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Wideband frequency-swept excitation in pulsed EPR spectroscopy

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ABSTRACT

Excitation of electron spins with monochromatic rectangular pulses is limited to bandwidths that are smaller than the spectral widths of most organic radicals and much smaller than the spectral widths of transition and rare earth metal ions. With frequency-swept pulses, bandwidths of up to 800 MHz have previously been attained for excitation and detection of spin packets at frequencies of about 9.6 GHz and bandwidths of up to 2.5 GHz in a polarization transfer experiment at frequencies of about 34 GHz. The remaining limitations, mainly due to resonator bandwidth and due to pulse length restrictions are discussed. Flip angles for state-space rotations on passage of a transition can generally be computed from the critical adiabaticity by the Landau-Zener-Stückelberg-Majorana expression. For hyperbolic secant pulses, the Demkov-Kunike model describes excitation for spin packets within and outside the sweep range. Well within the sweep range, the Bloch-Siegert phase shift is proportional to critical adiabaticity to a very good approximation. Because of the dependence of both flip angle and coherence phase on critical adiabaticity, it is advantageous to use pairs of amplitude and frequency modulation functions that provide such offset-independent adiabaticity. Compensation for the resonator response function should restore offset-independent adiabaticity. Whereas resonance offsets and Bloch-Siegert phase can be refocused at certain pulse length ratios, phase dispersion in coupled spin systems cannot generally be refocused. Based on the bandwidth limitations that arise from spin dynamics, requirements are derived for a spectrometer that achieves precise spin control over wide bands. The design of such a spectrometer and hardware characterization by EPR experiments are discussed.

1. Introduction

The excitation bandwidth of monochromatic rectangular pulses in electron paramagnetic resonance (EPR) spectroscopy is of the order of 100 MHz. Very few paramagnetic species have spectra narrower than that. For example, spectral width for the widely used nitroxide spin labels ranges from about 180 MHz at X-band frequencies (~ 9.6 GHz) to about 450 MHz at W-band frequencies (~ 94 GHz). Spectra of triplet states of organic molecules, of transition metal complexes, and of rare earth ion complexes are usually wider than 1 GHz. Therefore, most experiments in pulse EPR spectroscopy are geared to the regime where only part of the spin packets of an inhomogeneously broadened EPR line is excited [1].

Such experiments have severe shortcomings. First, sensitivity may be lost by detecting the signal from only a fraction - sometimes a very small fraction - of all spin packets. In particular this applies to experiments where the excitation bandwidth could be increased without increasing the noise bandwidth of detection, such as electron spin echo envelope modulation (ESEEM) spectroscopy, its two-dimensional form of HYSCORE, electron-nuclear double resonance (ENDOR), and all pulsed electron-electron double resonance (ELDOR) experiments. Second, two transitions can be correlated in an experiment only if both of them are within the excitation bandwidth. Although ELDOR schemes enable correlation beyond the bandwidth of pulses at a single frequency, such approaches come at the expense of further sensitivity loss. This limitation also applies to ESEEM experiments, where the detected nuclear frequencies are differences of two transitions that must be excited in the same experiment. Third, spin packets at resonance offsets of the order of the excitation bandwidth of rectangular pulses follow spin dynamics that is not usually intended. The fraction of such spin packets is relatively large if the spectral line width is much larger than the excitation bandwidth. Therefore, spin control is much less precise in EPR spectroscopy than in NMR spectroscopy. As a result, each additional pulse causes sensitivity loss and often introduces coherence transfer pathways that lead to unwanted signal contributions. Such contributions cannot always be removed by phase cycling. Accordingly, multi-pulse techniques

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[2], which are prominent in NMR, are rarely used in EPR spectroscopy.

Related problems in broadband heteronuclear decoupling in liquid-state NMR, magnetic resonance imaging (MRI), and solid-state NMR of quadrupole nuclei have been addressed by application of frequency-swept pulses [3–7]. During the past decade or so, arbitrary waveform generators (AWGs) have become sufficiently fast to cover the full bandwidth of a few Gigahertz of microwave (MW) components in the pulse EPR spectrometers that are used for application work in the life sciences, in catalysis, and in materials research. Recently, the first commercial AWG setup with 1.6 GSa/s clock rate has been introduced by Bruker. Via Bruker's intermediate MW frequency concept, this setup allows for EPR experiments at S band (~ 4 GHz), X band, Q band (~ 34 GHz), W band, and in the 263 GHz mm band. During the past few years the new opportunities due to shaped-pulse excitation with AWGs have been explored mainly by groups who worked with home-built setups [8–24]. This work has revealed a great potential for frequency-swept excitation in pulsed EPR applications, but also some limitations that need to be considered in pulse sequence and spectrometer design. Here we present a critical review of these results and fill some gaps in previous description of spin dynamics during frequency-swept pulses.

The limitations of excitation by shaped pulses depend strongly on the type of spin system. Complications arise in multi-level systems and, in particular, for distributions of spin Hamiltonian parameters. Unfortunately, both these complications are typical for pulsed EPR applications. Many of these applications require separation of hyperfine or electron-electron dipole-dipole couplings from other interactions in macroscopically disordered systems. In our discussions, we always have such applications in mind.

This perspective article is structured as follows. First we consider passage of a two-level system, i.e., excitation of a single transition during a frequency sweep. We discuss the concept of critical adiabaticity Q_{crit}, the dependence of an equivalent flip angle on Q_{crit} for linearly frequency-swept (chirp, WURST) and hyperbolic secant (HS) pulses, the compensation of the resonator response function that is necessary for attaining wideband uniform excitation of spin packets, and Bloch-Siegert phase shifts that arise during frequency-swept pulses. We then turn to passage of multi-level systems. In such systems, longitudinal and transverse interference effects arise in passage of several transitions that are connected by shared energy levels. The three-level system is treated separately, as it still allows for an analytical description of the outcome of a linear or HS frequency sweep. We further discuss the ladder topology, as it is encountered for electron group spins $S > 1/2$, and systems where several energy levels are connected by a loop of allowed transitions.

Since most pulsed EPR experiments require echo formation, we then turn to refocusing of the phase dispersion induced by a frequency sweep and of the phase dispersion caused by the Bloch-Siegert effect. In multi-level systems, additional phase dispersion may arise from couplings and we discuss under which conditions such phase dispersion can be refocused.

We then consider additional limitations that are not caused by spin dynamics, but are rather imposed by instrumentation. First, we inquire how well hardware must be characterized in order to achieve reasonably precise spin control within the spin dynamics limits and how spurious excitation frequencies can be avoided. We then discuss what detection bandwidth can be achieved at the current level of spectrometer technology and point out that unobserved spins can be excited over a much wider band. From these considerations we derive a spectrometer design specification. We conclude with a short assessment of the new possibilities and open questions.

2. Passage of the two-level system

2.1. Critical adiabaticity

Any real band-limited waveform $y(t)$ can be expressed in terms of an amplitude modulation (AM) function $v_1(t)$ and a frequency modulation (FM) function $f(t)$ [25]

$$y(t) = v_1(t)\cos\left(2\pi\int_0^t f(t')\mathrm{d}t' + \phi_0\right), \tag{1}$$

where ϕ_0 is the initial phase. We define a frequency-swept pulse as a waveform with a monotonous FM function. Therefore, any transition between two levels with a resonance frequency $\omega_0/2\pi$ that is within the frequency band $[f_{min}, f_{max}]$ is passed exactly once. For the moment we consider a two-level system, i.e., only one transition in the spin system is passed.

The situation is most easily pictured in a frame that always rotates with the instantaneous frequency $f(t)$ (Fig. 1) [26]. In such a frame the microwave field, represented by a vector $\vec{\omega}_1$ of length $2\pi v_1(t)$, is at a fixed angle ϕ_0 in the xy plane, i.e., along the x axis for $\phi_0 = 0$. The effective field $\vec{\omega}_{eff}(t)$ seen by the spin changes its amplitude and direction due to the variation of the resonance offset $\Delta\omega(t) = \omega_0 - 2\pi f(t)$ and of the amplitude $\omega_1(t) = 2\pi v_1(t)$.

We now consider a sweep that starts far below resonance ($\Delta\omega \gg \omega_1$) with the magnetization vector along the direction z of the static magnetic field. If the change of the orientation of the effective field is slow compared to its amplitude, the magnetization vector closely follows the effective field. For a sweep ending up far above resonance, the effective field and the magnetization vector end up along $-z$. This is called adiabatic passage and inverts the spin state. Adiabaticity of the resonance passage can be quantified as [27]

$$Q(t) = \frac{\omega_{eff}}{|\mathrm{d}\theta/\mathrm{d}t|} = \frac{\sqrt{\Delta\omega^2 + \omega_1^2}}{|\mathrm{d}\theta/\mathrm{d}t|} \tag{2}$$

$$= \frac{\left(\omega_1^2 + \Delta\omega^2\right)^{3/2}}{|\omega_1(\mathrm{d}\Delta\omega/\mathrm{d}t) - \Delta\omega(\mathrm{d}\omega_1/\mathrm{d}t)|}, \tag{3}$$

with $Q(t) \gg 1$ throughout the pulse providing a good approximation to an adiabatic sweep. An adiabatic sweep generally inverts the spin state, even if this state is not an eigenstate of $\hat{S}_z$. In other words, adiabatic passage corresponds to a state-space rotation by flip angle π around an axis in the xy plane. Accordingly, coherence inversion, understood as exchange of the single elements $\hat{S}^+$ and $\hat{S}^-$ of the density matrix, is also effected if $Q \gg 1$ during the whole sweep. Maximum coherence generation from polarization requires a diabatic passage with $Q < 1$ (*vide infra*).

For arbitrary FM and AM functions, spin packets with different resonance frequency ω_0 experience a different time dependence of adiabaticity $Q(t)$ and thus, unless $Q(t) \gg 1$, different spin state transfer. This is detrimental to uniform broadband excitation and to precise spin control. For some pairs of AM and FM functions, on-resonant adiabaticity at $\Delta\omega(t_0) = 0$, i.e., at the time t_0 of passage, is independent of ω_0. Such frequency sweeps with *offset independent adiabaticity* (OIA) achieve the same transfer for all spin packets within the excitation band [28]. For a given spin packet, adiabaticity Q still varies with time during the sweep and attains a minimum on passage ($\Delta\omega = 0$). This minimum value is critical for transition probability [27] and is thus called critical adiabaticity Q_{crit} [16]

$$Q_{crit} = Q(t_0) = \frac{\omega_1(t_0)^2}{|\mathrm{d}\theta/\mathrm{d}t|_{\Delta\omega=0}} \tag{4}$$

By inserting $\Delta\omega = 0$ into Eq. (3) we have