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Review

Combining NMR spectroscopy and quantum chemistry as tools to quantify spin density distributions in molecular magnetic compounds

Martin Kaupp[a,*], Frank H. Köhler[b,*]

[a] Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
[b] Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

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ABSTRACT

NMR signal shifts of paramagnetic molecules are a measure of the spin density at the respective nuclei. The success of the method depends heavily on the analysis of the various shift contributions which are reviewed. While traditional treatments were based on ligand-field theory, recent progress is due to quantum chemical approaches. The restrictions of the analyses are compared. Solution- and solid-state results are considered and emphasis is laid on the distinction of spin density in s- and p-type orbitals. Specific examples are nitronyl nitroxide radicals and paramagnetic metallocenes. The latter demonstrate how the analysis may depend on the spin state of the molecule.

1. Introduction

The present review is closely related to molecular magnetism which receives much attention because the assembly of neutral molecules and ions having unpaired electrons (magnetic building blocks) lead to new magnetic materials [1]. Examples are bulk magnetic materials with high Curie or Néel temperature [2], spin-crossover materials [3], photomagnets [4], chiral magnets [5], and magnetic clusters or nanomagnets [6]. The overall magnetic behavior of the building blocks is commonly traced to their spin states which are well understood [7]. However, since the desired new magnetic properties arise from the interaction between the unpaired electrons of the building blocks, a key question is: What happens on the way from one building block to the next? Actually, the unpaired spins are usually not localized on one atom, for instance, on the transition metal of a coordination compound. The metal atom must rather be regarded as a spin source from which the spin is transferred partially to the atoms of coordinated ligands. The fraction of a spin is termed spin density, which is usually given in atomic units (a.u.) to emphasize the fractional character. It may also be quoted per volume (Å^{-3}) to indicate that spin density is

* Corresponding authors.
E-mail addresses: kaupp@mail.uni-wuerzburg.de (M. Kaupp), f.h.koehler@lrz.tu-muenchen.de (F.H. Köhler).

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associated with a shape. The spin density has a sign. That is, it orients itself parallel or antiparallel with respect to an external magnetic field or reference field. With suitable magnetic interaction, the spins may orient, thus giving the material a particular magnetic behavior.

The spin densities delocalized to the atoms at the periphery of magnetic building blocks will interact with each other upon assembly to the material. In the crystal lattice of magnetic compounds mutual spin transfer between the building blocks gives rise to parallel or antiparallel spin alignment typical for ferro- or antiferromagnetic interaction, respectively. The scenario may be comparatively well arranged as in Prussian blue-type magnets with up to six almost equivalent interactions per hexacyanometalate [8]. But it may also be complicated as in crystals of organic radicals where various close contacts between the molecules add up to the final magnetic interaction [9]. In any case, the knowledge of the spin density distribution within the building blocks, and their mutual interaction, are key points for the understanding and the design of magnetic materials. Experimental spin maps of the building blocks and of the final materials uncover the mechanism(s) generating the spin at the various atoms [10], and once this is known the synthetic chemist can modify the building blocks in order to achieve the desired magnetic interaction.

NMR spectroscopy of paramagnetic compounds [11] ("pNMR") is a method for determining the spin density distribution [10,12]. Most notably, it may be applied to solids which are magnetically undiluted, that is, to genuine magnetic materials by using established high-resolution techniques [13], while solution NMR studies are commonly used for the study of isolated magnetic building blocks. Changes of the spin density distribution upon assembling the material would then be detected by comparative studies in solution and the solid state. Other advantages of NMR spectroscopy are the relatively low cost and high resolution as compared to neutron diffraction [14] and the direct access to the sign of the spin density and again the resolution as compared to EPR spectroscopy [15]. Note, however, that NMR and EPR provide information under complementary experimental conditions because of the different electron relaxation regimes. A review on various experimental methods for the determination of spin densities is in progress [16].

As outlined below, the conversion of NMR data to spin densities is not always straightforward, due to a variety of contributions to the observed chemical shifts. The analysis may be hampered by missing data from other measurements. Also, the signal assignment of complicated ^{1}H and ^{13}C NMR spectra (and hence the assignment of the spin densities) to specific nuclei may be ambiguous, and sometimes the signals may not be detected at all because they appear in unexpected spectral ranges or because the nuclear relaxation is unfavorable. In these and other cases, it is highly desirable to theoretically reproduce or predict the NMR data and to relate them to the spin densities. This requires to go beyond the usual formalism of chemical shift tensors for diamagnetic systems (see, e.g. Ref. [17] and references therein). There have thus been substantial efforts over the past decade to compute NMR chemical shifts of open-shell (paramagnetic) species quantum chemically, usually within the framework of density functional theory (DFT). Initial studies were often restricted to the contact shifts only, which are sometimes accessible in a relatively straightforward way from computed isotropic hyperfine coupling constants [18,19], or to the anisotropy contributions from anisotropic hyperfine couplings [20]. Recently, a more general quantum-chemical framework has been developed that allows access to all relevant terms, including those beyond the contact term, and for the entire shift tensors, in a first-principles approach [21–25]. Here we will draw attention to these recent developments and describe the state-of-the-art situation of the interplay between experiment and theory of paramagnetic NMR signal shifts, and how these may be used to extract the spin density distribution in open-shell compounds.

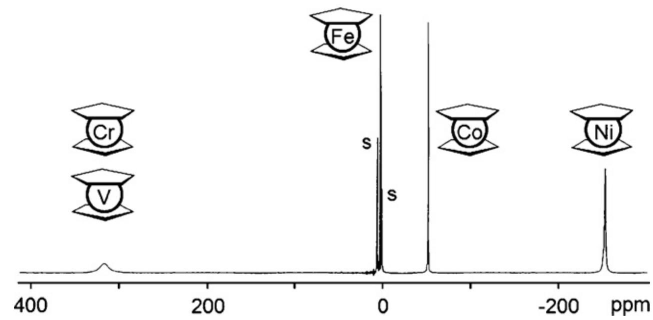

Fig. 1. ^{1}H NMR spectrum of a mixture of Cp_2V, Cp_2Cr, Cp_2Fe, Cp_2Co, and Cp_2Ni dissolved in toluene-d_8 at 32 °C. The signals of Cp_2V and Cp_2Cr coincide; S = residual proton signals of the solvent.

2. Theoretical background

2.1. General formalism

The NMR signals of paramagnetic compounds are usually much broader and more shifted than those of their diamagnetic analogues. A typical example is given in Fig. 1 which shows the ^{1}H NMR spectrum of a mixture of vanadocene (S = 3/2), chromocene (S = 1), cobaltocene (S = 1/2), nickelocene (S = 1), and diamagnetic ferrocene. The signal broadening is due to the effect of the electron spin on the nuclear spin relaxation [26] while the signal shift can be thought of as being mainly determined by the average local magnetic field of the unpaired electrons which in turn is related to the spin density.

The formalism of the chemical shifts of open-shell magnetic compounds has been developed over decades and is described in several text books [11,12]. Here we will not follow the course of the historical developments, which were often formulated within the framework of ligand-field theory, with recourse to spin susceptibilities as intermediate quantities, and with the point-dipole approximation. Instead we would like to start from a rather compact formalism that has been outlined recently within a quantum chemical framework [22–25]. This description has the advantage of containing all terms derived previously in a compact representation, based on the terms of the EPR spin Hamiltonian. The formalism allows straightforward inclusion of the effects of zero-field splitting (ZFS) for systems with S > 1/2 [25], and it is currently the most suitable basis for quantum chemical calculations. We will, however, identify wherever possible the relation to the terms appearing in the more traditional treatments [11,12,27]. For simplicity we will outline mainly the formalism for systems with S = 1/2 [22,23], where ZFS is absent. Following the derivation of Moon and Patchkovskii [22], the shift tensor of nucleus N at temperature T, $\boldsymbol{\delta}_T(N)$, for a system with S = 1/2, without thermally accessible electronically excited states, is given by Eq. (1). Hrobárik et al. [24] showed that for small ZFS contributions, this equation provides also excellent results when used in DFT calculations of ^{1}H and ^{13}C shifts for metallocene complexes with S > 1/2 (see below). When ZFS effects are large, the extended formalism of Pennanen and Vaara [25] has to be used (see further below).

$$\boldsymbol{\delta}_{\boldsymbol{T}}(N) = \boldsymbol{\delta}_{orb}(N) + \frac{S(S+1)\beta_e}{3kT\gamma(N)}\mathbf{g}.\boldsymbol{A}^{\dagger}(N) = \boldsymbol{\delta}_{orb}(N) + \boldsymbol{\delta}_{HF,T}(N) \qquad (1)$$

In Eq. (1), S is the spin multiplicity, β_e the Bohr magneton, $\gamma(N)$ the nuclear gyromagnetic ratio, and $\mathbf{g}$ and $\mathbf{A}$ are the g- and hyperfine tensors, respectively. $\boldsymbol{\delta}_{orb}(N)$ is the orbital part of the shift tensor. It is formally temperature-independent and analogous to the