# Ligand field splitting and magnetic exchange interaction in KNiF3. An application of molecular quantum

Wachters, Arthur Johannes Hubertus

## SUMMARY

A non-empirical method is used to obtain a better theoretical understanding of the crystal field splitting and the magnetic exchange interaction of transition metal ions placed in halogenide lattices. As subject of our theoretical investigation we have chosen the compound $KNiF_3$. Although, in particular, the crystal field splitting of this compound has received considerable previous theoretical attention, this has not lead to simple physical interpretation of its properties. We have shown that even within the ionic electrostatic model more than half of the crystal field splitting can be explained, provided that the Born repulsion is taken into account. The antiferromagnetic exchange interaction between two nickel ions in $KNiF_3$ could satisfactorily be described by the Heitler-London method using orthogonal orbitals and including charge transfer states as a first order perturbation. Our results confirm the theory of Anderson, i.e., that the magnetic coupling is mainly due to kinetic exchange interaction. In contrast to previous qualitative approaches our treatment has the advantage that quantitative information can be obtained about the various contributions to the exchange interaction.

The technique employed is a modification of the Hartree-Fock (H-F) method due to Roothaan. In this method the molecular orbitals are described by a linear combination of basis functions, centered on the atoms of the molecular system. The method is discussed in chapter two.

As basis functions we have used contracted Gaussian-type orbitals. The atomic basis sets are of "double zeta" quality, i.e., for $Ni^{2+}$ we used a (14|9|5) set contracted to (8|4|2), and for $F^-$ a (10|6) set contracted to (4|2). The optimization of the orbital exponents and the contraction of the basis sets are discussed in chapter three.

In chapter four we give the results of the H-F calculations on an $NiF_6^{4-}$ cluster. The calculations are performed by use of the computer program IBMOL IV. The crystal field splitting, defined as the energy difference between the first excited state ($^3T_{2g}$) and the ground state ($^3A_{2g}$) of the cluster, can reasonably well be interpreted in the well-know ionic electrostatic model. However, the origin of the splitting should not be sought so much in the Madelung part of the

potential, but first of all in the Born repulsion part of the potential. The influence of the remainder of the crystal is studied in a point charge approximation. Furthermore the nuclear magnetic hyperfine parameters and Racah parameters are calculated and compared with experiment.

In the last chapter we give the results of the calculations on a linear system $Ni^{2+}F^{-}Ni^{2+}$ surrounded by ten negative point charges at the immediately neighbouring $F^{-}$ positions. From the results we were able to estimate the magnetic exchange interaction in $KNiF_3$ by second order perturbation theory. The most important contribution to the exchange interaction is due to the delocalization or kinetic exchange. The exchange interaction is shown to be very sensitive to the fluorine 2p and 2s orbital contributions of the open shell orbitals on the nickel ions. Of special interest is the role of the 2s orbitals, which is seldom considered in theoretical discussions. Its contribution compensates a large fraction of that of the 2p orbitals.