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Adiabatic and fast passage ultra-wideband inversion in pulsed EPR

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ABSTRACT

We demonstrate that adiabatic and fast passage ultra-wideband (UWB) pulses can achieve inversion over several hundreds of MHz and thus enhance the measurement sensitivity, as shown by two selected experiments. Technically, frequency-swept pulses are generated by a 12 GS/s arbitrary waveform generator and upconverted to X-band frequencies. This pulsed UWB source is utilized as an incoherent channel in an ordinary pulsed EPR spectrometer. We discuss experimental methodologies and modeling techniques to account for the response of the resonator, which can strongly limit the excitation bandwidth of the entire non-linear excitation chain. Aided by these procedures, pulses compensated for bandwidth or variations in group delay reveal enhanced inversion efficiency. The degree of bandwidth compensation is shown to depend critically on the time available for excitation. As a result, we demonstrate optimized inversion recovery and double electron electron resonance (DEER) experiments. First, virtually complete inversion of the nitroxide spectrum with an adiabatic pulse of 128 ns length is achieved. Consequently, spectral diffusion between inverted and non-inverted spins is largely suppressed and the observation bandwidth can be increased to increase measurement sensitivity. Second, DEER is performed on a terpyridine-based copper (II) complex with a nitroxide-copper distance of 2.5 nm. As previously demonstrated on this complex, when pumping copper spins and observing nitroxide spins, the modulation depth is severely limited by the excitation bandwidth of the pump pulse. By using fast passage UWB pulses with a maximum length of 64 ns, we achieve up to threefold enhancement of the modulation depth. Associated artifacts in distance distributions when increasing the bandwidth of the pump pulse are shown to be small.

1. Introduction

Only a fraction of all electron spins can typically be excited in pulsed electron paramagnetic resonance (EPR) spectroscopy due to the technically constrained excitation bandwidth of rectangular pulses. In fact, the width of the EPR spectrum often exceeds the excitation bandwidth by several multiples, as for instance for transition metal centers with spectral widths above 1 GHz at moderate fields or for nitroxide radicals at high fields. While partial spin excitation is advantageous in order to select particular orientations of spectroscopically resolved anisotropy parameters [1–3], the constrained excitation bandwidth limits the measurement sensitivity in many EPR experiments [4]. Accordingly, a lot of effort has been invested in the field to enhance the excitation bandwidth:

First, the microwave resonator and the available pulse power at microwave frequencies are key restrictions to the excitation bandwidth of rectangular (hard) pulses, such that a number of optimized microwave resonators and optimized spectrometers have been reported. Recent examples include [5–8] and several earlier contributions are found in [9,10]. Second, alternative excitations providing larger bandwidths have been investigated, namely composite pulses [11], stochastic excitation pulses for Fourier transform EPR [12], shaped sinc-pulses for EPR imaging at radio frequency [13] and multichromatic rectangular pulses for broadband spin pumping [14]. Third, shaped microwave pulses tailored from optimal control theory (OCT) for increased excitation bandwidth have been demonstrated at X-band frequency [15]. Considering the impact of OCT pulses in nuclear magnetic resonance (NMR) spectroscopy [16], the combination of OCT and EPR is promising and has already shown interesting applications of coherence pathway selection [17,18] and narrowband control [19] with shaped X-band pulses in the context of quantum information processing.

In order to experimentally realize shaped microwave pulses derived from OCT, fast arbitrary waveform generators (AWG) with up to 1 ns timing resolution to modulate amplitude and phase of a fixed microwave oscillator (LO) have been used. To date, the fastest commercially available AWGs even provide sub-ns timing resolution to directly synthesize microwave pulses, as demonstrated for rectangular pulses [20,21] and applied in rotational spectroscopy [22].

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In this study, an ordinary X-band spectrometer is extended by a 12 GS/s AWG to test the feasibility of ultra-wideband (UWB) inversion by adiabatic or fast passage pulses. Since UWB refers to spectral extent above 0.5 GHz [23], the excitation bandwidth exceeds the bandwidth of current microwave resonators. The aim of this study is therefore to establish compensation techniques of bandwidth effects distorting the excitation pulse and to demonstrate applications where UWB inversion surpasses conventional approaches. For an identification of bandwidth effects due to the entire excitation chain, adiabatic pulses of fairly basic shapes are examined, because these provide simple means of comparing actual experimental performance against simulated performance. As a result, bandwidth limitations and variations in group delay are found to influence inversion performance (*vide infra* adiabaticity). Compensation of those is based on a quasi-linear hardware model obtained upon processing data from transient nutation experiments, because the high power microwave amplifier is strongly non-linear. The validity of this quasi-linear model is discussed and enhanced inversion performance by pulse compensation is demonstrated experimentally. Then, suppression of spectral diffusion processes by virtually complete inversion of the nitroxide spectrum is shown to prolong longitudinal relaxation times obtained from inversion recovery (IR) experiments, thus allowing for the measurement of intrinsic longitudinal relaxation times by that experiment. Finally, double electron–electron resonance (DEER, also termed PELDOR) experiments with fast passage pulses on a copper-nitroxide complex are presented. Herein, enhanced modulation depth is shown when pumping the spectrally broad copper center with UWB pulses and observing the nitroxide spins.

2. Theory

2.1. Adiabatic inversion

Adiabatic inversion by phase and amplitude modulated pulses has been established in NMR since many years. While early implementations made use of frequency swept pulses of constant amplitude [24], later a number of optimized pulse shapes have been developed [25–27]. A unique property of adiabatic pulses is that the magnetization follows the effective field $\boldsymbol{\omega}_{\mathrm{eff}}$ and is relatively insensitive to inhomogeneities in the driving field B_1. The requirement for the magnetization to follow $\boldsymbol{\omega}_{\mathrm{eff}}$, expressed via the adiabaticity factor Q, is given by [25]

$$Q = \frac{\boldsymbol{\omega}_{\mathrm{eff}}}{|d\theta/dt|} \gg 1 \tag{1}$$

The factor $|d\theta/dt|$ is the instantaneous angular velocity of $\boldsymbol{\omega}_{\mathrm{eff}}$. Considering a linear frequency sweep (linear chirp), Q has its minimum at the time when a particular isochromat is on resonance and can be written as [25]

$$Q_{\mathrm{min}} = \frac{2\pi\nu_1^2 t_{\mathrm{p}}}{\Delta f} \tag{2}$$

where ν_1 is the nutation frequency, t_{p} the pulse length and Δf the total sweep width (all frequencies in Hz). UWB inversion performance ($Q_{\mathrm{min}}\Delta f$) therefore scales quadratically in ν_1, which is limited by the available microwave power and the resonator bandwidth, and linearly in the pulse length t_{p}, which is limited by relaxation or coherence transfer times required by the experiment. All other parameters being equal, UWB inversion performance scales linearly with microwave power.

In addition to a high adiabaticity factor Q, an adiabatic inversion pulse should rotate $\boldsymbol{\omega}_{\mathrm{eff}}$ from $+z$ to $-z$, which is usually fulfilled by smooth tails of the inversion pulse. For the chirped pulses used in this study, the pulse edges were therefore weighted with a quarter period of a sine, whose length is specified separately by t_{rise}. While slightly better suited pulses for frequency-selective adiabatic wideband inversion are found in the literature [26,28,29], it should be noted that in an ordinary EPR spectrometer the pulse modulation functions are distorted by a number of hardware imperfections:

The amplitude modulation function is most affected by the saturated traveling wave tube (TWT) amplifier and the bandwidth of the resonator. Such amplitude imperfections have an effect on ν_1 and their impact on the adiabaticity of linear chirps is quantified by Q_{min} in Eq. (2). The phase modulation function is perturbed by the phase response $\beta(f)$ of the excitation chain, which describes the relative phase offset of the driving field with respect to the phase programmed in the AWG. The influence of $\beta(f)$ on the adiabaticity requires separate analysis, which is presented in the following.

2.2. Dependence on group delay

UWB chirp pulses for adiabatic inversion in EPR raise the relevance and importance of the excitation chain's phase response $\beta(f)$, which, in general, has previously not been considered. In order to simplify the analysis for present consideration, the perturbation of the phase modulation function is modeled by the frequency domain phase response $\beta(f)$ evaluated at the instantaneous frequency f_{i} of the chirp. The analogous procedure is used for the perturbation of the amplitude modulation function by the amplitude response $\nu_1(f)$. Note that such an approximation has its limitations towards fast chirp rates ($\Delta f/t_{\mathrm{p}}$) and non-smooth amplitude and phase responses, $\nu_1(f)$ and $\beta(f)$. However, our current experimental results based on linear chirps indicate that the actual perturbation of the pulse modulation functions in time domain are approximated to a significant degree.

Accordingly, the influence of $\beta(f)$ is best seen in an accelerated rotating frame synchronized to the unperturbed phase modulation function, as illustrated in Fig. 1b. If the pulse is not subject to any phase shift β, the observer frame remains in phase with the effective field $\boldsymbol{\omega}_{\mathrm{eff}}$. The trajectory of $\boldsymbol{\omega}_{\mathrm{eff}}$ is therefore entirely in the x-z plane and the polar velocity ω_α constitutes the angular rate of change $\omega_\theta = d\theta/dt$ of the effective field. Consequently, any phase shift $\beta(f)$ moves $\boldsymbol{\omega}_{\mathrm{eff}}$ azimuthally off the x-z plane and reduces the adiabaticity by enhancing $|\omega_\theta|$, which becomes the root sum over the squared polar and azimuthal velocities, ω_α and ω_β.

Note that the construction described above is valid for any phase modulation function. For a linear chirp, the velocities at the time when a particular isochromat is on resonance with the instantaneous frequency f_{i} are

$$\omega_\alpha = \frac{\Delta f}{\nu_1(f_{\mathrm{i}})t_{\mathrm{p}}} \tag{3}$$

$$\omega_\beta = d\beta/df\,\frac{\Delta f}{t_{\mathrm{p}}} = -2\pi\tilde{\tau}_{\mathrm{g}}(f_{\mathrm{i}})\frac{\Delta f}{t_{\mathrm{p}}} \tag{4}$$

where $\tilde{\tau}_{\mathrm{g}}(f)$ denotes variations in the group delay with frequency and is related to the group delay, which is the negative phase-derivative with respect to angular frequency, via $\tilde{\tau}_{\mathrm{g}}(f) = \tau_{\mathrm{g}}(f) - \tau_{\mathrm{g}}(0)$. Neglect of overall pulse delays, $\tau_{\mathrm{g}}(0)$, prevents the unphysical situation of adiabaticity reduction due to frequency-independent delays in the excitation chain. However, any group delay *variations* undergone by the pulse prior to spin excitation persist and degrade the adiabaticity.

Under idealized conditions, the excitation chain operates linearly and its net excitation bandwidth is defined by the resonator. In this case, the perturbations of the intended pulse modulation functions are completely described by the linear transfer function