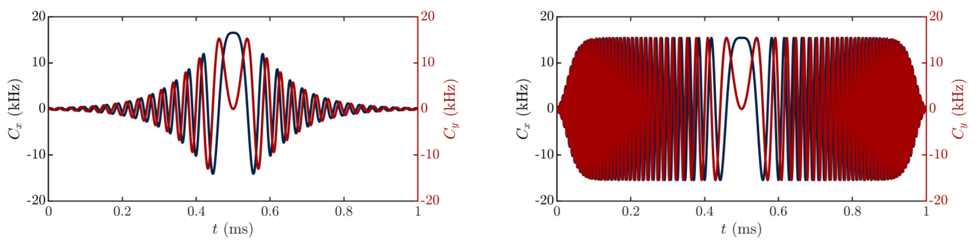
Improved design of frequency-swept pulse sequences

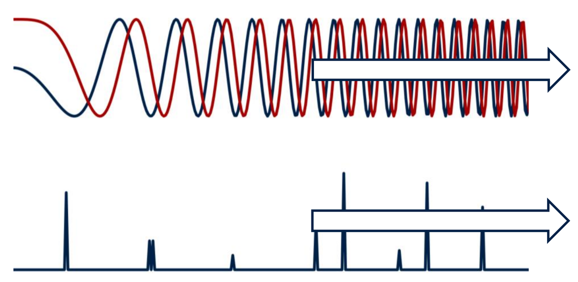
Jean-Baptiste Verstraete, Mohammadali Foroozandeh.
Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, UK.

1. Frequency-swept pulses

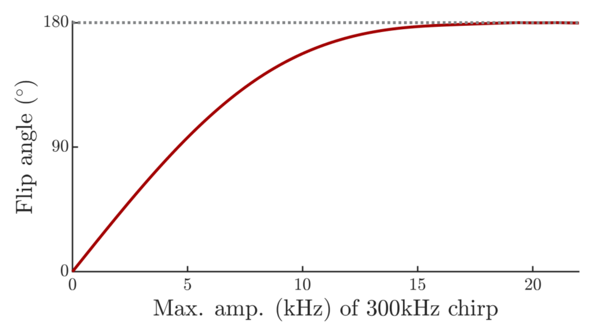
Common shapes
- Hyperbolic Sechant (HS): high selectivity (*left*)
- Chirp: large bandwidths (*right*)



Properties
- **Broadband**



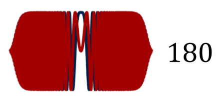
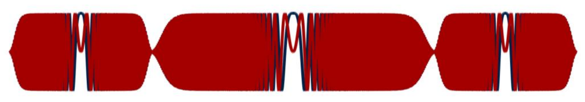
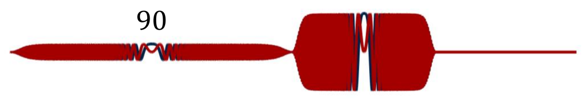
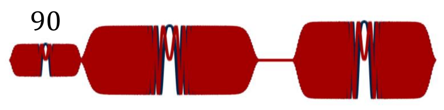
- **Adiabatic (B_1-tolerant)**

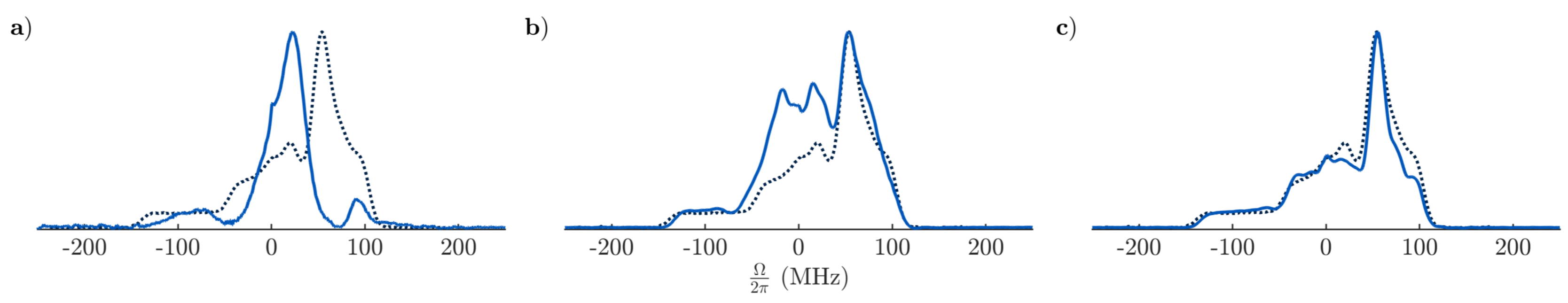


2. Basic blocks

Since FS pulses act on different frequencies at different times, we generally need more than one pulse to refocus the magnetisation.

The instantaneous flip approximation is used to calculate the duration of the pulses and their delays.

Scheme name	Application	B_1-tolerance	Representation with chirps
Single FS pulse	Inversion	Very high	
Double FS pulse	Compensated refocusing	Very high	
Triple FS pulse	Refocusing	Very high	
Kunz/ Böhlen-Bodenhausen (KB)	Excitation	Low	
ABSTRUSE/ CHORUS	Excitation	High	

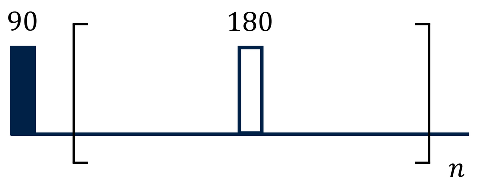


EPR spectra of bisnitroxide, a) Hahn echo with hard pulse, b) KB and c) CHORUS excitation [1], compared to the reference field sweep (dotted)

3. CHORUS-CPMG

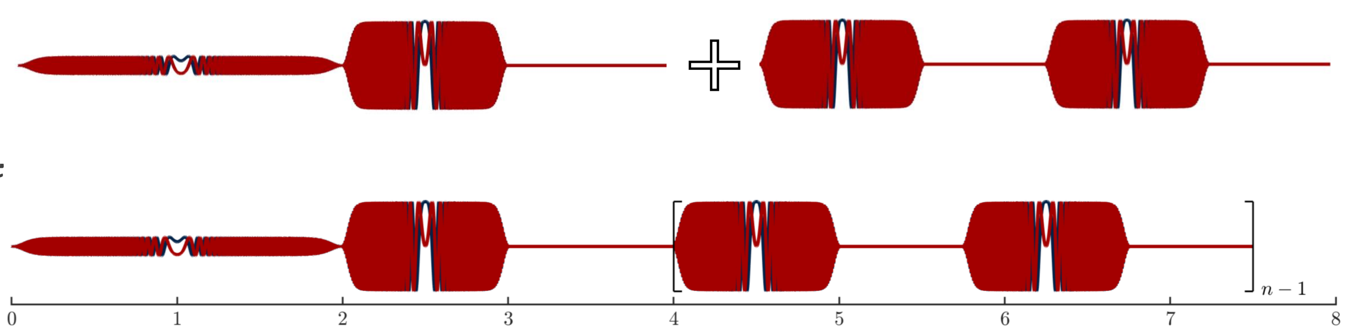
One can create new sequences by combining basic blocks. We illustrate this using a broadband, B_1-tolerant CPMG: CHORUS-CPMG.

- Conventional sequence

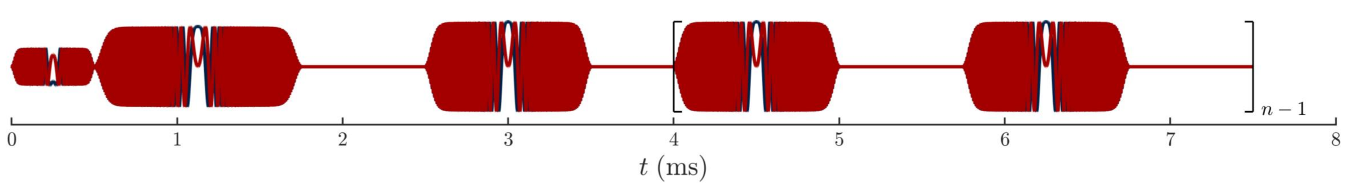


⇒ let's make a broadband version

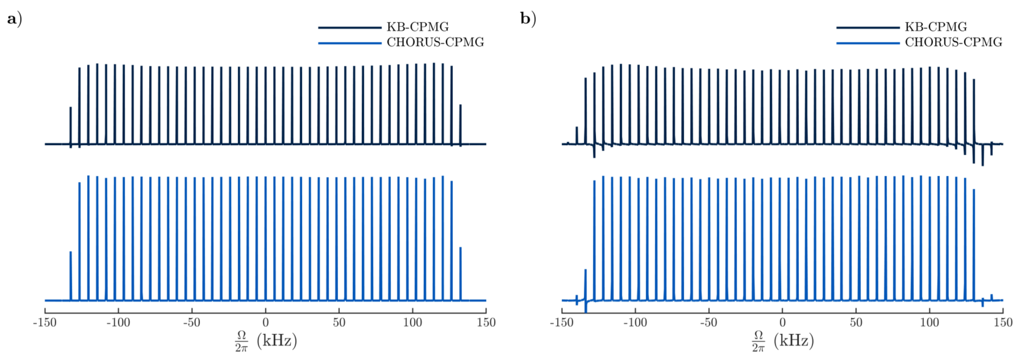
- KB-CPMG
  - Present in the literature but B_1-sensitive



- CHORUS-CPMG



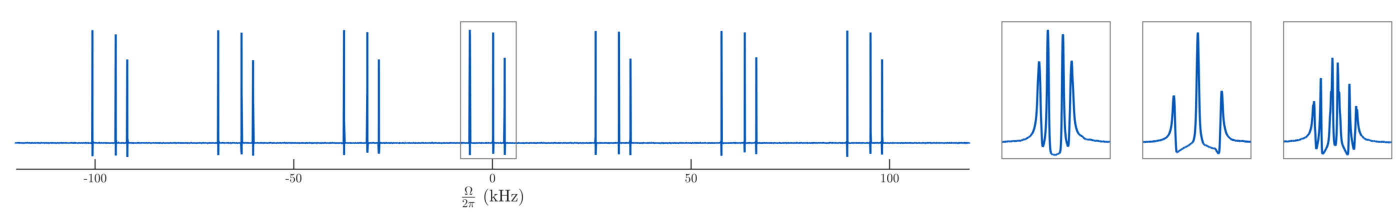
- Better sensitivity and phase stability



a) Simulated and b) experimental ¹H excitation profiles for both CPMGs with n=7 (at 400MHz Larmor frequency)

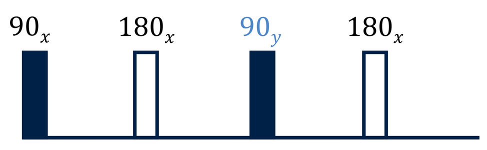
4. Suppression of J-modulation

Long sequences lead to phase distortion due to evolution of J-coupling. We present a broadband perfect echo sequence, PROCHORUS, to address this problem.



J-modulation in ¹⁹F spectra of pentaflurorobenzene using 6ms CHORUS

- Perfect echo **suppresses J-modulation** thanks to an additional quadrature 90° pulse [3].



- How to make frequency-swept version (PeRfect echO CHORUS)?

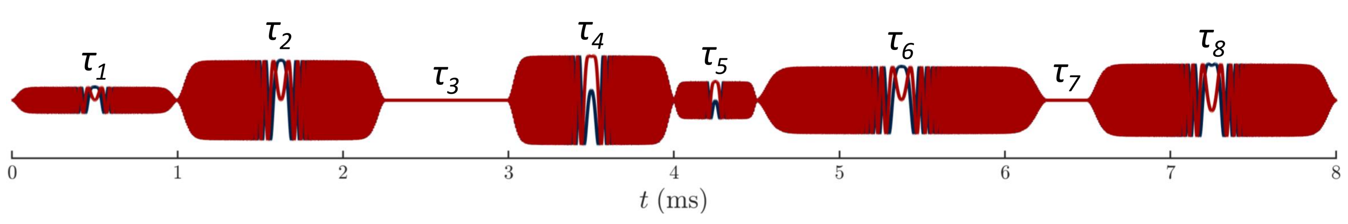
⇒ Refocusing conditions for an arbitrary offset in 3 equations:

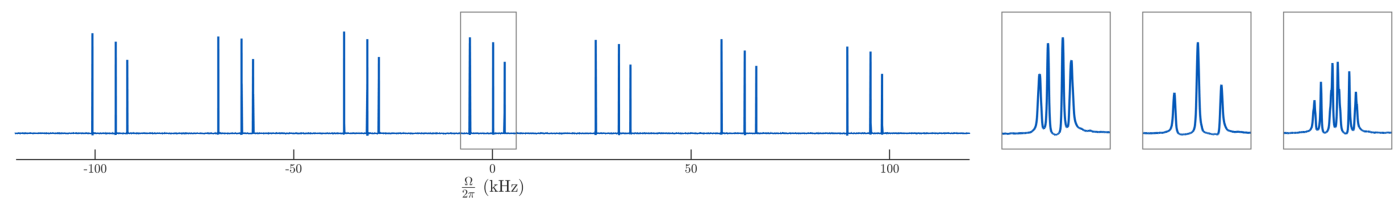
CS refocusing (CHORUS-like)

$$\begin{pmatrix} 1-\alpha & 2\alpha-1 & -1 & 1-2\alpha & \alpha & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1-\alpha & 2\alpha-1 & -1 & 1-2\alpha \\ 1-\alpha & 1 & 1 & 1 & 2\alpha-1 & -1 & -1 & -1 \end{pmatrix} \begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \\ \tau_4 \\ \tau_5 \\ \tau_6 \\ \tau_7 \\ \tau_8 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

J-coupling evolution (either side of the 90_y)

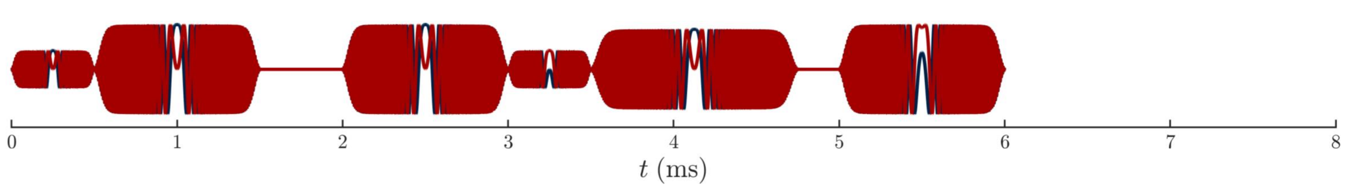
- Exact solution

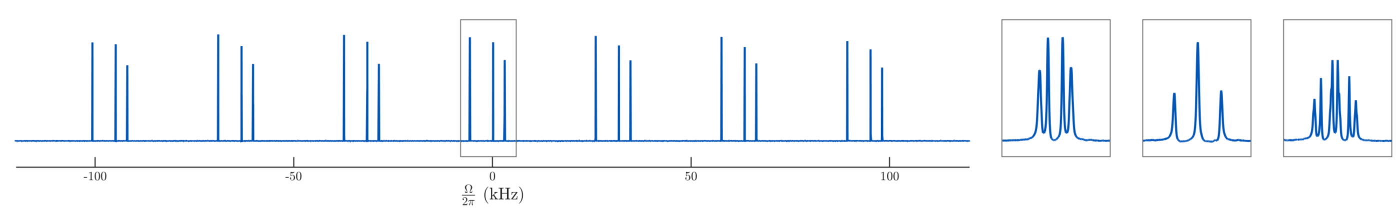




Suppression of J-modulation with 8ms uncompressed PROCHORUS

- Approximation

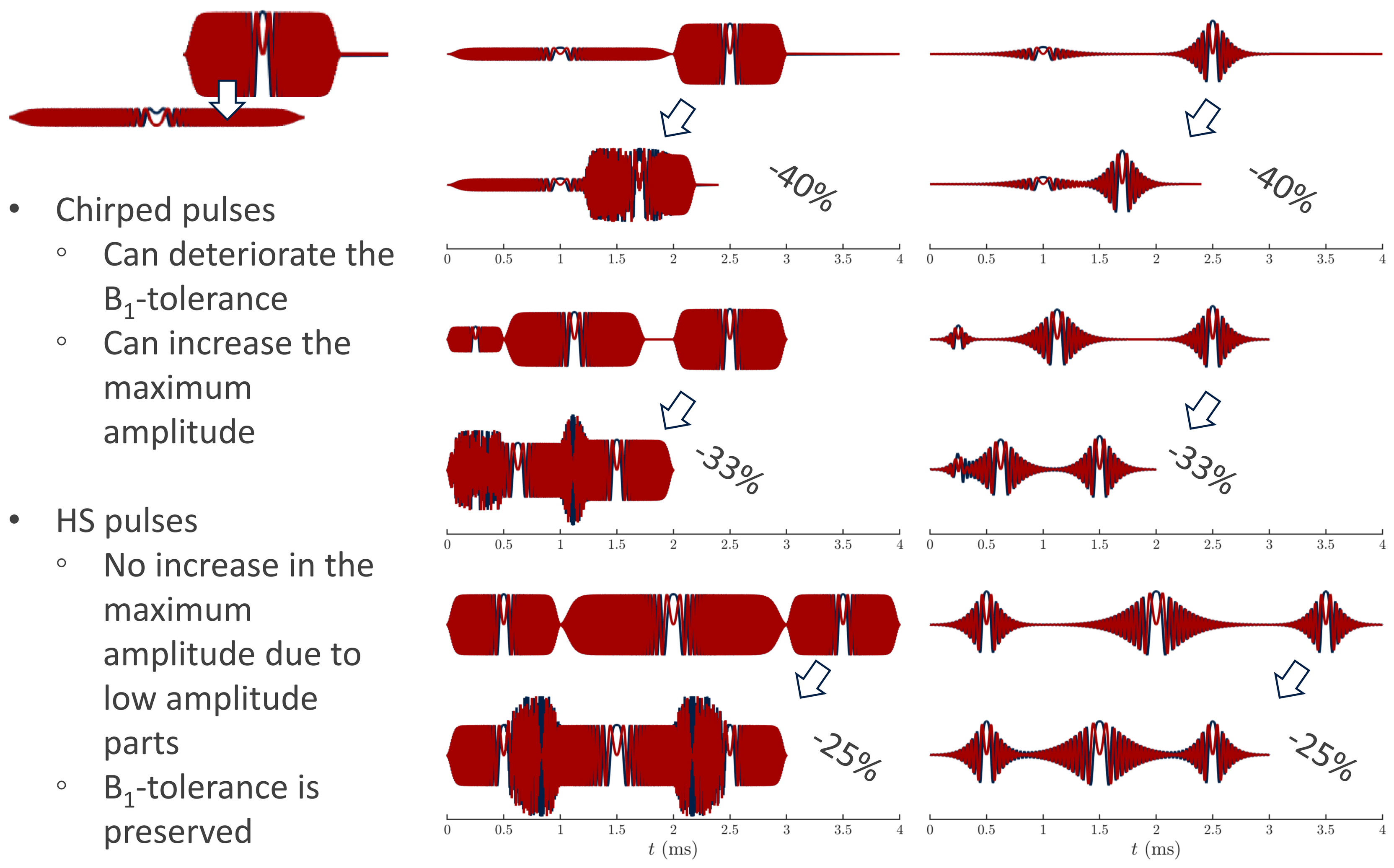




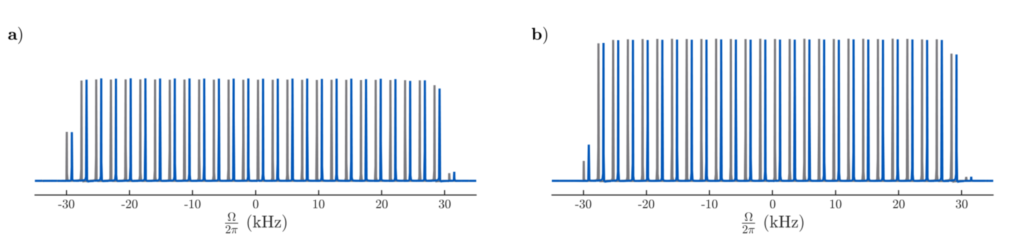
Suppression of J-modulation with 6ms compressed PROCHORUS

5. Pulse superposition

First proposed in 1993 [4] to reduce the duration of a Böhlen-Bodenhausen scheme but can be applied to other sequences.



- Chirped pulses
  - Can deteriorate the B_1-tolerance
  - Can increase the maximum amplitude
- HS pulses
  - No increase in the maximum amplitude due to low amplitude parts
  - B_1-tolerance is preserved



Experimental ¹H excitation profiles for normal (grey) and superposed (blue, +0.8kHz shift) a) KB and b) ABSTRUSE (at 400MHz Larmor frequency)

References
[1] J.-B. Verstraete, W. K. Myers, M. Foroozandeh. J. Chem. Phys. 154, 094201 (2021).
[2] K. Takegoshi, K. Ogura, K. Hikichi. J. Magn. Reson. (1969) 84, 611-615 (1989).
[3] V. L. Ermakov, G. Bodenhausen. Chem. Phys. Lett. 204, 375-380 (1993).
[4] J.-B. Verstraete, M. Foroozandeh. J. Magn. Reson., 107146 (2022).

Acknowledgements
- We thank the Royal Society and the EPSRC DTP for their support.

Poster download & links

Design your own frequency-swept pulse sequences

- Free open-source pulse generation and simulation toolboxes
  - MRChirpLab: MATLAB with fast simulation relying on Rodrigues formula
  - mrpypulse: Python version(less complete)
- JMR publication with this poster's new sequences [5]