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Review

Group-theoretical approaches in molecular magnetism: Metal clusters

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Dedicated to Professor Dante Gatteschi—to highlight his exceptional achievements and kudos.

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ABSTRACT

In this article I review the application of the group-theoretical approaches to a wide area of molecular magnetism dealing with metal clusters. The following main aspects are discussed: (1) irreducible tensor operator (ITO) approach that is based on the so-called "spin-symmetry". Use of this approach in molecular magnetism has given a revolutionary impact on the evaluation of the energy levels, thermodynamic and spectroscopic properties of high-nuclearity metal clusters. ITO approach facilitated development and applications of the isotropic and anisotropic spin-Hamiltonians and the study of the magnetic anisotropy in clusters containing orbitally degenerate metal ions; (2) group-theoretical classification (assignment) of the exchange multiplets based on both spin-symmetry and point symmetry that allows to analyze the non-Heisenberg forms of the exchange interaction and magnetic anisotropy in general terms, establishes selection rules for magnetic resonance transitions and facilitates computation of spin levels. This approach allows also to reveal the selection rules for the active Jahn–Teller coupling and to clear understand the interrelation between spin frustration and structural instabilities; (3) group-theoretical classification of the delocalized electronic and electron-vibrational states of mixed-valence compounds in terms of spin and point symmetries (including delocalization of the electronic pair) that essentially reduces the time of calculations and provides direct assess to the selection rules for different kinds of transitions. This becomes crucial in the dynamical vibronic problems inherently related to mixed-valency even for the truncated basis sets when the calculations become hardly executable not only in the case of strong vibronic coupling but even provided that the vibronic coupling is moderate. The proposed approach includes the design of the symmetry adapted vibronic basis and can enormously extend computational abilities in the dynamical problem of mixed-valency.

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1. Introduction

Contemporary molecular magnetism pioneered by Dante Gatteschi originates from classical magnetochemistry and represents an interdisciplinary field of science that incorporated basic concepts of physics, chemistry and material sciences. The objects of molecular magnetism include molecular metal clusters, i.e., molecular assemblies consisting of a finite numbers of exchange coupled ions, represent the so-called class of zero-dimensional magnets [1–15]. These systems are of current interest in many areas of research and applications, like molecular magnetism and biochemistry and have perspective applications as single molecular magnets (SMM) [1,2,8–10] and multifunctional nanomaterials. As it was recently demonstrated, coexistence of ferromagnetism and metallic conductivity can be reached in one molecular material [16,17]. One of the most important trend in the spin-crossover area is focused on the molecule-based multifunctional materials [18,19]. Organic molecules of increasing sizes and large numbers of unpaired electrons are also being explored as building blocks for molecular-based magnets [20,21]. The modern trend in molecular magnetism is focused on the possibility to use molecular clusters as magnets of nanometer size, which exhibit magnetic bistability and quantum tunneling of magnetization at low temperatures. The first 10 years of activity summarized in the review article of Gatteschi and Sessoli [3] showed that the fundamentals of the field are established and the SMMs are expected to provide important nano-technological applications as the memory storage units of molecular size and as a novel route to a spin-based implementation of quantum information processing [22–25].

The understanding of the magnetic and spectroscopic properties of nanoscopic objects between molecules and bulk magnets require special theoretical concepts. In this paper we will review the theoretical tools of molecular magnetism based on symmetry concepts. First, we shortly summarize the background of the irreducible tensor operators (ITO) approach and give some selected examples illustrating the efficiency of the ITO technique in different kinds of problems related to the field of the exchange interactions in metal clusters (Section 2). For a long time the treatment of the metal clusters has been restricted to comparatively simple systems comprising a reduced number of magnetic centers. Gatteschi with coworkers (Gatteschi and Pardi [26], Bencini and Gatteschi [4]) introduced in molecular magnetism a very efficient approach based on the use of the ITOs of the full rotation group [27–29]. The ITO approach has given a revolutionary impact on the consideration of high-nuclearity clusters including mixed-valence clusters and orbitally degenerate systems. ITO approach allows to avoid evaluation of the spin functions of the system and to construct directly the matrix of the spin-Hamiltonian which takes into account all kinds of the exchange terms, or more common effective Hamiltonian containing orbitally-dependent exchange interactions (see Refs. [13,14,30–35]).

Then (Section 3) we consider exchange clusters consisting of orbitally non-degenerate ions for which spin–spin interactions are the most important (hereunder, spin-clusters) while the orbital magnetic contributions are small and act as anisotropic corrections. We show how the exchange multiplets within the isotropic Heisenberg–Dirac–Van Vleck (HDVV) scheme can be correlated with the exact terms of the system (full spin and irreducible representation of the point group) [13,14,30]. Using selected examples we illustrate also how the symmetry assignment of the spin multiplets allows to select active non-Heisenberg terms in the exchange Hamiltonian and to reduce the matrices of the HDVV Hamiltonian that is crucially important for the treatment of high-nuclearity spin-clusters. Group-theoretical classification allows also to directly use the pseudoangular momentum representation and in this way to establish the selection rules for the EPR transitions and exact rules for crossing/anticrossing of the magnetic sublevels. This theoretical tool allows also to find the conditions under which the spin-vibronic Jahn–Teller coupling is active and consequently one can expect manifestations of structural instability in a spin-cluster. This is shown to be especially important for the spin-frustrated systems whose magnetic properties are essentially affected by even small structural distortions (static or/and dynamic) [36]. In Section 4 the group-theoretical classification is applied to mixed-valence systems with the delocalized electrons and holes and to the systems with partial electron delocalization [14] in which localized and itinerant electrons coexist and interact. In Section 5 the symmetry aspects of the dynamical electron-vibrational (vibronic) problem in mixed-valence (MV) compounds are discussed. It is shown how to construct the symmetry adapted vibrational and electron-vibrational states [37]. This can to essentially reduce the sizes of the enormously large matrices that appear while solving the dynamical vibronic problems. The procedure is exemplified by classification and evaluation of the vibronic states for a trimeric mixed-valence system with a delocalized electron. Finally, in Section 7 we shortly mention application of ITO in the problem of orbital degeneracy in the exchange and double exchange when the HDVV model in invalid even as an approximation [35,38].

The aim of the paper is to illustrate in an easily accessible way how the symmetry concepts can be applied to the study of the molecular magnets and what are the main advantages one can gain. Consequently, the main emphasis is put on the computational