Coherence Transfer by Passage Pulses in Electron Paramagnetic Resonance Spectroscopy

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Supplementary Information

1. Phase extraction and inhomogeneity

This section describes the extraction of the linear scaling factor $s_Q$, which relates adiabaticity to phase. The extraction requires quantification of critical adiabaticity $Q_{crit}$ as well as of the dynamical phase shift by the refocusing pulse. In addition to $s_Q$ extraction, supplementary information on $B_1$ inhomogeneity is provided.

The dynamical phase shift was separated from other phase shifts by taking the phase difference between experiments with upward and downward sweeps. The two-dimensional dynamical phase profile obtained with $B = 0.8$ GHz and $t_p = 800$ ns is shown in Fig. S1a. The relationship between $s_Q$ and $\Omega$ shown in the main text was calculated from this profile. The phase contribution which increases with $|\Omega|$ can be readily identified, as for instance by the shape defined by the yellow regions. Note that at higher $Q_{crit}$, as for instance in the turquoise regions, an asymmetry with respect to $\Omega$ can be observed. This is related to quantification of $Q_{crit}$ for $\Omega \neq 0$ and is explained further below.

Fig. S1b shows experimental phases versus $\Omega$ for upward (orange) and downward (blue) sweeps with $Q_{crit} = 1$. The two curves were corrected by a linear phase profile. Such a correction is not necessary when taking the phase difference. Extraction of the phase difference from primary phase data solely requires proper phase unwrapping (removal of discontinuities). Phase contributions other than the dynamic phase are obtained by taking half the sum of the upward and downward sweep data, as indicated by the black curve in Fig. S1c. The gray curve underneath shows an approximation to the overall instrumental phase of the spectrometer, which was calculated from the frequency response $\nu_1(\Omega)$ of the spectrometer’s excitation arm [1].

The above described separation between the dynamic phase due to the refocusing pulse and the instrumental phase is not perfect. The dashed green vertical line in panels (b) and (c) indicates one apparent feature in the instrumental phase. (d) Normalized frequency responses $\nu_1(\Omega)$ obtained at a reduced drive level [1, 2]. Only if instrumental phase perturbations are larger than on the order of 20 degrees (data not shown), the influence on $s_Q$ is negligible. Note that the phase lag related to the sweep direction of the chirp pulse is a limitation for pulse compensation assuming instantaneous phase response (zero phase lag) [2].
 errors from neglect of phase lag, compensation is successful. Here, the instrumental phase perturbation was small enough to exclude an influence on adiabaticity.

Quantification of the critical adiabaticity $Q_{\text{crit}}$ requires knowledge of the amplitude-dependent frequency response $v_1(\Omega, a_{S})$ of the spectrometer’s excitation arm, where $a_{S}$ is the amplitude of the digital pulse synthesized by the AWG. We have used the frequency profile obtained with the digital amplitude $a_{S}^{\text{ref}}$ of a refocusing pulse with $Q_{\text{crit}} = 1$ to calculate offset independent adiabaticity pulses [2]. This procedure yielded the constant critical adiabaticity $Q_{\text{crit}}(\Omega)$ at the specific digital amplitude $a_{S}^{\text{ref}}$. Adiabaticity factors at different amplitudes $a_{S}$ were obtained by multiplication with $v_1(a_{S})^2/v_1(a_{S}^{\text{ref}})^2$, where $v_1(a_{S})$ was experimentally obtained at $\Omega = 0$. While this is an accurate description of $v_1(\Omega, a_{S})$ at $\Omega = 0$, it does not necessarily hold for $\Omega \neq 0$: The normalized $v_1(\Omega)$ profile at $a_{S}^{\text{ref}}$ is shown in green in Fig. S1d, together with a profile obtained at full-scale digital amplitude (violet). For offsets $\Omega < 0$, the two profiles are comparable, such that adiabaticities for negative offsets are reasonably accurate. However for offsets $\Omega > 0$, the full-scale profile had reduced relative field strength $v_1$, such that adiabaticities at positive offsets and large $a_{S}$ were overestimated. The largest digital amplitude $a_{S}$ in the experiment was 0.4 and resulted in an adiabaticity factor of 8.9.

The dependence of the dynamic phase on $Q_{\text{crit}}$ for different offsets $\Omega$ is shown in Fig. S2a. At $\Omega = 0$ (dashed curves), the experimental phase (blue underneath red) fits well to a linear relationship (red). The same applies for $\Omega/(2\pi) = -0.35$ GHz (solid blue underneath solid red). For $\Omega/(2\pi) = 0.35$ GHz, however, the experimentally obtained dynamic phase is not linear. This non-linearity is due to the overestimation of large adiabaticities at positive offsets (see above). To avoid an influence on $s_{Q}$, quadratic functions were fitted to experimental data and the linear component was used as $s_{Q}$. In doing so, non-linear curves were automatically linearized at small $Q_{\text{crit}}$ values, which were the most accurate for all offsets $\Omega$. As seen in Fig. 4a in the main text, the resulting $s_{Q}(\Omega)$ profile shows wiggles, which are not reproduced in the simulation. These wiggles are probably also due to $Q_{\text{crit}}$ quantification. Within the central frequency slice $|\Omega| < 100$ MHz, the wiggles in experimental $s_{Q}$ values result in a variation of dynamic phases by roughly ±1% (see $s_{Q}$ values below).

For reference, the simulated dependence of $\phi_{0}$ on $Q_{\text{crit}}$ (blue) for $t_{p} = 800$ ns and $B = 0.8$ GHz (dotted lines) as well as $B = 1.6$ GHz (solid lines) is shown in Fig. S2b. Both curves show reasonable agreement to a linear relation (red). In the simulation with $B = 0.8$ GHz, the reduction to $\tilde{\tau}_{1}$ after the first pulse (see main text) was omitted. Accordingly, small $Q_{\text{crit}}$ have a non-linear contribution due to incomplete coherence inversion (see inset). When extracting $s_{Q}$ from simulated data including the reduction to $\tilde{\tau}_{1}$, a slight dependence on the chirp bandwith $B$ was observed: $s_{Q} = -3.34$ and $s_{Q} = -3.74$ for $B = 0.8$ GHz and $B = 1.6$ GHz, respectively. The experimental value for $s_{Q}$ with $B = 0.8$ GHz varied between -3.1 and -3.18 within the central frequency slice $|\Omega| < 100$ MHz due to the wiggles in $s_{Q}(\Omega)$. For the discussion of inhomogeneity below, we will assume a value of -3.5 for $s_{Q}$.

As mentioned in the main text and pointed out previously [3], inhomogeneity in $B_{1}$ reduces the refocusing efficiency. Using $s_{Q}$, the refocusing efficiency $R_{\text{inh}}$ for inhomogeneous $B_{1}$ distribution can be written as spatial integral

$$R_{\text{inh}} = \iint_{D} \cos(s_{Q} \cdot Q_{\text{crit}}(x) - \phi_{\text{max}}) \, dx$$

where $D$ is the spatial extent of the sample, $Q_{\text{crit}}(x)$ the spatial variation in $Q_{\text{crit}}$ due to $B_{1}$ inhomogeneity, and $\phi_{\text{max}}$ the phase which maximizes the integral. As an example, we have assumed a uniform distribution of $B_{1}$ within ±10% and calculated $R_{\text{inh}}$ as a function of $Q_{\text{crit}}$ (dashed red line in Fig. S2a). Combination with the transfer efficiency $T$ (dashed blue line) results in optimum refocusing (black) at reduced critical adiabaticity $Q_{\text{crit}}$. The influence of the inhomogeneity on the optimum $Q_{\text{crit}}$ for refocusing is shown in Fig. S2d. The influence of inhomogeneity on the transfer efficiency $T$ has not been taken into consideration.

Experimentally, the distribution in $B_{1}$ may not be uniform. Nev-
ertheless, one can expect a similar behavior for different distributions: The quadratic dependence of $Q_{\text{crit}}(x)$ on $B_1$ leads to a monotonic increase of the spatial dynamic phase shift when increasing $B_1$, thus reducing $R_{\text{inh}}$ when increasing $Q_{\text{crit}}$. It is worth mentioning that a linear scaling of the spatial phase shift with $B_1$ [3], and therefore a square-root dependence on $Q_{\text{crit}}$, cannot change the refocusing efficiency $R_{\text{inh}}$ when increasing $Q_{\text{crit}}$. For a spatial distribution $B_1(x) = B_1 \cdot (1 + \Delta(x))$, the variation of spatial phase shift would remain the same for any $B_1$.

Another experimental aspect is the combined influence of dynamic phases and instrumental phases. Importantly, the phases which depend on frequency offset $\Omega$ may not lead to interference in FT spectra, as long as the phase shifts across homogeneous linewidths are negligibly small. The spatial dynamic phases due to inhomogeneity, however, always interfere, unless one explicitly compensates dynamic phases with the AB−STRUSE scheme [3].

The influence of $Q_{\text{crit}}$ inhomogeneity on the transfer efficiency $T$ is discussed in the main text. In addition to the results shown in the main text in Fig. 2, Fig. S3 shows the inversion $I$ for a 2-mm diameter Herasil rod with height of 4 mm. The relaxation times of this sample were comparable to the ones of the extended height 2-mm diameter Herasil sample. However, the sample shown here has less contributions from fringe fields of the resonator. Accordingly, a better fit between experiment and simulation is achieved.

![Figure S3: Inversion of the echo signal (black) in a 2-mm diameter Herasil rod with 4 mm height and simulation with $T_\text{s} = 1 \mu s$ (red). The dashed green lines are the predictions due to Eq. 5 in the main text. (a) Original data. (b) Semi-logarithmic plot.](image)

In our simulated data, the difference $\Delta \phi$ of the dynamical phase from the dynamical phase at the center of the sweep $\phi_0$ exhibits a rather nice linear dependence on critical adiabaticity $Q_{\text{crit}}$ for moderate offsets $\Omega$ from the center of the sweep, as is seen in Fig. S4a for resonance offsets $\Omega = -0.6$ GHz and $\Omega = 0.6$ GHz in a sweep from -0.8 GHz to 0.8 GHz. The slope of the linear function differs slightly between negative and positive resonance offsets. For offsets closer to the edge of the sweep ($\Omega = -0.75$ GHz and $\Omega = 0.75$ GHz), significant deviations from the linear dependence are observed at small $Q_{\text{crit}}$.

2. AWG Spectrometer

All chirp echo experiments were performed on a home-built AWG spectrometer [1]. In order to increase the sensitivity of the spectrometer, the receiver was extended by a switchable variable-gain amplifier. A schematic of the entire spectrometer is shown in Fig. S5. Only the components inside the orange box differ from the previous description in [1]. The variable-gain amplifier was assembled out of $A_2$ and $R_1$ (see Table S1). Two switches $S_2$ and $S_3$ are used to activate this amplifier during detection. During excitation, the two switches are connected via a fixed attenuator (tiny dashed black line). In this way, one has the ability to observe the leakage of excitation pulses with the ADC at an adequate level. The ADC itself was upgraded to 2 GS/s sampling rate and the high-pass filter $F_3$ was installed to reject noise in the first Nyquist zone from 0 to 1 GHz. Almost all phase measurements showed artifacts at the crossing of the Nyquist zone at 1 GHz, which corresponds to a microwave frequency of 9 GHz and to a frequency offset $\Omega = -0.25$ GHz. For proper synchronization between the AWG and the ADC, the sampling rate of the AWG needed to be changed from 12 GS to 8 GS/s.

Note that at the time of writing, $L_1$ has been placed in front of $S_1$ to avoid damage of the protection switch $S_1$. In fact, ultra-wideband excitation often leads to a considerable amount of power to be blocked by the receiver.

![Figure S5: Layout of the spectrometer showing the main signal path (dark gray) and control triggers (light gray). The orange box indicates the changes made with respect to the layout shown previously [1]. The added components are listed in Table S1.](image)

3. Generation of nuclear coherence by one or two passage pulses

For an electron-nuclear spin system with $A, B \ll \omega_0$ a single passage pulse generates only a small fraction of nuclear coherence, independently of critical adiabaticity (Fig. S6(A)). Coher-
Supplementary Information

<table>
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<tr>
<th>Label</th>
<th>Device</th>
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<tbody>
<tr>
<td>$S_2$, $S_3$</td>
<td>Minicircuits ZASWA-2-50DR</td>
</tr>
<tr>
<td>$A_e$</td>
<td>Herotek AF01-6362513B</td>
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<td>$R_1$</td>
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<td>$F_3$</td>
<td>Minicircuits SHP-600+ or SHP-900+</td>
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<tr>
<td>ADC</td>
<td>SP Devices ADQ412-4G PCIe</td>
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Table S1: Component listing for Figure S5

ence with much larger amplitude is generated on one of the forbidden electron-nuclear transitions (Fig. 7 of the main text). If such a passage pulse, performed at optimum $Q_{\text{crit},1}$ for generating electron-nuclear coherence and phase cycled $[+ (+x) - (-x)]$, is followed by a second passage pulse, the electron-nuclear coherence (red dotted line in Fig. S6) is transferred to nuclear coherence on both transitions (blue solid and dotted lines) with maximum transfer being achieved at $Q_{\text{crit},2} = 2 \ln(2)/\pi$ (vertical black dotted line). At larger $Q_{\text{crit},2}$, nuclear coherence amplitude decreases and amplitude of coherence on the other forbidden electron-nuclear transition increases. In the adiabatic limit at very large $Q_{\text{crit},2}$ the transfer from one forbidden transition to the other forbidden transition is complete, which is the same result as for a non-selective $\pi$ pulse acting on the same spin system in the same initial state.

References


Figure S6: Coherence generation and transfer in a system consisting of an electron spin $S = 1/2$ and a nuclear spin $I = 1/2$ with nuclear Zeeman frequency of $\nu_I = -51.66$ MHz, secular hyperfine coupling $A/(2\pi) = 6.43$ MHz and pseudo-secular hyperfine coupling $B/(2\pi) = 3.37$ MHz. (a) Zoomed view of coherence amplitudes after a passage pulse of duration $t_p = 240$ ns with $B/(2\pi) = 0.5$ GHz starting from thermal equilibrium. Electron coherence on allowed transitions is depicted by green lines $[(1 \leftrightarrow 3)$ solid, $(2 \leftrightarrow 4)$ dotted], coherence on forbidden electron-nuclear transitions by red lines $[(2 \leftrightarrow 3)$ solid, $(1 \leftrightarrow 4)$ dotted], and nuclear coherence by blue lines $[(1 \leftrightarrow 2)$ solid, $(3 \leftrightarrow 4)$ dotted]. The vertical black dotted line denotes $Q_{\text{crit}} = 2 \ln 2/\pi$ and the horizontal black dotted line the amplitude of coherence on the two forbidden transitions after an ideal $\pi/2$ pulse. Compare to Figure 7 in the main text. (b) Coherence amplitudes after a second passage pulse of duration $t_p = 240$ ns with $B/(2\pi) = 0.5$ GHz with the initial state corresponding to the situation with maximum coherence on transition $(1 \leftrightarrow 4)$ after the first pulse ($Q_{\text{crit},1} = 5.75$), assuming $[+ (+x) - (-x)]$ phase cycling of the first pulse. The vertical black dotted line denotes $Q_{\text{crit},2} = 2 \ln 2/\pi$ and the horizontal black dotted line the amplitude of nuclear coherence at anti-blindsots of a $\pi/2 - \tau - \pi/2$ nuclear coherence generator realized with ideal pulses. Color code is the same as in panel (a).