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Mechanisms of dynamic nuclear polarization in insulating solids

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ABSTRACT

Dynamic nuclear polarization (DNP) is a technique used to enhance signal intensities in NMR experiments by transferring the high polarization of electrons to their surrounding nuclei. The past decade has witnessed a renaissance in the development of DNP, especially at high magnetic fields, and its application in several areas including biophysics, chemistry, structural biology and materials science. Recent technical and theoretical advances have expanded our understanding of established experiments: for example, the cross effect DNP in samples spinning at the magic angle. Furthermore, new experiments suggest that our understanding of the Overhauser effect and its applicability to insulating solids needs to be re-examined. In this article, we summarize important results of the past few years and provide quantum mechanical explanations underlying these results. We also discuss future directions of DNP and current limitations, including the problem of resolution in protein spectra recorded at 80–100 K.

1. Introduction

The history of dynamic nuclear polarization (DNP) dates from 1953 when Overhauser proposed that irradiation of electron paramagnetic resonance (EPR) transitions could result in the enhancement of the polarization of coupled nuclei [1]. Shortly thereafter, Carver and Slichter performed the first DNP experiments that confirmed the Overhauser effect (OE). In particular, they observed enhanced ^{7}Li signal intensities obtained from Li metal dispersed in mineral oil [2]. The enhancement was also observed in solutions of Na^{+} in liquid NH_3 [3]. The first DNP mechanism documented for insulating solids was the solid effect (SE) and was described by Jefferies [4,5] and Abragam and coworkers [6,7]. Five years later, the cross effect DNP mechanism was observed by Kessenikh [8,9], and subsequently discussed in more detail by Hill and Hwang [10,11] and Wollan [12,13]. The goal of many of these early efforts was to understand the physics underlying DNP and to develop experiments that produced polarized targets for neutron scattering experiments. Indeed, preparation of polarized targets remains an area of active interest in experimental particle physics, most recently using pulsed DNP methods (*vide infra*). For the interested reader there are excellent reviews of these early experiments [14–17].

In the 1980s and early 1990s, efforts to incorporate DNP into magic angle spinning (MAS) and other solid state NMR experiments were initiated by Wind et al. [18], Yannoni [19–21] and Afeworki and Schaefer [22]. These experiments used klystron microwave sources and were performed primarily at a magnetic field of 1.4 T (60 MHz/40 GHz ^{1}H/electron Larmor frequencies) although one experiment at 1.9 T was reported [23]. However, these experiments were limited to low fields because of the paucity of microwave sources operating above 40–50 GHz. In 1993 Becerra et al. [24] introduced the gyrotron as a microwave source for DNP experiments at 5 T (140 GHz for electrons), with the specific aim of developing an experimental approach that would permit DNP at higher magnetic fields used for contemporary NMR experiments. These magnetic fields require microwave sources that ideally operate at the 10–100 W level in the ~140–660 GHz frequency range, corresponding to magnetic fields of ~5–23 T and ^{1}H Larmor frequencies of ~200–1000 MHz. Subsequently, gyrotron based DNP/NMR spectrometers operating at 250 GHz/380 MHz and 460 GHz/700 MHz were successfully constructed [25–28]. In addition, DNP/NMR instruments operating at 263 GHz/400 MHz, 395 GHz/600 MHz and 527 GHz/800 MHz are now available commercially. The accessibility of this new instrumentation has stimulated a variety of new applications as well as investigations of new DNP mechanisms.

In this review, we discuss key aspects of several known DNP mechanisms including continuous wave (CW) and time domain DNP. We present recent experimental results together with some new quantum mechanical treatments. Our analysis builds on the work by Hu et al. [29]. However, we emphasize the use of perturbation theories (both time independent and time dependent; non-degenerate and degenerate). Furthermore, we include the effects of MAS in CE DNP that have been considered recently [30,31]. Our discussion focuses primarily on the mechanisms of

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DNP in insulating solids at high fields. For other aspects of DNP such as instrumentation, radical development, and applications, we refer the reader to other reviews by Ni et al. [32], Barnes et al. [33], Maly et al. [34], and Nanni et al. [35]. However, we do include a discussion of the effects of low temperature on resolution in spectra of proteins.

The paper is organized as follows. In Sections 2.1 and 2.2, we discuss CW DNP mechanisms in which the microwave fields are treated as time-dependent harmonic perturbations, while the remaining terms in the Hamiltonian are viewed as static. Diagonalization of the static Hamiltonian is conveniently approximated using time independent perturbation theory, without obscuring any conclusions. In the case of CE DNP (Section 2.2), despite the magic angle spinning, the Hamiltonian can also be regarded as static at each rotor angle. Section 3.1 deals with pulsed DNP methods using low microwave power including DNP in the nuclear rotating frame (NRF DNP) and the dressed state solid effect (DSSE) in which the microwave fields are treated as perturbations. In Section 3.2, we discuss two time-domain DNP experiments: nuclear orientation via electron spin locking (NOVEL) and the integrated solid effect (ISE), where the microwave fields are large and can no longer be treated as perturbations. Section 4 discusses resolution in low temperature spectra and some future directions of DNP.

2. CW DNP

2.1. Narrow EPR spectrum

The first class of DNP mechanisms in insulating solids involves radical dopants that satisfy the inequality $\delta, \Delta < \omega_{0I}$, where δ, Δ and ω_{0I} are the homogenous electron paramagnetic resonance (EPR) linewidth, the breadth of the EPR spectrum and the nuclear Larmor frequency, respectively. In this case, DNP is mediated by the Overhauser effect and/or the solid effect. The influence of MAS can be conveniently ignored because the EPR spectrum is narrow and therefore the electron energy levels are only weakly modulated by the sample rotation. The molecular structures of four narrow-line polarizing agents are shown in Fig. 1a–d and include 1,3-bisphenylene-2-phenylallyl (BDPA), sulfonated-BDPA (SA-BDPA), trityl OX063 and Gd^{3+}-DOTA. These polarizing agents have a small g-anisotropy or, in the case of Gd^{3+} a narrow $-½ \rightarrow ½$ central EPR transition due to molecular symmetry. However, the EPR lines are broadened by the proton hyperfine couplings (BDPA and SA-BDPA), residual g-anisotropy (trityl OX063), or second order zero field splitting (Gd^{3+}-DOTA).

2.1.1. Overhauser effect

The Overhauser effect was the first DNP mechanism proposed for systems with mobile electrons, namely conducting solids and liquids. The effect is operative in a two-spin system consisting of one electron and one nucleus (Fig. 1e), and relies on the presence of the zero quantum (ZQ) and double quantum (DQ) relaxation pathways with differing relaxation rates. The imbalance between the two rates, (Γ_0 and Γ_2 in Fig. 1e) leads to an enhancement in nuclear polarization. In particular, upon microwave irradiation near the single quantum (SQ) EPR transition, the DQ and ZQ relaxation, mediated by molecular tumbling in liquids and translational motion of electrons in conducting solids, redistribute the populations via fluctuations of the anisotropic and isotropic couplings, respectively. This results in a Zeeman field profile that is symmetrically centered at the frequency of the EPR transition. In liquids, the DQ transition is generally the dominant relaxation pathway, and leads to the observation of negative DNP enhancements for ^{1}H. However in insulating solids, we recently observed a significant OE DNP with a *positive* enhancement, indicating that the ZQ term is dominant [36]. This is illustrated in Zeeman field profiles of Fig. 1g–i where the positive enhancement in the center of the profiles is assigned to the OE. In addition, quantum mechanical simulations predict an OE even though the samples are insulators. In contrast to some other CW DNP mechanisms, the OE relies on allowed EPR transitions, requires much less microwave power, and appears to scale favorably with the magnetic field as is also illustrated in the panels in Fig. 1g–i.

To date the OE in insulators has only been observed for BDPA and its derivative SA-BDPA. In addition, perdeuteration of BDPA resulted in an order of magnitude decrease in DNP efficiency but, more importantly, in a sign change of the OE enhancement from positive to *negative* as well. This result and the fact that ~5 MHz ^{1}H couplings are present in BDPA, SA-BDPA suggest that ^{1}H–e^- hyperfine coupling is essential for the OE. This also provides an explanation of why the OE is not observed for the trityl radical. In particular, trityl was designed to eliminate all ^{1}H couplings in order to have a narrow line to enhance Overhauser effects in solution!

Efforts are underway to improve the efficiency of the OE with the synthesis of new narrow-line radicals with hyperfine couplings larger than those found in BDPA. Furthermore, theoretical and experimental research is needed to fully understand the origin of cross relaxation mechanisms responsible for the OE in insulating solids.

2.1.2. Solid effect

The solid effect (SE) is similar to the OE in that it involves a two-spin process between an electron spin S and nuclear spin I. The Zeeman field profiles for the SE (plus the OE) are shown in Fig. 1g–i and the SE is responsible for the negative and positive signal enhancements at $\omega_{SE} = \omega_e \pm \omega_{0I}$. In the secular approximation, the static Hamiltonian for such a system can be written as

$$H = \omega_{0S} S_z - \omega_{0I} I_z + A S_z I_z + B S_z I_x \tag{2.1.1}$$

where the first two terms are the electron and nuclear Zeeman interactions, and the last two terms the secular and pseudo-secular hyperfine couplings, respectively. Using first order perturbation theory we rewrite H as

$$H = H^{(0)} + H^{(1)} \tag{2.1.2}$$

where the small perturbation $H^{(1)}$ is the pseudo-secular hyperfine coupling term in (2.1.1). The unperturbed Hamiltonian $H^{(0)}$ is already diagonal in the direct product basis set. The energy levels and the corresponding eigenstates of H can then be evaluated using perturbation theory. The direct product states are not eigenstates of H and there is a small but essential mixing of these states due to the pseudo-secular hyperfine coupling (Fig. 1f). The degree to which the states are mixed is given by the factor q [37]

$$q \approx \frac{B}{2\omega_{0I}} \tag{2.1.3}$$

As a result, the nominally forbidden ZQ and DQ transitions become slightly allowed and can be driven by the microwave field, yielding an enhancement in the nuclear polarization that is positive or negative depending on the field position relative to the position of the EPR line. We refer to the plots shown in Fig. 1g–i as Zeeman field profiles. Note that in this CW DNP experiment the coefficient of state mixing is proportional to ω_0^{-1}, and therefore the transition probability is $\sim \omega_0^{-2}$. Thus, the SE enhancements decrease significantly at higher fields, which is a characteristic of continuous wave (CW) DNP experiments. On the other hand, the transition rate can be improved by increasing the microwave field strength [38,39]. Another approach is to use a radical whose EPR