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Coen de Graaf · Ria Broer

Magnetic Interactions in Molecules and Solids

Springer

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To W.C. Nieuwpoort

Preface

Magnetic interactions are not only fascinating from an academic viewpoint, they also play an increasingly important role in chemistry, especially in the chemistry that is aimed at designing materials with predefined properties. Many of these materials are magnetic, either in their ground states or by external perturbation and have found their way into real-world applications as molecular switches, sensors or memories. Although magnetic interactions are commonly orders of magnitude weaker than other interactions like covalent bonding, due to these interactions small changes in composition or external conditions may have huge consequences for the properties. Think for example of perovskite-type manganese oxides, where chemical doping affects the interplay between magnetic and electric properties, leading to *giant* or *collossal* magnetic resistance. An obvious example dealing with molecular (non-bulk) moieties can be found in the design of single-molecule magnets. Obtaining systems with tailor-made properties heavily depends on our knowledge of the interactions between local magnetic sites.

This textbook aims to explain the theoretical basis of magnetic interactions at a level that will be useful for master's students in chemistry. Although it has been written as a volume in the series "Theoretical and Computational Chemistry", the book is intended to be also helpful for students of physical, inorganic and organic chemistry. Most chemistry textbooks give only a brief general introduction, whereas textbooks treating magnetic interactions at a more advanced level are mostly written from the perspective of solid-state physics, aiming at physics students.

This volume gives a treatment of magnetic interactions in terms of the phenomenological spin Hamiltonians that have been such powerful tools in chemistry and physics in the past half century. On the other hand, it also explains the magnetic properties using many-electron quantum mechanical models, first at a simple level and then working towards more and more advanced and accurate treatments. Connecting the two perspectives is an essential aspect of the book. It makes clear that in many cases one can derive magnetic coupling parameters not only from experiment, but also, independently, from accurate *ab initio* calculations. Combining the two approaches leads, in addition, to a deeper understanding of the

relation between physical phenomena and basic properties and how we can influence these. Think for example of magnetic anisotropy and spin-orbit coupling.

Throughout the book the text is interlarded with exercises, stimulating the students to not only read but also verify the assertions and perform (parts of) derivations by themselves. In addition, each chapter ends with a number of problems that can be used to check whether the material has been understood.

The first chapter of this volume introduces a number of basic concepts and tools necessary for the development of the theories and methods treated in the following chapters. It explains various ways to generate many-electron spin-adapted functions, gives an introduction to perturbation theories and to effective Hamiltonian theory. Chapter 2 treats atoms with and without an external magnetic field. This is followed by a chapter on systems containing more than one magnetic center. In this chapter the phenomenological Hamiltonians are introduced, beginning with the Heisenberg and the Ising Hamiltonian and ending with Hamiltonians that include biquadratic, cyclic or anisotropic exchange. Chapter 4 explains how quantum chemical methods, reaching from simple mean field methods to accurate models, can help to understand the magnetic properties. The simple models can give a qualitative understanding of the phenomena. The more accurate models, such as post Hartree-Fock models like DDCI, CASPT2 and NEVPT2 or broken symmetry models based on density functional theory, are able to produce accurate predictions of the energies and wave functions of the relevant states. Making accurate computations is one thing, mapping the results back onto the intuitive models yielding parameters that can be compared with the ones deduced from experiments is another. Effective Hamiltonian theory is a powerful tool to make these connections, as shown in Chap. 5. The last chapter explains how the magnetic interactions in solid-state compounds can be treated, with embedded cluster models and with periodic approaches. It gives an account of the double exchange mechanism in mixed valence systems, explaining the Goodenough-Kanamori rules. Finally, an account is given of spin wave theory for (anti-)ferromagnets.

The book covers a full Master's course, but a shorter course can be distilled from it in many ways. One of them includes Chap. 2, the first two sections of Chap. 3 and optionally one of the subsections of 3.4 to get acquainted with the spin Hamiltonian formalism. After that, Sects. 4.1.1 and 4.1.2 combined with Sects. 4.3.1, 4.3.2 and 4.3.4 can be studied to connect the quantitative and qualitative computational viewpoints of magnetic interactions. From Chap. 5, we recommend to include Sects. 5.1.1 and 5.3, which provide us with the basic tools for analysis. If time permits, one can close the short course with a brief account on some issues related to the solid state: Sects. 6.3 and 6.5 provide some basic notions on this topic.

We end by noting that the outstanding book by the late Prof. Olivier Kahn, O. Kahn, Molecular Magnetism, VCH Publishers, 1993, has been an inspiration for the entire book.

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Acknowledgments

This book can be considered to a large extent as a product of sharing knowledge in the so-called *Jujols* community over the past 25 years. Without the continual interactions during conferences, visits and intense collaborations on many aspects of the theoretical description of magnetic phenomena in molecules and solids, this book would never have reached the degree of completeness and clarity that we hope to have reached. Special thanks are due to Jean-Paul Malrieu, Nathalie Guihéry, Carmen Calzado, Rosa Caballol, Rémi Maurice, Celestino Angeli, Nicolas Ferré, Eliseo Ruiz, Joan Cano, Remco Havenith, Alex Domingo and Gerjan Lof for inspiration, clarifications, resolving doubts, affirmations, corrections, proofreading, etc., during the process of writing the book. We are grateful to the late Olivier Kahn, for sharing his broad and deep knowledge with us, in person, but also through the great legacy of his book on molecular magnetism.

Contents

Acronyms

AF	Antiferromagnetic
BS	Broken Symmetry
CAS (n, m)	Complete Active Space with n electrons and m orbitals
CASPT2	Complete Active Space second-order Perturbation Theory
CASSCF	Complete Active Space Self-Consistent Field
CI	Configuration Interaction
CISD	Configuration Interaction of Singles and Doubles
CSF	Configuration State Function
DDCI	Difference Dedicated Configuration Interaction
DFT	Density Functional Theory
F	Ferromagnetic
GK	Goodenough-Kanamori
HS	High Spin
HTH	Hay-Thibeault-Hoffmann
IR	Irreducible representation
KS	Kohn-Sham
LDA	Local Density Approximation
LMCT	Ligand-to-Metal Charge Transfer
LS	Low Spin
MLCT	Metal-to-Ligand Charge Transfer
MO	Molecular Orbital
MR	Multideterminantal/Multiconfigurational reference; Multireference
NEVPT2	N-Electron Valence state second-order Perturbation Theory
NH	Non Hund
QDPT	Quasi Degenerate Perturbation Theory
REKS	Restricted Ensemble Kohn-Sham
RHF	Restricted Hartree Fock
ROKS	Restricted Open-shell Kohn-Sham
VB	Valence Bond
WF	Wave function

ZFS	Zero-field splitting
ψ, φ, ϕ	one-electron functions, orbitals
Ψ	N-electron wave function
Φ	Slater determinant
$\widetilde{\Psi}$	Projection of Ψ on a model space
$\widetilde{\Psi}'$	Normalized projection of Ψ on a model space
$\widetilde{\Psi}^{\perp}$	Orthonormalized projection of Ψ on a model space
$\widetilde{\Psi}^{\dagger}$	Biorthogonal projection of Ψ on a model space
$\widetilde{\Psi}'^{\dagger}$	Normalized biorthogonal projection of Ψ on a model space
$E^{(n)}$	n-th order correction to the energy
$\Psi^{(n)}$	n-th order correction to the wave function