pNMR: The roots of the matter

Foundations and future challenges for theory and experiments of paramagnetic NMR

Book of abstracts

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Theory of pNMR chemical shielding in open shell molecules

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The chemical shift and other parameters in the nuclear spin Hamiltonian can be calculated ab initio as electronic structure properties of the molecule. The theoretical foundation for closed shell molecules was given by Ramsey. We present a natural extension of Ramsey's theory to treat molecules with an arbitrary electronic spectrum. This includes paramagnetic systems with a degenerate ground state of spin or spin-orbit character, or systems where this degeneracy is lifted by a small zero-field splitting. In each case the chemical shift dependends on the thermal occupation of these electronic states and is therefore a temperature-dependent quantity. We also discuss how the paramagnetic shift can be expressed as a contraction of Zeeman and hyperfine coupling tensors, of all ranks required by the size of the degeneracy.

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pNMR shieldings and couplings in the SDS realm

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We introduce the current workhorse of pNMR shielding tensor and chemical shift prediction as presented originally in the classic paper by Kurland and McGarvey [1], and elaborated recently in a modern quantum-chemical setting [2,3]. This method formulates the hyperfine shielding in terms of the EPR parameters appropriate to the ground multiplet, split by zero-field splitting (ZFS) interaction of the form of the SDS Hamiltonian. Using *ab initio* multiconfigurational methods, as opposed to DFT, in the calculation of the critical ZFS and *g*-tensors [4], good agreement with experiment can be obtained for non-trivial 3d transition-metal systems, with potential to suggest reassignment of signals [5].

The detailed analysis in terms of the various contributions to the *g*-tensor and hyperfine coupling [3,4] enables systematic formulation of the long-distance point-dipole approximation [6], whereby pseudocontact shift calculations in very large systems become feasible. Such computations enable either predicting shifts in, *e.g.*, metalloproteins from a known structure of metal coordination, or alternatively constraining the local structure by demanding agreement of the experimental and computational shifts.

We furthermore describe the results of incorporating scalar relativistic effects both in the calculation of the ZFS and *g*-tensors, and particularly in the hyperfine coupling tensor, for 3d and heavier transition metal complexes [7]. Promising results are also obtained for lanthanide systems [8].

Theory and computational methods for the paramagnetic enhancement of the spin-spin coupling tensor have been formulated [9]. The results indicate significant changes of the coupling constants for nuclear pairs in the vicinity of the paramagnetic center. The enhancement does not decay in the same way with the number of bonds between the coupled atoms, as the standard spin-spin coupling tensor of diamagnetic systems. Therefore the paramagnetic terms may become quite important upon the development of experimental pNMR methodology.

We demonstrate the operation of the analysis script of the pNMR shielding tensor based on quantum-chemical calculations of the EPR tensors. The long-distance approximation [6] and the break-down into physical contributions [3,4] are presented. Similarly, the analysis of the spin-spin coupling enhancement [9] is shown in action.

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[6] L. Benda, J. Mareš, E. Ravera, G. Parigi, C. Luchinat, M. Kaupp and J. Vaara: *First-principles calculation of pseudo-contact shifts in a paramagnetic metalloprotein*, submitted (2016).

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[8] V. Gowda *et al.*, *in preparation* (2016).

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Theory of chiral discrimination in paramagnetic NMR spectroscopy

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Magnetic resonance spectroscopies, despite being among the most useful characterization techniques due to their high sensitivity to tiny details of the geometrical and electronic structure of molecules, are blind to chirality. However, it has been recently proposed by Buckingham [1] and Buckingham and Fischer [2] that NMR could be used to achieve chiral discrimination for closed-shell chiral molecules, via the detection of a molecular electric polarization **P** rotating in a plane perpendicular to the NMR magnetic field [1,2], and having opposite orientation for the two enantiomers of a chiral species. In solution, the induced chiral polarization **P** is proportional to the pseudoscalar $\sigma^{(1)}$, isotropic average of a third-rank tensor known as the *shielding polarizability* [1-3] However, computational estimates of $\sigma^{(1)}$ in diamagnetic molecules suggest that it is generally too small to be detected [1-5].

Here we present a theory of NMR chiral discrimination which is valid for molecules in solution with a ground state of arbitrary degeneracy [6]. We describe the response of the degenerate system in terms of a *generalized shielding polarizability* tensor defined as an analytical third-derivative of the electronic free energy [6-9]. The proposed theory predicts previously unexplored orientational contributions to the macroscopic rotating chiral electric polarization **P,** which are proportional to the chiral molecule's magnetic anisotropy, and to the square of the inverse temperature. Ab initio calculations for ten Dy3+ complexes that are also single-molecule magnets [10], show that **P** can be more than 1000 times larger than in diamagnetic molecules, making paramagnetic NMR chiral discrimination amenable to room temperature detection [6].

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pNMR Computations from long-range PCSs in proteins to shifts in extended solids

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In my lecture I will report on recent advances obtained in the computational description of pNMR shifts in collaborations within the pNMR ITN. In close cooperation with the Oulu and Florence groups, we have tackled the long-range pseudo-contact shifts (PCSs) in an entire (cobalt-substituted) protein.[1] This has been made possible by combining modern first-principles formalisms of pNMR shifts with a) a point-dipole approximation for the long-range hyperfine anisotropies, b) DFT-optimized structures, and c) multi-reference perturbation computations for *g*- and *D*-tensors. The extreme structure dependence of the PCS-correlations will be highlighted and connected to the local molecular and electronic structure around the metal center. This has led, among other things, to a reconsideration of the originally refined PDB structure. The computations also allow us to look at shifts closer to the metal site, into the blind sphere caused by paramagnetic line broadening. I will also report on efforts, together with the Cambridge group, to extend pNMR shift calculations for extended solids beyond the contact term only, and to combine accuracy and computational efficiency using the CP2K code.

[1]. L.Benda, J.Mareš, E. Ravera, G. Parigi, C. Luchinat, M.Kaupp, J.Vaara, to be submitted.

New Opportunities for paramagnetic environments using ultra-fast MAS

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The capability to perform MAS NMR with spinning rates at 100 kHz and higher now admits experiments in solid-state NMR of materials and biological samples, which were not possible before. On the other hand, spinning rates as high as 100 kHz also alter typical experimental conditions, for example in cross polarization experiments. The talk, after introducing the technological challenges of ultrafast MAS hardware, will also present some of these typical experimental conditions and discuss examples of NMR spectra obtained at those high speeds.

Overview of relaxation theory in paramagnetic systems

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The presentation will introduce various aspects of paramagnetic relaxation and will cover topics such as Curie spin relaxation, contact and pseudo-contact shifts, and paramagnetic relaxation enhancements. The geometric dependence of the dipolar effects involving an electron spin will be discussed. Applications such as distance measurements, contributions of the g-tensor, and determination of the binding mode of ligands will also be highlighted.

Ab initio modelling of paramagnetic relaxation in metal complexes in solution

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Nuclear spin relaxation is a powerful probe of dynamics and structure in complex environments,

but theory and calculations are required to access the information.

Paramagnetic relaxation is particularly challenging, but the theoretical framework is well established [1].

For an ab initio treatment of paramagnetic relaxatrion [2], we need to follow molecular dynamics,

electron spin dynamics and nuclear spin relaxation, partially occurring on similar time-scales.

Recent advances in quantum chemistry makes it possible to realize this, by allowing for a frequent sampling

of the zero-field splitting of the paramagnetic metal complex in extended molecular dynamics simulations [3-5].

However, the effort is only worthwhile if the quantum chemical calculations is reliably accurate and

reasonably affordable, to allow for sufficient sampling. Hence, different computational schemes must

be critically evaluated [6-7].

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Selective inversion of ^{13}C resonances by DNP-driven and paramagnetically enhanced nuclear cross relaxation

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Dynamic nuclear polarization enhances NMR sensitivity by transferring large electron spin polarization to surrounding nuclei under microwave irradiation. Ideally the polarizing agent and the molecule of interest are connected by an efficient spin-diffusion pathway so that enhanced nuclear polarization can be effectively transferred and paramagnetic effects on the analyte are minimal. Furthermore, nuclear spin-lattice relaxation should be rather slow so that large polarization enhancement can be accumulated.

If the biomolecule of interest is carrying a paramagnetic moiety such as a lanthanide binding tag, spin-lattice relaxation is enhanced and accumulated DNP enhancement is concomitantly reduced. Additionally, we have observed that for ^{13}C, which is not directly hyperpolarized by DNP due to absence of ^{13}C and inefficient ^{13}C-^{13}C spin-diffusion in the bulk solvent matrix, a selective inversion and negative enhancement of methyl resonances is observed under microwave irradiation. This enhanced inverted polarization is then spread throughout the protein by homonuclear spin-diffusion. At the same time, we observe a second species of proteins, where no inversion, but a positive direct enhancement of a severely broadened NMR spectrum is observed.

We present a model, where enhanced ^{1}H polarization is transferred from the polarizing agent via spin-diffusion through the solvent to the protein where heteronuclear cross relaxation is occurring with methyl ^{13}C. The cross relaxation rate is strongly enhanced by the presence of the paramagnetic ion which leads to selective amplification of inverted signal intensity. On the other hand, proteins which are in close proximity to a polarizing agent molecule experience direct enhancement of ^{13}C while suffering from severe broadening by the presence of the nitroxide polarizing agent.

We show that this effect is rather robust and in fact occurs under different conditions with or without paramagnetic cross relaxation enhancement and might be interesting for selective NMR of functional groups or molecules susceptible for the observed ^{1}H-^{13}C polarization transfer. Potential applications are discussed in regards to multi-dimensional correlation spectroscopy of large biomolecules or one-dimensional spectroscopy of complex mixtures.

Radicals for Efficient Solid-State Dynamic Nuclear Polarization

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Dynamic nuclear polarization (DNP) currently attracts considerable attention as it has recently evolved into one of the most efficient methods to increase the sensitivity of NMR experiments. Of particular interest is the possibility to do high-field DNP at low temperatures in situ to increase the sensitivity of magic-angle spinning (MAS) solid-state NMR spectroscopy (1). In this approach, samples are usually dissolved or impregnated with a solution containing stable exogenous paramagnetic centres such as nitroxides or trityls, which act as the polarization source. Most solid-state DNP NMR experiments are carried out in the presence of dinitroxide polarizing agents as they can transfer polarization through the cross-effect (CE) mechanism, which is one of the most efficient mechanisms for DNP at high magnetic fields.

With the recent introduction of dinitroxides of high molecular weight like TEKPol (2) or AMUPol (3), signal enhancements (ε) of between 100 and 200 are routinely obtained at 9.4 T (400 MHz proton frequency) and 100 K on a wide variety of samples, ranging from biomolecules to materials. These enhancement factors are however still far from the predicted maximum values and many efforts are still devoted in the rational design of polarizing agents of optimized geometries and electronic properties.

We have recently investigated a series of new dinitroxides belonging to the BTurea, PyPol, bTbK and TEKPOL families in frozen organic solutions (4). Clear relationships were established between the electronic relaxation properties of these molecules, their level of deuteration and their DNP efficiency. These results will be discussed together with the impact of very fast magic angle spinning on their DNP performance.

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2D NMR Measurement and Prediction of Full Paramagnetic Shift Tensors of Quadrupolar Nuclei

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Using the symmetry pathways formalism, we analyzed various 2D NMR methods for separating and correlating the paramagnetic shift and quadrupolar coupling frequency contributions in static polycrystalline samples. We illustrate our approach on a series of polycrystalline $MCl_2 \cdot 2\, D_2O$ samples (M=Cu, Ni, Co, Fe, Mn), using a simple motional model of rapid hopping of D_2O about their C2 axes for relating the observed motionally averaged quadrupolar and paramagnetic shift tensors to their instantaneous tensors. For the quadrupolar coupling a simple model for the efg tensor orientation along the O--D bond predicts a coupling in excellent agreement with previously measured values. Our analysis of the full deuterium paramagnetic shift tensor reveals that a delocalized point dipole model can be sufficient for predicting the paramagnetic shift tensor given an appropriate model for the molecular magnetic susceptibility of the paramagnetic site.

Paramagnetic NMR and scattering analyses of the structures, compositions, and properties of cerium-doped solid-state phosphors

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The local environments of dilute rare-earth ions are known to have crucial influences on the macroscopic optical properties of certain oxide materials, though these have been challenging to characterize and understand. For example, calcium scandate, $CaSc_2O_4$, when substituted with small amounts (<1%) of the activator ion Ce^{3+} to replace Ca^{2+}, exhibits excellent luminescence properties, though about which little is understood. Solid-state ^{45}Sc and ^{43}Ca NMR measurements conducted at very high magnetic fields (19-23 Tesla) exploit the local effects of paramagnetic Ce^{3+} dopant ions on the peak positions and spin-lattice relaxation times of nearby NMR-active nuclei, yielding enhanced spectral resolution. A combination of paramagnetic NMR measurements and X-ray and neutron scattering analyses establish distinct atomic environments near the Ce^{3+} ions over a range of material compositions, which are correlated with the macroscopic luminescent properties of Ce-doped $CaSc_2O_4$. The results provide insights and design criteria that are expected to be useful for the discovery, optimization, and development of novel and efficient phosphor materials for optoelectronics or solid-state lighting applications.

In situ spectroscopic imaging of batteries containing paramagnetic materials

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Operando NMR of lithium-ion batteries is a powerful tool to follow changes in lithium-ion batteries. The two powerful facets of NMR, imaging and spectroscopy, bring meaningful information. We combine both in spectroscopic images to monitor in situ the paramagnetic electrodes of a battery while it is charged and discharged.

Standard methods such as chemical shift imaging work very well for liquid electrolyte and metallic lithium [1,2]. The current challenge is for the paramagnetic electrodes. Paramagnetism generates extremely short transverse relaxation times, so that the solid paramagnetic electrodes are absent from the standard spectroscopic images so far [3].

We obtain for the first time a spectroscopic image of a full battery, including the paramagnetic electrodes. We designed a sequence specifically for fast relaxing signals and we apply it on our home-made in situ electrochemicall cell with an extremely strong pulsed field gradient (30 T•m-1) to obtain a resolution of 100um.[4] The spectroscopic images identify the source of limitation in the battery performance.

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Measuring and interpreting paramagnetic shifts in materials science and biology

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Paramagnetic systems are of the utmost importance in many fields of science, including chemistry, materials science, and biology. In the NMR of such materials the hyperfine interaction induces a "paramagnetic shift", which is an indispensable tool for the assignment and interpretation of the spectra. There are significant challenges in measuring and interpreting the paramagnetic shifts, which we explore in this presentation. In the first part we outline the full form of the paramagnetic shift tensor, and show how it can be linked to both the EPR and bulk magnetic properties of the system. Whilst this full form is very complicated, it can be shown that for different types of material different parts of the hyperfine interaction dominate the shift. We explore this point in more detail in the second part using some specific examples of battery materials and metalloenzymes. For all these cases we outline the experimental strategy for acquiring the high-resolution NMR data, and show how the shifts may be understood and interpreted. In particular we compare the similarities and differences of the specific nature of the important contributions to the shifts for all these systems.

Solid state NMR studies of paramagnetic, inorganic Ni(II) materials and complexes

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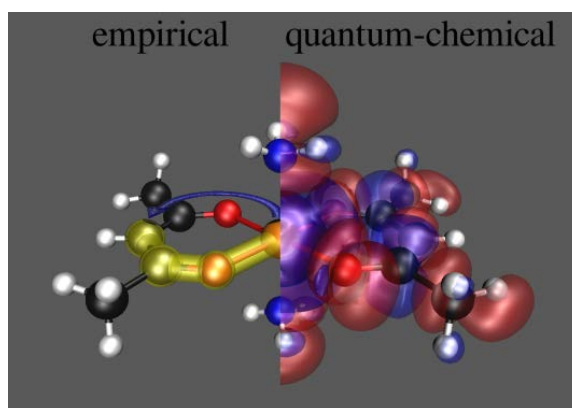
A series of Ni(II) acetyl acetonate complexes [Ni(II)(acac)$_2$L$_2$] with L = H$_2$O, D$_2$O, NH$_3$, ND$_3$, and PMe$_2$Ph has been investigated by ^{1}H, ^{2}H, and ^{13}C solid state NMR (SSNMR) in combination with first-principles calculations at various levels of approximation for the different physical contributions to the pNMR shifts appearing in the theory. Assignment of the single pulse ^{13}C MAS NMR spectra based on paramagnetic shifts only using the conventional "the closer to the paramagnetic center, the larger the paramagnetic shift" and the first-principles calculations suggest contradicting assignments. Thus, additional SSNMR experiments and synthesis of selectively labelled complexes were performed to resolve these ambiguities.

Preliminary ^{2}H, ^{13}C and ^{27}Al results from SSNMR studies of layered, inorganic Ni(II) and Fe(III) materials demonstrate that detailed structural information can be obtained from SSNMR. However, the studies also demonstrate some of the experimental challenges in SSNMR studies of paramagnetic complexes with respect to sample quality and background signals.