given by the sum of the occupied orbital energies \( \varepsilon_{I} \) and the first-order energy is equal to the HF energy. Second-order perturbation theory (MP2) leads to the following estimates of the total correlation energy and the first-order wave function:

\[
E^{(2)} = -\sum_{i<j} \sum_{a<b} \frac{\left\langle \Phi_{ij} | \hat{H}^{(1)} | \varphi_{a} \varphi_{b} \right\rangle^{2}}{\varepsilon_{a} + \varepsilon_{b} - \varepsilon_{i} - \varepsilon_{j}}
\]

(1.39)

\[
\Psi^{(1)} = \sum_{i<j} \sum_{a<b} C_{ij}^{ab} | \Phi_{ij} \rangle \text{ with } C_{ij}^{ab} = \frac{\left\langle \Phi_{ij} | \hat{H}^{(1)} | \varphi_{a} \varphi_{b} \right\rangle}{\varepsilon_{a} + \varepsilon_{b} - \varepsilon_{i} - \varepsilon_{j}}
\]

(1.40)

The ingredients for \( E^{(2)} \) and \( \Psi^{(1)} \) are easily obtained from the preceding HF calculation, which makes MP2 a very efficient and simple method to estimate the electron correlation effects. However, for a multireference wave function the Møller Plesset partitioning of the Hamiltonian is not possible and other schemes have to be developed. One such scheme is the complete active space second-order perturbation theory (CASPT2) developed by Andersson and Roos [88-90]. On the basis of a CASSCF wave function the method calculates the second-order estimate of the remaining electron correlation energy and the first-order estimate of the wave function. \( \hat{H}^{(0)} \) is a sum of Fock-type one-electron operators that reduces to the Møller-Plesset operator in case of a single configurational reference wave function.

\[
\hat{H}^{(0)} = \sum_{pq} f_{pq} \hat{E}_{pq} \quad \text{with } f_{pq} = -\left\langle 0 | [ [ \hat{H}, a_{q}^{\dagger} ], a_{p} ]_{+} | 0 \right\rangle
\]

(1.41)

Here \( | 0 \rangle \) is the CASSCF reference wave function and \( \hat{E}_{pq} \) an excitation operator defined as the product of the creation operator \( a_{p}^{\dagger} \) and the annihilation operator
1.4 The N-electron wave function

In equation (1.41) and in all following (and previous) equations the following indices are used for the different classes of orbitals:

- $i, j, \ldots$ inactive orbitals
- $t, u, v, \ldots$ active orbitals
- $a, b, \ldots$ virtual or secondary orbitals
- $p, q, r$ and $s$ general

Contrary to the Møller-Plesset $\hat{H}^{(0)}$, the one-electron operators in this zeroth-order Hamiltonian has non-zero matrix elements between the different orbital spaces and is only diagonal within the three different subspaces. Therefore, an extra diagonalization step is needed to obtain the corrected energy and wave function. Analogous to the ICMRCI method, the first-order wave function $|\Psi^{(1)}\rangle$ is constructed by an internally contracted expansion of all configurations connected to single and double excitations from the CASSCF wave function:

$$|\Psi^{(1)}\rangle = \sum_{pqrs} C_{pqrs} \hat{E}_{pq} \hat{E}_{rs} |0\rangle$$

These configurations span the so-called first-order interaction space and can be classified into eight different classes according to the number of electrons created in the virtual orbitals:

- **Internal** (no external electrons)
  $$\hat{E}_{ti} \hat{E}_{uv} |0\rangle$$
  $$\hat{E}_{ui} \hat{E}_{uj} |0\rangle$$

- **Semi-internal** (one external electron)
  $$\hat{E}_{at} \hat{E}_{uv} |0\rangle$$
  $$\hat{E}_{ai} \hat{E}_{tu} |0\rangle, \hat{E}_{ui} \hat{E}_{au} |0\rangle$$
  $$\hat{E}_{ut} \hat{E}_{uj} |0\rangle$$

- **External** (two external electrons)
  $$\hat{E}_{at} \hat{E}_{bu} |0\rangle$$
  $$\hat{E}_{ai} \hat{E}_{bt} |0\rangle$$
Chapter 1: General introduction and theoretical framework

The internally contracted character of the first-order wave function strongly reduces the number of parameters but complicates the expressions of $E^{(2)}$ and the coefficients of $|\Psi^{(1)}\rangle$, because the construction of the third-order density matrix is needed. However, as with the NOCI, once implemented [88-90] a very efficient method is obtained.

In all perturbational schemes which are based on Fock-type zeroth-order Hamiltonians, configurations can appear in the first-order wave function with an expectation value of $\hat{H}^{(0)}$ which is very close to (or even lower than) the expectation value of the reference wave function. This leads to very small (or even negative) energy denominators in the expressions for $E^{(2)}$ and $C^{(1)}$, thereby causing a breakdown of the perturbation theory. In fact, TM materials are rather susceptible to this phenomenon. As a consequence of the competition between one-electron energy terms (kinetic energy and nuclear attraction) and two-electron terms (electron-electron repulsion), orbital energies do not strictly follow the aufbau principle in these compounds. The orbital energies of the partially filled TM-3d orbitals are in general not as high as the orbital energy of the ligand-2p orbitals. Hence, the expectation value of $\hat{H}^{(0)}$ for a configuration connected to excitations from the ligand-2p to the TM-3d orbitals is often smaller than the expectation value of $\hat{H}^{(0)}$ for $|0\rangle$.

In the case of CASPT2, which has a more complex form of $\hat{H}^{(0)}$, the situation is not as simple as sketched above, but intruder states may appear as well and special action needs to be undertaken in such cases. A large interaction matrix element between such an intruder state and the reference wave function indicates that it is inevitable to include that state in the reference wave function. On the other hand, it can also happen that the intruder state does not have a large interaction with the reference wave function. At the cost of losing any significance of the first-order wave function, the intruder state can be artificially shifted up in energy by adding an arbitrary value to the expectation value of $\hat{H}^{(0)}$ of this intruder state. In this way the (near-) degeneracy which makes the perturbation theory divergent is avoided. Roos and Andersson [91] introduced a so-called level shift technique for CASPT2 and successfully applied it to various systems, e.g., to the notorious problem with the potential energy curve of Cr2. This technique shifts all configurations in the first-order interaction space (1.43a-h) up in energy by an amount $\mu$, which leads to the following second-order energy and coefficients of the first-order wave function:

$$\hat{E}_{ai} \hat{E}_{bj} |0\rangle$$

(1.43h)
\[ E^{(2)} = \sum_j \frac{|\langle j | \hat{H}^{(1)} | 0 \rangle|^2}{\varepsilon_j - E^{(0)} + \mu} \quad (1.44) \]

\[ \tilde{C}_j = \frac{- \langle j | \hat{\tilde{H}}^{(1)} | 0 \rangle}{\varepsilon_j - E^{(0)} + \mu} \quad (1.45) \]

in which \(|j\rangle\) is a configuration in the first-order interaction space and \(\varepsilon_j\) the expectation value of \(\hat{H}^{(0)}\) of this configuration. Under the assumption that \(\varepsilon_j - E^{(0)} \gg \mu\), the second-order energy thus obtained can be corrected for the applied shift by

\[ E^{(2)} - \tilde{E}^{(2)} = \mu \left( 1 - \frac{1}{\tilde{\omega}} \right) \quad (1.46) \]

Here \(\tilde{\omega}\) is the weight of the CASSCF wave function in \(\tilde{\Psi}^{(1)}\) obtained with the applied level shift \(\mu\). In principle, this weight reaches 1 at very large values of \(\mu\). The correction of the second-order energy, however, is not complete (as will be illustrated in the next chapter) and in order to obtain meaningful results it is essential to apply the same level shift in the CASPT2 for the state which is used as the relative zero of energy. Equation (1.46) shows that as soon as \(\tilde{\omega}\) for the state affected by an intruder state and the state at zero energy coincide, the correction for both states is the same and does not need to be considered anymore. This makes the relative energies of the two states only weakly dependent on the size of the applied level shift, provided that the intruder state has a small interaction matrix element and \(\mu\) does not get extremely large. For all clarity, it is always preferable to solve the problem of the intruder states by extending the reference wave function. Sometimes, however, such an extension is not possible because the wave function expansion would become too long. In these cases the level shift can be helpful to repair the divergence of the second-order energy estimate.

1.5 ELECTRON CORRELATION IN TM MATERIALS

The energy difference between the (hypothetical) exact non-relativistic energy and the Hartree-Fock energy is generally called the correlation energy. Various attempts have been made to divide the electron correlation energy into different contributions. We will follow the scheme which divides the correlation...
energy in dynamical (mainly atomic) electron correlation, and non-dynamical electron correlation.

Dynamical correlation effects arise from the instantaneous electron-electron repulsion. Electrons avoid each other more effectively than predicted by the Hartree-Fock method. Non-dynamical electron correlation effects are caused by the inability to describe the N-electron wave function with a single CSF only; configurations that lie low in energy often strongly mix with the Hartree-Fock CSF. For example, a closed-shell molecule near its equilibrium distance usually do not show large non-dynamical electron correlation effects and the correlation energy is largely caused by dynamical correlation only. On the contrary, if bonds are formed or broken, important effects will arise from non-dynamical correlation. As with all other divisions, the division into dynamical and non-dynamical electron correlation is not entirely unambiguous. A well-known example is the Be atom. The ground state of this atom can be described by a 1s$^2$2s$^2$ configuration. Large contributions to the wave function are observed from configurations connected to double excitations from the 2s orbital to the 2p orbital. This can be considered to be a non-dynamical electron correlation effect. However, it is equally valid to ascribe it to dynamical electron correlation, because the spatial extent of a 2p orbital is larger than of a 2s orbital and hence the electron-electron repulsion is reduced.

In many TM materials the electron correlation effects are very important. The localized nature of the 3d electrons in the ionic insulators causes large dynamical correlation effects and the open-shell character of the TM ions forces one to go beyond the Hartree-Fock description of the N-electron wave function to account for the non-dynamical correlation. Apart from the multiconfigurational character of the wave function due to the appearance of more than one d$^8$ CSF, the reference wave function may contain large contributions of configurations that arise from excitations representing ligand-p to TM-d charge transfer. In the following sections some methods will be discussed to calculate and analyze the importance of the different dynamical and non-dynamical correlation effects on the electronic structure of this class of materials.

$FOCI + CEC$

It is rather straightforward to account for the non-dynamical electron correlation that arises from the fact that in general the 3d$^n$L$^m$ states in TM materials cannot be described accurately with a single CSF. The different 3d$^n$L$^m$
CSFs can be either included in a small MCSCF or in a CI using the orbitals optimized for an average of the different 3d^nL^m states.

The First-Order Configuration Interaction (FOCI) method as applied by Janssen and Nieuwpoort [16, 67, 92, 93] provides a way to include the non-dynamical electron correlation effects arising from the 3d^{n+1}L^{m-1} charge transfer (CT) configurations. A reference wave function is constructed by considering all internal replacements within the TM-d shell and the ligand-p shell

\[ \Psi^{\text{ref}} = C_1 | \ldots 3d^nL^m | + C_2 | \ldots 3d^{n+1}L^{m-1} | + C_3 | \ldots 3d^{n+2}L^{m-2} | + \ldots \]  

(1.47)

In this expression the terms that are schematically denoted by Slater determinants represent linear combinations of all Slater determinants of a particular type, rather than individual Slater determinants. In first approximation the coefficients c2 of the single CT configurations are expected to be very small because there is almost no direct interaction with the 3d^nL^m configurations.

In the FOCI approach the reference wave function (1.47) is extended with configurations connected to single and double excitations under the restriction of at most one external electron. In analogy to the terminology used in equation (1.43) for CASPT2, these configurations will be referred to as semi-internal configurations.

\[ \Psi^{\text{FOCI}} = \Psi^{\text{ref}} + C_1 | \ldots 3d^{n-1}L^ma | + C_{l+1} | \ldots 3d^nL^{m-1}a | + \ldots \]  

(1.48)

In these configurations ‘a’ refers to an orbital in the virtual space. Solving the secular equations leads to a drastic increase of C2 in the wave function with respect to its value in the reference wave function. The main source of this increase lies in the large interaction matrix elements between the CT and the semi-internal configurations [16, 92, 93]. The effect of the interaction with these semi-internal configurations can be regarded as relaxing the CT configurations, bringing them down in energy.

The FOCI approach is well suited for studying the non-dynamical correlation effects due to the CT configurations. Dynamical correlation effects, on the other hand, cannot be treated because these effects are connected to configurations with at least two external electrons. In fact, in any CI approach the treatment of dynamical correlation is rather cumbersome for TM materials. An accurate treatment of the effect can only be achieved by configuration expansions which are too large to be handled by the current computer resources in almost all cases.
A semi-empirical approach was proposed by Pueyo and Richardson [94]. Their
correlation energy correction (CEC) approach is based on the assumption that the
dynamical correlation for transition metal ions surrounded by other ions (either
in a molecule or in a solid) can be deduced from that in the isolated TM ion. The
correction is determined by comparing the excitation energies of the calculated
HF atomic $3d^n$ states to the experimental ones. The corrections can then be added
to the FOCI energies as was done by Janssen and Nieuwpoort in their study of the
electronic structure of bulk NiO [67, 93].

**CASSCF / CASPT2**

The CASSCF / CASPT2 approach is a very suitable method to include both
non-dynamical and dynamical electron correlation in the description of the
electronic structure of TM materials. The non-dynamical correlation is accounted
for by a CASSCF wave function that is constructed so as to include all near-
degenerate configurations; the remaining, mostly dynamical, electron correlation
is estimated by CASPT2. Contrary to the FOCI+CEC method, there is no need for
empirical parameters in this approach. However, a drawback is that the inclusion
of the different non-dynamical correlation effects is not as straightforward as it is
in the FOCI+CEC method. Similarly difficult is the analysis of the importance of
these effects.

Obviously, a CASSCF with an active orbital space consisting of five TM-d
orbitals and $n$ 3d electrons can only account for the non-dynamical correlation
arising from the different $3d^nL^m$ configurations. The largest part of the configu-
rations treated in the subsequent CASPT2 account for the dynamical correlation
of the electrons. Nevertheless, there are some configurations which are con-
nected with charge transfer processes and hence some non-dynamical correlation
is included in the CASPT2, be it not completely because the interaction matrix
elements between excited configurations are not considered.

The matrix schematically depicted in Figure 1.1 shows which matrix
elements are treated in the FOCI approach and in the CASSCF/CASPT2 based on
a reference function with $3d^nL^m$ configurations only. The elements in the first
row of the matrix are taken into account in the CASSCF/CASPT2 method. In
FOCI all matrix elements are accounted for and in this way the interaction
between CT configurations and semi-internal configurations is included. As
stated in the previous section this causes a drastic increase of the charge transfer
configurations in the wave function. Because there is no direct interaction
1.5 Electron correlation in TM materials

**FIGURE 1.1** Interaction matrix elements between configurations treated in FOCI or CASPT2.

<table>
<thead>
<tr>
<th>3dnLm</th>
<th>3dn+1Lm-1</th>
<th>3dnLm-1a</th>
<th>3dn+1Lm-2a</th>
<th>3dn-1Lma</th>
</tr>
</thead>
<tbody>
<tr>
<td>3dnLm</td>
<td>E1</td>
<td>α2</td>
<td>α3</td>
<td>α4</td>
</tr>
<tr>
<td>3dn+1Lm-1</td>
<td>α2</td>
<td>E2</td>
<td>β3</td>
<td>β4</td>
</tr>
<tr>
<td>3dnLm-1a</td>
<td>α3</td>
<td>β3</td>
<td>E3</td>
<td>γ4</td>
</tr>
<tr>
<td>3dn+1Lm-2a</td>
<td>α4</td>
<td>β4</td>
<td>γ4</td>
<td>E4</td>
</tr>
<tr>
<td>3dn-1Lma</td>
<td>α5</td>
<td>β5</td>
<td>γ5</td>
<td>δ5</td>
</tr>
</tbody>
</table>

Note that FOCI uses the matrix elements of $\hat{H}$, and CASPT2 the matrix elements of $\hat{H}^{(0)}$. The character a in the configurations denote a singly occupied virtual orbital.

between the 3dnLm and the 3dn+1Lm-1 configurations, $\alpha_2$ (being a matrix element of $\hat{H}^{(0)}$) is very small, implying that the CASSCF/CASPT2 approach cannot take into account the effect in the way FOCI does.

The extension of the active space with ligand-p orbitals does not help to overcome this problem. Such an active space would result in a CASSCF wave function containing the same configurations as in the reference wave function for the FOCI (equation 1.47). For the same reason as in the FOCI approach, the coefficient of the charge transfer configuration will be very small. Although in a subsequent CASPT2 the matrix elements of the second row of the matrix in Figure 1.1 are considered as well, hardly any change will be observed compared to the previous CASSCF/CASPT2. This is caused by the contracted nature of the first-order wave function; each external configuration is weighted by the coefficients of the CASSCF wave function (see section on CASPT2 in §1.4). Because the coefficient of the charge transfer configuration is nearly zero, the inclusion of $\beta_3$, $\beta_4$, and $\beta_5$ with CASPT2 does not lead to an increase of the importance of the charge transfer configurations.

Instead of adding the ligand-2p orbitals, a better choice for extending the active space is to add a set of virtual orbitals of the same symmetry character as the TM-3d orbitals. These virtual orbitals turn out to form a second shell of TM-d orbitals, the so-called 3d’ shell [95-98]. This active space treats a large part of the d-d electron correlation effects in a variational manner, and hence avoids the large overestimation of the d-d correlation energy that was observed in the CASPT2 treatment of this effect [98]. No charge transfer configurations are included in the CASSCF wave function. Again, the corrected wave function contains some configurations connected to charge transfer excitations. In addition
to the first row of matrix elements treated in the CASSCF/CASPT2 with an active space of the TM-3d orbitals, the matrix elements of the last row of the matrix in Figure 1.1 are also included. This means that at least part of the matrix elements between the CT configurations and so-called relaxing configurations are included.

An important part of the charge transfer effects can be included in the CASSCF wave function by further extending the active space with occupied ligand-2p orbitals. A schematic representation of the resulting wave function is:

\[
\Psi^{\text{CAS}} = C_1 | \ldots 3d^n L^m | + C_2 | \ldots 3d^{n+1} L^{m-1} | + C_3 | \ldots 3d^n L^{m-1}a | + \\
+ C_4 | \ldots 3d^{n+1} L^{m-2}a | + C_5 | \ldots 3d^{n-1} L^m a | + \ldots \tag{1.49}
\]

This wave function is similar to the FOCI wave function (1.48). Apart from the \(3d^n L^m\) and \(3d^{n-1} L^{m+1}\) states it also contains some external configurations, namely those in which 3d’ orbitals (in equation (1.49) represented by the character a) are occupied. Two differences remain between this wave function and the FOCI wave function. In the first place, there is a difference in the number of virtual orbitals. In the FOCI study of the 3d^8 states in bulk NiO [93] more than 70 virtual orbitals were included, whereas only 5 virtual orbitals (the TM-3d’ orbitals) are included in this CASSCF wave function. On the other hand, contrary to FOCI, the orbitals are optimized in the CASSCF. This not only leads to optimal occupied orbitals, but also to optimal TM-3d’ orbitals, thus maximizing the effect of the external configurations. The combination of these two differences makes it hard to judge to what extent relaxation of the CT excitations is included in this CASSCF wave function. Nevertheless, we believe that with the CASSCF/CASPT2 approach based on this active space all important effects are included in the description of the \(3d^n L^m\) states.

Another strategy to reach the best choice of active space for the CASSCF and electrons to be correlated in the CASPT2 is based on the following considerations. Four effects are important to obtain a reasonable description of the \(3d^n L^m\) states. In the first place, there is the mixing of the different \(d^n L^m\) CSFs in the wave function for which an active space containing the TM-3d orbitals is sufficient. Secondly, there is the large dynamical correlation effect of the valence electrons, namely the ligand-p and the TM-3d electrons. For this purpose the active space should contain the ligand-p orbitals, the TM-3d orbitals and a set of correlating orbitals, the TM-3d’ and the ligand-p’ orbitals. This ensures a correct treatment of the largest part of the dynamical correlation due to these valence electrons; the remaining part can be estimated by CASPT2. In the third place we need to include the electron correlation effects due to the semi-core electrons on the TM-ion, the
TM-3s and 3p electrons. A sufficiently accurate treatment of this effect can be obtained by perturbation theory. Finally, it is necessary to account for the non-dynamical correlation effects caused by the configurations connected to CT excitations. An active space containing the TM-3d, 3d' and some ligand p-orbitals seems to be appropriate for this.

In summary: an accurate treatment of the most important electron correlation effects requires a CASSCF wave function constructed from an active space containing the ligand-p, p' and the TM-3d, 3d' orbitals and the subsequent CASPT2 should correlate the TM-3s, 3p and 3d, and the ligand-s and p electrons. However, this choice of active space leads to a computational problem which is far too large to be handled even with the largest computers available nowadays. Hence, by reducing the number of active orbitals, the treatment of some electron correlation effects needs to be transferred to the CASPT2. By putting the ligand-p' in the virtual space and the largest part of the ligand-p to the inactive space —only keeping the ligand-p orbitals that are important for the configurations connected to CT excitations— the active space is reduced greatly at the cost of treating the dynamical correlation of the ligand-p electrons perturbationally. This seems to be not a very severe approximation, because the differential effect of correlating the ligand-p electrons is expected to be small for electrons in doubly occupied ligand-p orbitals, although the total contribution is rather large. Therefore, the influence of this effect can be accurately estimated by perturbation theory.

In short, a CASSCF calculation with an active space containing the TM-3d, 3d' and some ligand-p orbitals followed by a CASPT2 that correlates the TM-3s, 3p and 3d, and the ligand-s and p electrons is believed to give a reasonable description of the electron correlation effects in the different 3d^nL^m states.

**Restricted Active Space SCF**

With the RASSCF method [80] a more specific choice of the configurations treated in the multiconfigurational wave function can be made. This makes it possible to include more orbitals in the active space and therefore allows for a more rigorous treatment and analysis of the non-dynamical correlation effects due to the charge transfer processes. However, no efficient computer implementation exists as yet for a subsequent perturbational treatment of the remaining dynamical electron correlation effects.
To include and to analyze the importance of the charge transfer configurations, the active space can be divided in the following way. RAS1 consists of all ligand-p orbitals with the same symmetry character as the TM-d orbitals. Configurations connected to single and/or double excitations out of this space are included, i.e. allowing one or two holes in RAS1. The TM-d and d' orbitals are put in the RAS2 space, ensuring a proper treatment of the large d-d electron correlation. Furthermore, it accounts for the matrix elements between charge transfer configurations and the most important configurations that relax the d-orbitals for the charge transfer excitation. Finally, RAS3 is either empty, i.e. no additional dynamical correlation is included in the wave function or electrons can be included here to treat (part of) the dynamical correlation.

The division of the active space that is expected to include efficiently the charge transfer configurations is the following: the ligand-p orbitals are treated in RAS1 including configurations connected to single and double excitations; the TM-d orbitals in RAS2; and as many virtuals as possible in RAS3 with the restriction of at most one electron. However, this restriction introduces severe convergence problems and no reasonable results can be obtained [99]. This is not completely understood yet but can probably (at least partly) be ascribed to the fact that the optimization of the orbitals is based on the inclusion of single excitations in each iteration. This problem is avoided when double excitations are treated as well. An additional advantage of this division of the orbitals over the subspaces is that without losing the most important part of the d-d electron correlation the CI expansion within RAS2 is significantly reduced compared to the CI expansion obtained with the TM-d and d’ orbitals in RAS2.
1.6 REFERENCES

Chapter 1: General introduction and theoretical framework


