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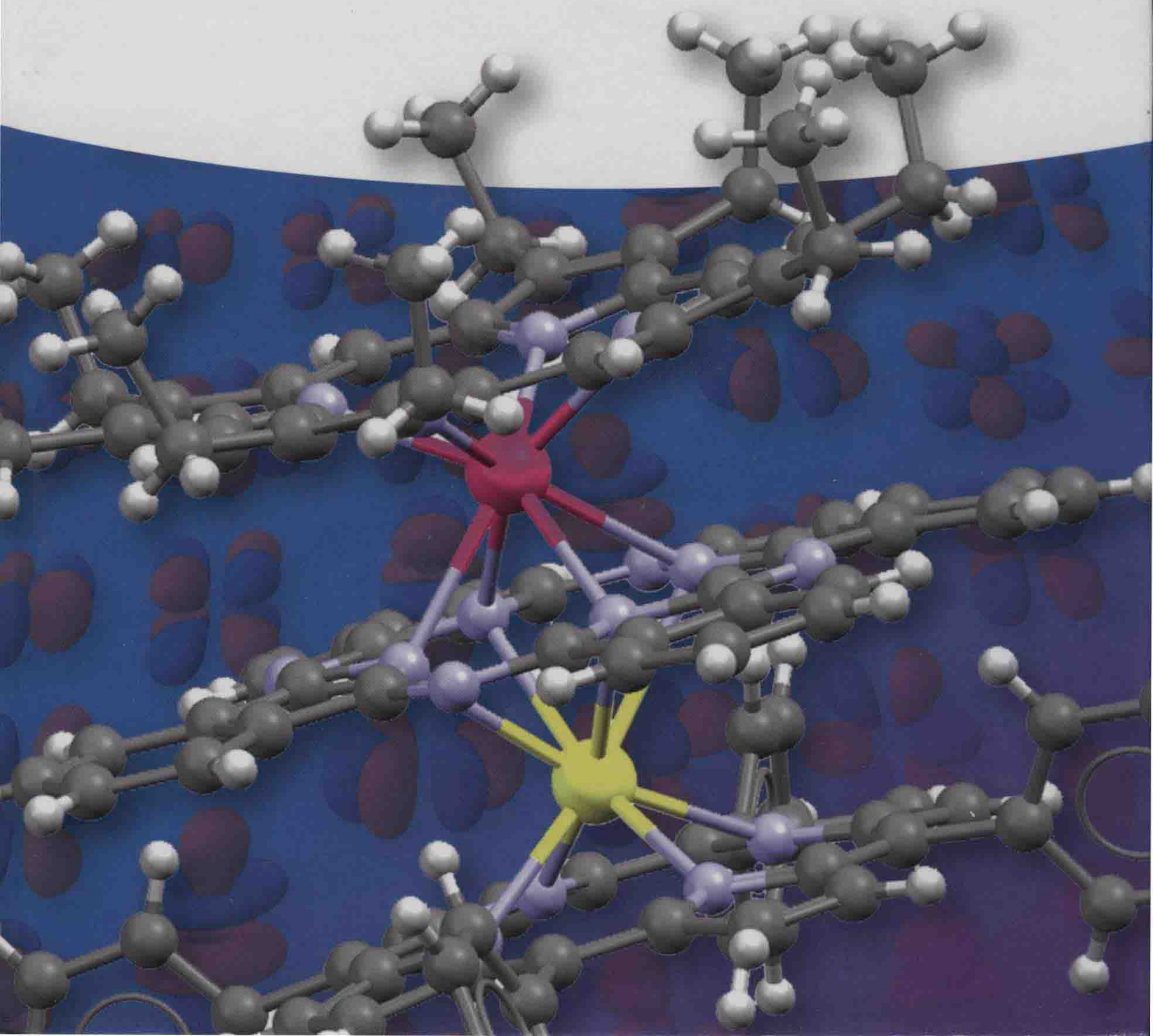
Introduction to Molecular Magnetism

From Transition Metals to Lanthanides



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Preface

The last years have seen an explosive increasing interest for the development of molecular magnetism, that is, for the magnetic properties of materials based on molecules. These materials have properties, which are related to those of the classic magnets, based on inorganic materials such as metals, just think about iron, or oxides such as magnetite but have interesting properties also for simple molecules. It was in the 1980s of last century that it was realized that magnetism developed with molecules could give rise to novel properties. In particular, it was discovered that beyond bulk magnetism mentioned earlier, it was possible to make new magnetic materials in which chemical engineering played a major role. The new field was called Molecular Magnetism (MM) and gave rise to new physics of which single molecule magnets (SMM) and single chain magnets (SCM) were understood by many researchers as a breakthrough to new materials.

The development of MM required a chemical background, which was not easily available to physicists, and a physical background, which was hard to understand for chemists. The field actually developed, thanks to the efforts of pioneers who explored the new field and translated the awkward local languages in something that could be understood by everybody. As will be discussed in the present book, it is tempting to identify the book *Magneto-Structural Correlations in Exchange Coupled Systems* edited by R. D. Willet, D. Gatteschi, and O. Kahn, with the first attempt to develop a common language between chemists and physicists who explored Molecular Magnetism. From a more chemistry-based approach, Kahn's book *Molecular Magnetism* has been the unique tool allowing chemists to understand magnetism. There have been many other edited books covering the various aspects of the new research area, but it must be highlighted that the book that can be considered as the predecessor of the present one was *Molecular Nanomagnets* by D. Gatteschi, R. Sessoli, and J. Villain, which was focused on the role of the size of molecular magnets in determining the properties.

In the last few years, there has been an exponential growth of molecular magnets based on lanthanide ions, which had been neglected at the beginning. Having been among the first to explore molecular magnets we conceived the idea of writing a book, which reported the unique approach needed for Ln. The original format was limited to these ions, but the contact with the publisher convinced us to write something with a wider appeal. The title then became *Introduction to Molecular*

Magnets, which highlights that the book wants to cover the basic aspects of the field, and the specification "from transition metals to rare earths" clarifies that the dominant interest is on Ln, transition metals being the starting point.

The book has benefited from the comments and corrections provided by several colleagues, namely Roberta Sessoli, Federico Totti, Mauro Perfetti, Lorenzo Sorace, Lapo Bogani, and Alessandro Lascialfari. We thank Alessandro Barbieri and Matteo Mannini for their help in preparing photos and figures.

Given the age of the authors, the book is dedicated to our families: to sons and daughters, Luca and Clara Benelli, Silvia and Alessandra Gattesch, the grand children Duccio Benelli and Marta and Lorenzo Mencaroni and of course to the grandmothers Rossella and Ninetta.

Florence, January 6, 2015

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1 Introduction

1.1 A Nano History of Molecular Magnetism

The two terms *molecular* and *magnetism* that appear in the title of this book are here used in a well-defined scientific and technological frame; on the other hand, both of them are also often used, with different meanings, that influences how the scientific version is understood by specialists. Here we will not present a history of the concept of a molecule or a magnet, but we will highlight some general concepts in a scientific field that is developing fast. In order to be understood, it is necessary to make clear immediately what is meant by the title.

Actually, there is a specification ("From transition metals to lanthanides") which is meant to indicate that the present book starts from what has been done in the last few years mainly using transition-metal ions. The novelty is the focus on lanthanides. Another possible subtitle could be "An f orbital approach to molecular magnetism".

Molecules, whatever the word means, are gaining space not only among specialists but also among lay people. The adjective "molecular" is attributed to an increasing number of scientific disciplines, and often the transition of a discipline to a molecular stage is a moment of its explosive development. Molecular biology, the branch of biology that deals with the chemical basis of biological activity, is a significant example. Chemistry is THE molecular science, covering the synthesis, reactivity, and functionality of matter down to the scale of 1 Å. There is no doubt that expressions containing "molecular" must be understood as a quality mark to the scientific approach, giving the impression of a set of activities investigating matter at the most fundamental scale, with as much detail as possible. The great success achieved so far in several molecular sciences is generating more and more molecular sciences. A short visit to Wikipedia shows as diverse substantives to go with "molecular," such as molecular pharmacology, psychiatry, therapy, endocrinology, microbiology, ecology, genomic, and so on. A tantalizing expression is "molecular foundry," but it has nothing to do with a workshop producing metal alloys with a molecular approach. In fact, it is a Department of Energy (DOE) program framed in nanoscience where the "foundry" provides researchers with instrumentation and expertise. Again, molecular implies something special.

Introduction to Molecular Magnetism: From Transition Metals to Lanthanides, First Edition.
Cristiano Benelli and Dante Gatteschi.

The present book will deal with molecular systems that possess magnetic properties, beyond the ubiquitous presence of diamagnetism, and the term *molecular magnetism* (MM) is to be understood as an indication of detailed studies at the molecular level, and as a coming of age of a discipline. There is no doubt that magnets came about much earlier than molecules. The latter term has a well-defined origin, both in time and space: the modern concept of a molecule appeared in France in the early seventeenth century, mole meaning a small mass. The English word "molecule" is documented in 1678, while Gassendi used it in 1658. The concept of molecule was worked out by Descartes as "bodies so small that we cannot perceive them and of which everybody is composed." With time, the modern concept of molecule emerged, and it became apparent that the properties of matter rely on the structure and reactivity of molecules.

Magnetism is much older, and the meaning of the word is controversial, associating it either with the name of a shepherd who discovered the attraction between iron and lodestone, or to the region, Magnesia, where the discovery was made. Additionally, there is evidence of an early use of compasses in China. At any rate, magnetism attracted attention because it allows action at a distance, as exemplified by the magnetic interaction between lodestone and iron, and their reciprocal attraction.

This action at distance puzzled mankind for millennia, and, since movement was associated with the existence in the lodestone of a soul. After all, we are still using the expression "animal magnetism" to indicate the attraction between people. Pliny gave a more material description of the coupling, but in 1600 Gilbert still interpreted the phenomenology with the soul concept: "Magnetic attraction arises because the Loadstone hath a soul." A major breakthrough came rather unexpectedly by joining magnetism and molecules, when Coulomb tried to imagine how a molecule could become polarized in the process of magnetization. But it was the key experiment by Oersted, in 1820, that opened new perspectives in the understanding of magnetism by showing that an electric current influences the orientation of a compass needle. In fact, Ampere suggested that currents internal to the material were responsible of the magnetism and that the currents must be molecular, that is, microscopic rather than macroscopic.

The contribution by Faraday to the knowledge of magnetism cannot be underestimated. In fact, he found that magnetic properties of matter are much more widespread than just lodestone and iron. He discovered that almost the totality of substances is weakly repelled by an applied magnetic field and called these substances *diamagnets*. A less numerous class of compounds was weakly attracted by a magnetic field and was called *paramagnets*. After discovering and naming diamagnetism and paramagnetism, Faraday conceived the concept of a magnetic field, and this view provided an explanation for the action at a distance that startled so much the ancients. A visualization of a magnetic field is shown in Figure 1.1, as obtained with a network of magnetic needles.

The other giant step toward understanding magnetism was taken by Maxwell who provided the mathematical frame that allowed the description of electromagnetism. Pierre Curie investigated the temperature dependence of the

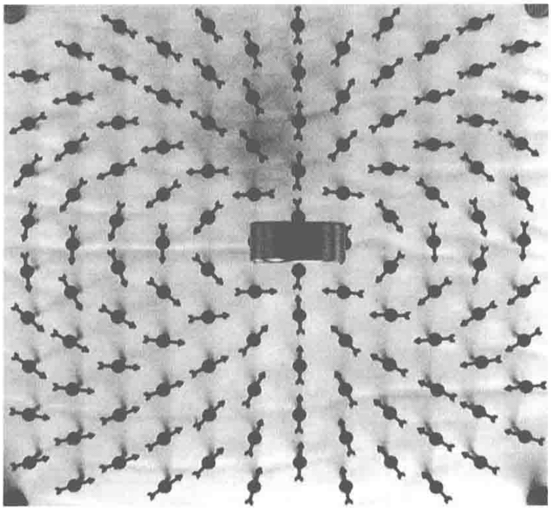

Figure 1.1 The power lines as described by an assembly of dipolar magnets. [Source: Prof. M. Verdaguer – Personal Communication].

magnetization, discovering the law that carries his name. The French title of his thesis, published in 1895, translates "Magnetic properties of matter at variable temperatures". Three types of magnetic bodies are introduced and a list of compounds corresponding to diamagnets, paramagnets, and ferromagnets are reported with a few examples. The only molecules listed are oxygen and nitric dioxide, which are present among paramagnets (weak magnets).

But one of the main actors on the magnetic scene was still missing: the electron. It took some time between the suggestion by Stoney (1874), the discovery by Thomson (1897) working with cathodic tubes and the understanding that the same electron was responsible for the chemical bond. Let us assign the merit for this to Lewis, who suggested the electron pair bond and substantially improved the ingenuous formalism of chemical formulas.

The last step was the development of quantum mechanics, which provided the tools for describing the magnetic properties, starting a revolution that we are still observing. Many new concepts were introduced, and some of them have had a fundamental impact on magnetism, most important among them spin and exchange. Today, with the centenary of quantum mechanics approaching (if we can assign an official date), there is an ever-increasing usage of quantum concepts and quantum phenomena, not only for basic science but for applications as well. Concepts such as quantum tunneling, coherence, decoherence, entanglement, and superposition, are no longer the initiatic jargon of a few scientists but the basic tools of everyday scientific life of chemists, physicists, materials scientists, biologists, and engineers. At the same time, there has been a shift in the size and number of objects under investigation. Typically, one investigates an ensemble containing a huge number of molecules, and what is obtained is an ensemble average. On the other hand, more and more experimental and theoretical tools allow addressing single molecules – a long way from Descartes and a complete paradigmatic shift.

We hope to have kindled some interest in a field that brings together the physical origins of magnetism with the chemical nature of molecules. One of the questions the book will try to answer is the following: does the above remark about a field acquiring a quality mark when becoming a molecular science also apply to MM?

1.2 Molecules, Conductors, and Magnets

Organic matter is often associated to electronic insulators but recently organic conductors have been synthesized and studied. Research has moved from molecular electronics to molecular spintronics. We will discuss the new exciting opportunities associated with the coexistence of electronic conduction with magnetic properties which provide unique opportunities for addressing individual molecules, storing, writing, and reading information in a single molecule, exploiting the quantum nature.

Molecular electronics is an example of a multidisciplinary approach as is well explained by R. Friend, a physicist who is one of the protagonists of molecular electronics:

> One of the big opportunities in this science is that it crosses traditional divides between subject areas. There's communication between physics and chemistry and materials and divide physics. Managing that communication has been hard work, but it has been really rewarding, as well. It hasn't felt at all like the ordinary mode of activity for a research program in the physics department. In fact, I spend more of my time going to chemistry conferences than I do going to physics conferences. I find what I can pick up at chemistry conferences extremely valuable. I'm constantly trying to better understand what chemists are trying to do.
>
> *R. Friend*

Magnetism is a property traditionally associated with metallic and ionic lattices. Till very recently, magnets were exclusively metals (Fe, Co, Ni, Gd), alloys ($SmCo_5$, $Nd_2Fe_{14}B$), or oxides such as magnetite (Fe_3O_4). This does not mean that magnetic molecules do not exist, O_2 being a clear example. But oxygen is a paramagnet which needs an applied magnetic field to work as a magnet and low temperature. The inorganic materials referred to earlier have permanent magnetization below a critical temperature (often called the *Curie temperature*) that is well above room temperature.

The idea of using organic molecules to make a new type of magnet, that is, an "organic ferromagnet," is a logical consequence of an argument of the following type: if molecules can yield unusual properties such as electrical conductivity, why should they not be magnetic? A gold rush toward this goal started in the 1970s, and it seemed to be successful when a nitroxide radical was reported to