Theory of d electrons in magnetic insulators. Long range exchange and electronic structure.
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In the first two chapters we give a perturbation theoretical approach of the exchange interaction between two spins in a diamagnetic lattice. In chapter one we derive an expression for the exchange in the Hartree-Fock approximation, and obtain a simple formula for superexchange taking into account only cation-anion dp covalency. The various contributions to the exchange are discussed on the basis of the assumption that exchange takes place predominantly either at the anion in transition-metal compounds or at the cation in rare-earth compounds. Simple equations are derived for these exchange contributions and these are compared with exchange mechanisms as discussed in the literature. It is found that it is possible to give in this manner, using the Hartree-Fock second-order perturbation equation for the exchange, a unified basis for the various mechanisms proposed in literature.

In chapter two the distance dependence of the exchange is discussed using the equations derived in chapter one. The various contributions to the exchange are derived in detail for a number of simple model systems such as a three-center system consisting of a cation-anion-cation chain, a four-center cation-anion-anion-cation chain and a linear N-center cation-anion array. Only cation-anion dp covalency, anion-anion pp covalency and the on-site dd Coulomb interaction is taken into account. It is shown that as a result of the dp covalency, the spin of the magnetic electron spreads over the neighbouring anions. The range of the spin density distribution is equal to the range of the exchange interaction. The exchange interaction is mainly ascribed to so-called kinetic exchange, due to transfer of one electron (hole) through the diamagnetic lattice between the two magnetic cations. A path model is derived in which the exchange interaction is analyzed in terms of products of the various possible transfer integrals between nearest-neighbour atoms along paths leading from one magnetic ion to another. The exchange is of very long range when the empty magnetic state comes close to the top of the filled valence band. In this limit, however, perturbation theory is no longer valid.

In the next four chapters we give expressions for the exchange and electronic structure, using Green's function techniques, for a model taking into account explicitly the on-site Coulomb interaction between d electrons. The results go beyond the expressions obtained using perturbation theory.

In chapter three a model Hamiltonian is derived containing a filled valence band, magnetic d states, a covalent interaction of the d states with the band states and an on-site Coulomb interaction between d electrons. The electronic structure of model systems for crystals containing in each unit cell a magnetic ion.
(N-cation model) with one electron in a nondegenerate orbital is derived using the Green's function method. With the same method we also studied a model with a single magnetic ion with one electron in a nondegenerate orbital in a diamagnetic lattice. For the latter case the electronic structure and the spin density distribution is obtained. The connection with the Hubbard model is indicated and the effects of electronic correlation are discussed. For a model with two-cations interacting via the diamagnetic lattice (two-cation model) the superexchange is derived within the Hartree-Fock approximation. It is shown that the Hartree-Fock approximation breaks down when the empty state comes close to the top of the band. Equations for the various contributions to the exchange within the two-cation model are derived using two-particle Green's functions.

In chapter four the electronic energy levels are calculated for a crystal with a fully occupied valence band interacting with a nondegenerate d state. The occupation of d states, the density of d states, the effective on-site Coulomb interaction, relaxation effects and the spin splitting are calculated. The influence of the band profile and the degeneracy of d states are discussed.

In chapter five we calculate the range of the kinetic exchange and the spin density distribution for a number of simple model systems using the expressions derived in chapter three. Although the detailed behaviour of the exchange interaction and spin density distribution differ, qualitatively the same rules hold for both. It is found that the range of the exchange is larger in a one-dimensional than in a three-dimensional lattice. When the empty magnetic state approaches the top of the valence band the range of the exchange interaction increases while the magnitude of the exchange interaction decreases. The expression for the kinetic exchange, derived in chapter two using perturbation theory, are valid for small dp covalency when the empty state is far above the top of the valence band. In this limit also the path model developed in chapter two is valid. When the empty magnetic state approaches the top of the valence band it is shown that one should take into account in the calculation of the exchange the large spread of the two magnetic electrons.

In chapter six theory and experiment are compared. In the first part of this chapter we calculate the electronic structure of a number of d$^{10}$ compounds (Cu and Ag monohalides and Zn and Cd monochalcogenides) and d$^{n<10}$ compounds (transition-metal difluorides and monoxides and manganese monochalcogenides). The unperturbed energies of the valence band states and d states and the on-site Coulomb interaction between d electrons are obtained from spectroscopic tables. The valence band width is derived from band widths of main-group
compounds obtained from photoelectron spectra. The calculated electronic structure is compared with results of photoelectron spectra. In the second part of chapter six the metal-nonmetal separator line and the effective on-site Coulomb interaction is discussed. In the third part of chapter six experimental evidence is presented for long-range exchange interactions and spin density distributions. The kinetic exchange for a number of compounds (spinels and perovskites) is discussed using the path model developed in chapter two.