



The role of level anti-crossings in nuclear spin hyperpolarization



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ABSTRACT

Nuclear spin hyperpolarization is an important resource for increasing the sensitivity of NMR spectroscopy and MRI. Signal enhancements can be as large as 3–4 orders of magnitude. In hyperpolarization experiments, it is often desirable to transfer the initial polarization to other nuclei of choice, either protons or insensitive nuclei such as ¹³C and ¹⁵N. This situation arises primarily in Chemically Induced Dynamic Nuclear Polarization (CIDNP), Para-Hydrogen Induced Polarization (PHIP), and the related Signal Amplification By Reversible Exchange (SABRE). Here we review the recent literature on polarization transfer mechanisms, in particular focusing on the role of Level Anti-Crossings (LACs) therein.

So-called “spontaneous” polarization transfer may occur both at low and high magnetic fields. In addition, transfer of spin polarization can be accomplished by using especially designed pulse sequences. It is now clear that at low field spontaneous polarization transfer is primarily due to coherent spin-state mixing under strong coupling conditions. However, thus far the important role of LACs in this process has not received much attention. At high magnetic field, polarization may be transferred by cross-relaxation effects. Another promising high-field technique is to generate the strong coupling condition by spin locking using strong radio-frequency fields. Here, an analysis of polarization transfer in terms of LACs in the rotating frame is very useful to predict which spin orders are transferred depending on the strength and frequency of the B_1 field. Finally, we will examine the role of strong coupling and LACs in magnetic-field dependent nuclear spin relaxation and the related topic of long-lived spin-states.

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1. Introduction

1.1. Spin hyperpolarization

Nuclear Magnetic Resonance (NMR) is a very versatile spectroscopic tool, which is used in many areas of science such as physics, chemistry, and biology. Furthermore, Magnetic Resonance Imaging (MRI), based on the same principles, is now a ubiquitous diagnostic tool in clinical medicine and medical research. However, a weakness of NMR is its low sensitivity. Essentially this is because the nuclear magnetic moments are very small and, therefore, their

interactions with magnetic fields are much weaker than the thermal energy, kT . This leads to very small population differences between nuclear spin levels (spin polarization), to which NMR signals are directly proportional. Typically, at thermal equilibrium the Boltzmann polarization is of the order of 10^{-4} . The sensitivity of NMR has increased during the last decades, for instance, by using higher magnetic fields, cross-polarization methods [1,2], INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) and similar techniques [3], remote detection methods [4], and cryo-probes [5,6]. Other promising approaches address the problem of low thermal spin polarization by selective population of nuclear spin energy levels (see Fig. 1.1). These methods, collectively called “hyperpolarization” include Dynamic Nuclear Polarization (DNP) [7–9], Spin Exchange Optical Pumping (SEOP) [10], Optical Nuclear Polarization (ONP) [11,12], Chemically Induced Dynamic Nuclear Polarization (CIDNP) [13–15] and Para-Hydrogen Induced Polarization (PHIP) [16,17]. Some of these methods achieve NMR signal enhancements of several orders of magnitude, thus making new

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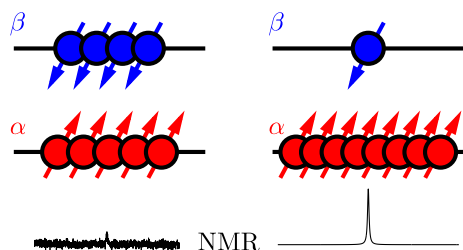


Fig. 1.1. Nuclear spin state populations for thermally polarized (left) and hyperpolarized (right) ensembles of spins $\frac{1}{2}$ and their NMR spectra. For protons the actual population difference at equilibrium is typically one in 10^4 .

NMR and MRI applications possible [18–33]. We will not discuss all these hyperpolarization methods but focus on methods that (may) involve polarization transfer between nuclei, such as CIDNP, PHIP and its recent offspring, Signal Amplification By Reversible Exchange (SABRE) [34].

CIDNP is observed in the products of chemical reactions involving radical pairs (RPs). The effect originates from the fact that electron singlet-triplet mixing in RPs is nuclear spin-state dependent. PHIP and SABRE exploit the huge non-equilibrium populations of the *para*-spin isomer of H_2 . In the case of PHIP, the symmetry of the NMR-silent *para*- H_2 is broken by a catalytic hydrogenation reaction (usually an addition to a double or triple C–C bond). SABRE does not require a hydrogenation reaction: instead, polarization transfer occurs in a transient complex (*para*- H_2)-(catalyst)-(substrate) and hyperpolarization is then observed in the dissociated substrate.

1.2. Polarization transfer and the role of LACs

SABRE relies entirely on polarization transfer from *para*- H_2 to the substrate. However, CIDNP and PHIP can also be used to transfer primary polarization to other nuclei, which may be protons or insensitive nuclei such as ^{13}C or ^{15}N . The resulting signal enhancement allows NMR and MRI experiments that would be impossible otherwise [20,35–40]. In principle, polarization transfer occurs either *via* cross-relaxation or by coherent spin mixing in nuclear spin coupled networks. As we will discuss later, at low magnetic fields coherent spin mixing is the dominant mechanism, while cross-relaxation is more likely to contribute at high fields (for an early discussion of polarization transfer in CIDNP, see Ref. [41]).

In PHIP experiments, some early observations of polarization transfer were explained in terms of cross-relaxation [42,43]. However, it was soon realized that at low magnetic fields, where the strong coupling condition prevails, coherent spin mixing is a powerful alternative [16,17,44]. In principle, the theory of polarization transfer in strongly coupled spin systems is well developed [44–46]. Essentially, the behavior of a spin-system is described by the time-dependent nuclear spin density matrix, which is obtained by solving the Liouville–von Neumann (LvN) equation (see Section 5) using a relatively simple Hamiltonian (including Zeeman and J-coupling interactions), a time-dependent magnetic field to account for field cycling, and possibly kinetic parameters to reflect chemical and relaxation process. Recently, Adams et al. [46] have provided an extensive density matrix theory for the SABRE experiment. Nevertheless, we have found it crucial [47] to consider an approximate treatment of polarization transfer using the notion of Level Anti-Crossings (LACs), also referred to as avoided crossings. LACs occur at magnetic fields where spin energy levels tend to cross or approach each other. Due to spin–spin interactions, the levels split at the crossing point and the actual crossing is avoided. This occurs only in the strong coupling limit and, therefore, LACs and strong coupling are related concepts.

Now if the density matrix theory provides a rigorous description of the evolution of a nuclear spin-system it is legitimate to ask why one would need an analysis in terms of LACs to account for magnetic field dependent polarization transfer. The reason is the following. Except for the simplest cases, solving the LvN equation for the time evolution of the density matrix for variable fields is a formidable computational problem. It can be successful when all magnetic parameters (chemical shifts and J-coupling constants) are known. However, when this is not the case, for instance, for ligands in a metal-organic catalyst, the inverse problem (i.e. extracting the magnetic parameters) becomes unwieldy. In that case, diagonalization of the Hamiltonian matrix at various magnetic fields in order to find the LACs is a much smaller computational problem. From an analysis of these LACs, one can then obtain a qualitative picture of the polarization transfer and its field dependence. Simulations based on the full LvN equation can then confirm this. This procedure worked well for field dependent SABRE effects [47], which apparently could not be interpreted using density matrix theories alone [48]. A further advantage of the LAC analysis is that the sign of net polarization and multiplet effects can be obtained for each LAC region using qualitative sign rules (see Section 9.1). Thus, LACs provide a detailed insight in the polarization transfer process that cannot easily be obtained from the full density matrix theory.

1.3. Scope of the review

The focus of this review is on polarization transfer processes in nuclear spin hyperpolarization experiments and the role of LACs therein. Although during the last decade several reviews have appeared on CIDNP [49–52], and also on PHIP and SABRE [17,53,54], we will start with a short overview of these hyperpolarization methods so that the review can be read as a stand-alone article. We will then discuss the concept of LACs in relation to strong coupling in nuclear spin systems as well as the formal density matrix theory of coherent spin mixing.

An overview of experimental methods for CIDNP, PHIP, and SABRE also includes methods for field cycling, since low field polarization transfer experiments require controlled changes in magnetic field. It is also possible to create strong coupling conditions by spin-locking magnetization in a strong radio-frequency (B_1) field. Again, LACs occur, now dependent on the B_1 field and the theory for spin mixing under these conditions is presented.

Finally, we will review recent examples of hyperpolarization transfer and their analysis in terms of LACs.

2. Chemically Induced Dynamic Nuclear Polarization (CIDNP)

2.1. Origin of CIDNP

Products of reactions involving radical pairs may show NMR lines with strongly enhanced intensities. In most cases, these CIDNP effects originate from the so-called Radical Pair Mechanism (RPM) [55–57]. The essential feature of the RPM is the (somewhat counterintuitive) notion that nuclear spins affect the chemical reactivity of radical pairs. This is possible because of the strong conservation of electron spin angular momentum during chemical reactions. To understand this, let us consider the following stages in the lifetime of a RP in solution (CIDNP can also be observed in the solid state [58–62], but this will not be discussed here).

- i. *Birth of the RP.* Just after formation of a spin-correlated RP its electronic spin state is the same as that of its precursor. Thus, for thermal reactions this is the singlet state, while for photochemical reactions it can be either singlet (S) or triplet (T).

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