Localized states in transition metal oxides
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Summary

This thesis is concerned with the investigation of the electronic structure of a number of insulating transition metal (TM) crystalline materials by using wave-function based embedded cluster calculations. Quantities and properties of interest studied in this work are related to the local ground-state electronic configuration, elementary, low-energy spin and charge excitations, and to core level excitation processes.

Attempts to characterize and understand the electronic structure of solid TM compounds like oxides, halides, and silicides, began already in the 1940’s. The main motivations at the time came from the issue of the Mott metal–insulator transition, the problem of magnetic ordering in insulators, and the problem of itinerant ferromagnetism. More recently, phenomena such as heavy fermion behavior, high-temperature superconductivity, colossal magnetoresistance, and spin-Peierls phase transitions have revived interest in these systems. Nevertheless, although considerable effort has been put into the field, many of the transition metal materials are poorly understood. The proper treatment of various competing physical effects, like electron localization as a result of strong electron–electron interactions and band-like behavior as a result of orbital overlap and translational symmetry, remains one of the most difficult problems in solid state physics.

Within the quantum chemical approach the cluster method is directed to solving the Schrödinger equation for a small but relevant part of a larger system. Certain properties of crystalline solids, e.g. effects connected with the existence of isolated defects and impurities in an otherwise perfect infinite lattice, molecule–surface interactions, localized 3d or 4f electronic states in transition metal or rare earth compounds etc., are well suited to investigation by cluster methods. In the present work calculations were performed on clusters containing one or more TM sites plus the adjacent anions. The cluster is embedded in some effective potential that accounts for the crystal Madelung field and for short-range Pauli and exchange interactions due to the finite charge distribution of the nearest neighbors, respectively.

Core level x-ray photoelectron spectra in NiO and MnO: importance of inter-atomic hole screening

Much of the progress on the understanding of the electronic structure of transition metal compounds has been obtained through photoemission and inverse photoemission
SUMMARY

experiments. By such techniques one is able in principle to measure the binding energy of electrons in atoms, molecules, and solids. However, a full understanding of the spectra requires the solution of the many electron problem. The valence electron removal and electron addition spectra in transition metal compounds are governed by two main effects: \( d - d \) correlations and metal \( 3d - 2p \) interactions. In the case of core level photoexcitation, the core–valence interactions and relaxation effects following the core ionization play also an important role. Due to these electron–electron interactions, the spectral weight is distributed over several features and a straightforward interpretation is often not possible.

We discuss the different origins of the x-ray \( 3s \) photoelectron spectra for MnO and NiO on the basis of a non-orthogonal configuration interaction (NOCI) study. In the two compounds, different physical mechanisms lead to \( 3s \) hole final states with completely different characteristics, although at first glance the two spectra seem to have similar features. In particular, the spectra for MnO and for NiO both contain an intense satellite peak at \( \approx 6 \) eV higher binding energy than the main line. In NiO, the main peak and the satellite were previously both assigned to high-spin final states and they both were found to have considerable charge transfer (O \( 2p \rightarrow TM 3d \)) character. In MnO, the main line is assigned to a high-spin final state, and we find, in agreement with previous \textit{ab initio} studies, that it has negligible charge transfer (CT) character. The strong peak at about 6 eV higher binding energy in MnO cannot be attributed to a high-spin final state. Instead, our work assigns the weak satellite at \( \approx 10 \) eV as arising from a high-spin final state with dominant CT character. We can say thus that intra-atomic effects dominate the Mn \( 3s \) XPS spectra and the contribution of charge transfer effects is quite small. Our interpretation for manganese oxide contradicts model Hamiltonian studies that find heavy \( 3d^n - 3d^{n+1}L \) configurational mixing for the Mn \( 3s \) hole final states.

For the Ni \( 3s \) photoelectron spectrum of nickel oxide, we extend a previous non-orthogonal CI, which was restricted to the analysis of the character of the high-spin final states, to low-spin couplings. We find that the \( 3s \) XPS spectrum is well described in terms of only few key configurations, related to three major physical mechanisms: multiplet splitting, ligand to metal charge transfer, and intra-atomic electron correlation. Our results indicate that the final \( 3s \) hole states are strong mixtures of non-CT (NCT) and CT configurations, and it is not possible to describe the states as being either NCT or CT states. The shoulder observed at about 2 eV in the Ni \( 3s \) XPS is well accounted for by a low-spin state with strongly mixed NCT–CT character. So-called non-local screening, inter-TM-site charge transfer, effects — invoked for explaining a similar feature in the Ni \( 2p \) XPS of NiO — are apparently not essential for describing this part of the \( 3s \) spectrum.

\textbf{Mn} \( K \)-edge excitations in LaMnO\(_3\)

LaMnO\(_3\) is being intensively studied as parent compound of the so-called colossal magnetoresistance perovskite-type manganites. Magnetoresistance, the variation of electrical resistance with magnetic field, is crucial to several areas of technology, such as magnetic data storage, and much of the impetus for the present interest in the manganites stems
from the possible utility of their magnetoresistive properties.

LaMnO$_3$ is insulating at all temperatures. The formal electronic configuration of the Mn ion is Mn$^{3+}$ $3d^4$. In (nearly) $O_h$ site symmetry, it has a high-spin ground-state arising from the weak-field configuration $t^2_{2g}e^1_g$. The two-fold orbital degeneracy is lifted by Jahn–Teller (JT) distortions of the MnO$_6$ octahedra and by the ordering of the occupied $e_g$ orbitals on neighboring ions. In addition to the JT distortion, the MnO$_6$ octahedra are tilted, so that the Mn–O–Mn angles become less than 180°. At high temperatures LaMnO$_3$ is paramagnetic, but below approximately 150 K it becomes an $A$-type antiferromagnet: using the $Pbnm$ reference system, in a given plane perpendicular to the crystal $c$ axis the magnetic moments on Mn sites are ordered ferromagnetically, but the moment direction alternates from plane to plane.

A number of authors reported recently to have found direct evidence of orbital ordering in LaMnO$_3$ by using resonant x-ray diffraction at the Mn $K$-edge. They argued that the azimuthal-angle dependence and the polarization analysis of the scattering for certain formally forbidden reflections probe the $d(3x^2−r^2)/d(3y^2−r^2)$ orbital arrangement in the ferromagnetic $ab$ planes. A simple theory of the resonant scattering mechanism was also provided, relating the peculiar angle dependence of the scattered intensity to some energy splitting of the Mn 4$p$ levels, $\delta p$. Initially, it was proposed that this splitting of the 4$p$ components and, consequently, the anomalous scattering is due to the Coulomb interaction between the 4$p$-like electron and the anisotropic charge distribution in the 3$d$ shell. Our calculations show, however, that the splitting of the manganese 4$p$ levels is mainly due to the Jahn–Teller distortion of the oxygen octahedron. Our results are in agreement with recent band structure and multiple scattering calculations, which also indicate that the structural distortion is the dominant mechanism leading to anomalous scattering.

We investigated the nature of the pre-edge features of the x-ray Mn $K$-edge absorption in LaMnO$_3$, by calculating explicitly Mn 1$s$ excitation energies associated with different 1$s$-hole final states. We confirm a previous assignment made on the basis of density functional band structure calculations, i.e. the low energy peaks, labeled $A$, correspond to 3$d$ states at adjacent Mn sites. Such $1s\rightarrow3d$ transitions acquire observable intensity through “indirect”, ligand-mediated, Mn 3$d$−(O 2$p$−) Mn 4$p$ mixing. In contrast to LaMnO$_3$, preliminary calculations for MnO indicate that the low-intensity pre-edge feature in this compound originate from on-site Mn 1$s$→3$d$ excitations. However, further investigation is needed in order to understand the nature of these differences.

**Electronic structure of ladder vanadates**

The vanadium oxides with ladder-type crystal structure can be denoted as $AV_2O_5$, with $A$ = Li, Na, Mg, or Ca. The transition metal ions, each roughly situated in the center of a pyramid of five oxygens, form layers in which one-dimensional vanadium chains are assembled in a planar network of two-leg ladders. The rungs are composed of two V ions, one on each leg of the ladder, connected by an oxygen.

For divalent $A$ elements, i.e. Ca or Mg, each vanadium ion is in the formal oxidation
state $V^{4+}$, which corresponds to a spin moment $S = 1/2$ at each V site. Spin moments on the same ladder interact antiferromagnetically. Antiferromagnetic $S = 1/2$ spin-ladder systems, with an even or an odd number of legs, have received considerable attention during the last years due to their unconventional spin excitation spectra. The isolated two-leg ladder, for example, has a finite spin-gap, i.e. a finite energy gap to the lowest spin excitation. In CaV$_2$O$_5$, the inter-ladder magnetic interactions are indeed weak. Various experiments indicate for this compound a rather large spin-gap of approximately 600 K. In contrast to CaV$_2$O$_5$, the inter-ladder interactions are much stronger in magnesium vanadate, which puts MgV$_2$O$_5$ outside the isolated ladder limit. The experimental data for this material is contradictory, and the existence of a spin-gapped state is an open question.

Substitution of the Ca$^{2+}$ or Mg$^{2+}$ ions with Na$^+$ or Li$^+$ will reduce the number of valence electrons on each $V-O_R-V$ rung. In a fully ionic model of the crystal with O$^{2-}$ and Li$^+/Na^+$ ions, there should be one $d$ electron per two vanadiums. The generally accepted picture for the electronic and magnetic structure of LiV$_2$O$_5$ consists of a "double-chain" charge ordered configuration: magnetic $V^{4+}$ ($S = 1/2$) chains on adjacent legs of different ladders are separated by nonmagnetic $V^{5+}$ ($S = 0$) double-chains. The one-dimensional character of the magnetic ordering is confirmed by magnetic susceptibility and neutron inelastic scattering data. So, although crystallographically LiV$_2$O$_5$ does have a ladder structure, its magnetic properties are well described in terms of an antiferromagnetic gapless chain model.

Among the ladder vanadates, the electronic structure of NaV$_2$O$_5$ is a matter of active debate. At room temperature, NaV$_2$O$_5$ is isostructural with the spin-ladder material CaV$_2$O$_5$. While in CaV$_2$O$_5$ one spin is attached to each vanadium site, in NaV$_2$O$_5$ the character of the electronic ground-state is less obvious. Early x-ray diffraction measurements reported two inequivalent sets of vanadium ions, and a model was proposed with alternating $V^{4+}$ ($3d^1$) and $V^{5+}$ ($3d^0$) linear chains. Above 34 K the temperature dependence of the magnetic susceptibility is indeed consistent with that of a $S = 1/2$ antiferromagnetic Heisenberg chain. The rapid decrease of the susceptibility below $T_c \approx 34$ K, a lattice distortion, and the opening of a spin-gap were at that time interpreted in terms of a spin-Peierls phase transition, where dimerization of the $V^{4+}$ ions occurs. However, later experiments showed that at room temperature all V ions are equivalent. Based on density functional band structure calculations and model Hamiltonian studies, NaV$_2$O$_5$ was associated with a "quarter-filled" $V^{4.5+} - V^{4.5+}$ insulating ladder system. In this interpretation each $d$ electron is not attached to a single V ion, but to a V 3$d$-V 3$d$ bonding orbital. The V-V rung "molecular" clusters are antiferromagnetically coupled along the legs of the ladder and form parallel $S = 1/2$ quasi-one-dimensional chains. X-ray diffraction and nuclear magnetic resonance measurements show that at least two inequivalent vanadium sites exist below 34 K. This inequivalency was attributed to a $2V^{4.5+} \rightarrow V^{4.5-\delta_c} + V^{4.5+\delta_c}$ charge ordering process. Several charge ordered models have been proposed for the low-temperature phase, based on either in-line or zigzag charge ordering. Recent experimental results, i.e. the temperature dependence of the dielectric function, the anomalous x-ray scattering at the vanadium K-edge, and the sound velocity data, seem to support a zigzag pattern. However, the charge ordering scenario apparently can not explain the low value of the transition temperature.
We investigated the electronic structure of NaV$_2$O$_5$ by wave-function based embedded cluster calculations. Our analysis is based on multiconfiguration wave-functions where the essential physical effects, i.e. the on-rung electron delocalization, the rung–rung superexchange, and the effect of local distortions, are quite accurately described. Because the strongest interactions take place inside the rung V–O$_R$–V unit, the use of an embedded cluster model — clusters including two VO$_5$ pyramids (one rung) or four VO$_5$ pyramids (two adjacent rungs) were used — is a reasonable first approximation.

The results presented in this thesis work indicate that the spin doublet ground-state of the V–O$_R$–V rung has actually predominant 3$d^1$–2$p^5$–3$d^1$ character, both above and below 34 K. In the high-temperature undistorted geometry, the main contribution to the doublet ground-state is given by a configuration where the unpaired electron on oxygen is low-spin coupled to the d electrons and spin density is equally distributed over the vanadium ions. A preliminary analysis of the effect of distorting the V 3$d^1$–O$_R$2$p^5$–V 3$d^1$ rung on the ground-state energy reveals that a broken-symmetry configuration, $d(V_i$–O$_R$) < $d(V_j$–O$_R$), with V$_i$–O$_R$ spin singlet formation and stronger V$_i$3$d$–O$_R$2$p$ bonding, can be energetically preferred. The energy gain calculated for this displacement is small, but relaxation of the other atoms in the crystal is expected to further stabilize the broken-symmetry configuration. We suggest that the energy gain upon the formation of such V–O pairs, when the bridging rung oxygen is shifted towards one of the adjacent V ions, determines the onset of the phase transition at 34 K. This model does involve charge redistribution, but not via significant V–V charge disproportionation. We argue that the antiferroelectric ordering which occurs in the vanadium–oxygen plane at the transition point is mainly connected to a subsequent zigzag rearrangement of the V and O ions, and not to V$^{4.5-\delta_c}$–V$^{4.5+\delta_c}$ charge ordering. Our results are able to explain the main features of the optical absorption and the antiferromagnetic interaction along the leg of the ladder. The calculations predict a reduction of the exchange coupling constant of about 25% when distorting the V–O$_R$–V rung. At the same time, structural distortions involving the leg oxygens induce alternation of the coupling constant and therewith spin-gap behavior. The calculations also predict ferromagnetic inter-ladder interactions with a high-temperature coupling parameter of 30–40 K.

We also analyzed the V–V magnetic interactions in CaV$_2$O$_5$. For the calcium compound the sign and the magnitude of the inter-ladder couplings are fairly well established. This permits us to test our computational schemes. Heisenberg exchange constants in excellent agreement with fits of the magnetic susceptibility have been obtained for the rung and leg interactions. We also obtained reliable estimates for the inter-ladder coupling, whose sign still is a matter of controversy. We confirm the ferromagnetic nature of this interaction, initially predicted on the basis of density functional calculations.