Spinach A Fast and General Spin Dynamics Simulation Library

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At the energies commonly encountered in chemical systems, the currently established models of reality (Dirac-Schrodinger, Quantum Field and General Relativity equations) are essentially exact and their general solutions are known. Given enough computing power, it is possible to predict, with absolute accuracy, any property of any chemical system. This situation is perhaps the greatest intellectual triumph of human kind, but for one important qualifier – the computing power required is exponential with the size of the system... "absolute accuracy", while achievable, is realistically limited to about five atoms; in the case of Magnetic Resonance spectroscopy – to about ten spins.

Progress can be made by using approximations – a simulation that is run with a finite time step, for a finite time and in the presence of decoherence can often be performed cheaper and faster than the implacably cruel $O(2^N)$ upper bound would suggest. It was that thought that started our work on *Spinach* – the intention was not to write another simulation package (there are plenty of excellent software tools around), but to test a particular hypothesis that we had about levels of spin correlation in magnetic resonance systems. Another idea was to build a Magnetic Resonance theory lab – to be just like an experimental lab, where all equipment is in the right place, things work as they should and exciting research is done into things unknown. A good lab cannot be bought, borrowed or inherited, it can only be built. And so it began.

The hypothesis quickly turned out to be true – practically encountered levels of spin correlation in liquid state Magnetic Resonance were remarkably low (Figure 1). It took a while to convince Peter Hore and Nicola Wagner-Rundell (who came to the opposite conclusion for their radical pair systems) that this was not a one-off coincidence, and eventually we published a paper together [1], noting in the abstract that "*it actually appears that a majority of states in large spin systems are not essential in magnetic resonance simulations and can safely be dropped from the state space*". This had the potential to accelerate all Magnetic Resonance simulations – the complexity scaling became polynomial rather than exponential with the size of the spin system. A few of our subsequent papers demonstrated that huge systems could be simulated on a laptop with the algorithms proposed [2–4], but the burning question was about the physical reasons for that impressive performance. Intriguingly, there were cases (reported by Jean-Nicolas Dumez, Paul Butler, Meghan Halse and Lyndon Emsley) where reduced state space simulations produced correct answers against all expectations to the contrary [5–7]. We did offer some qualitative justifications in the papers, and so did the Emsley group, but it wasn't until Alexander Karabanov came to Oxford for a three-month visit from Walter Köckenberger's group in Nottingham that quantitative accuracy conditions were established [8]. Meanwhile, the IK group (reinforced by Andreas Biternas, Gareth Charnock, Luke Edwards, Hannah Hogben, Matthew Krzystyniak, Dima Savostyanov and Zenawi Welderufael) kept publishing paper after paper with an order of magnitude or so acceleration reported in each. There were some systems where little acceleration was found to be possible (notably in Spin Chemistry and some solid state NMR/ESR systems), but there were also cases (most liquid state systems) where protein-sized molecules could be done in a matter of minutes, in time domain, in Liouville space and with full Redfield relaxation superoperators, including all cross-relaxation and cross-correlation terms [4]. That was big news and it earned us the front page of the *Journal of Magnetic Resonance* in February 2011 [9].

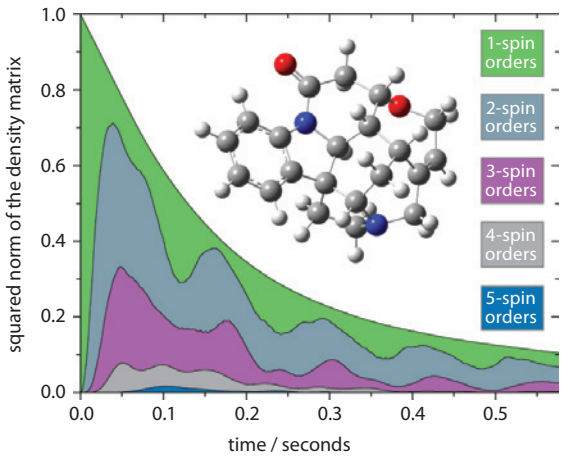

Figure 1. Numerical simulation of the density matrix norm dynamics during the evolution and detection period of a pulse-acquire NMR experiment on the 22-spin system of strychnine. All distances and magnetic parameters imported from a GIAO DFT B3LYP/EPR-II calculation. Bloch-Redfield-Wangsness relaxation superoperator (including DD, CSA and cross-correlation terms) was used with isotropic rotational diffusion correlation time of 200 ps.

We found two words in the Oxford English Dictionary that started with "spin": *spinach* and *spindle*. The latter was neutral, but the former carried with it the image of Popeye the Sailor cracking open a tin and becoming very powerful. The project was dubbed *Spinach* and we went on with the coding – complete SVN repository logs, detailing the code development history with individual authors, comments and dates listed, may be found on our web site (http://spindynamics.org).

At the time of writing, *Spinach* is unique in that it supports all forms of magnetic resonance spectroscopy under one roof (Figure 2): NMR, ESR, DNP, Spin Chemistry, Optimal Control, *etc*. To maintain this level of generality, the package is split into two major sections – the "kernel", which is a general algebraic abstraction containing core functions that are used in any simulation of a finite-state quantum system, and the "user-land", which is a collection of case-specific assumptions, experiment settings and examples. The user-land acts as a translation layer that interprets a specific simulation context, passes it to the kernel for processing and then interprets the answer. In this way, the clean generality of the kernel is safeguarded from the huge swarm of special cases that comprise the practical reality of Magnetic Resonance – all special cases are kept in the user-land.

The following features are, either entirely or at that level of generality, currently unique to *Spinach*:

1. Automatic detection of long-lived spin states (*e.g.* singlets). *Spinach* implements a very general case of Bloch-Redfield-Wangsness relaxation

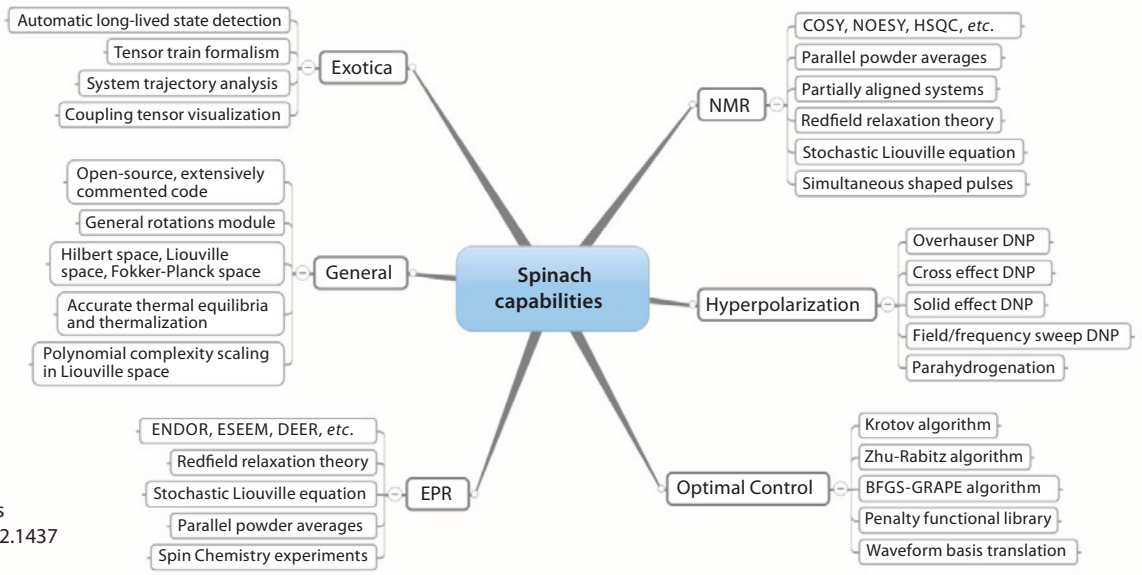

Figure 2. Summary of features available in *Spinach* version 1.2.1437 at the time of writing.

theory that includes all dipolar, quadrupolar, Zeeman and hyperfine mechanisms as well as all cross-correlations thereof. The null space of the relaxation superoperator (which is often sizable) contains the states that are immune to relaxation [10].

2. Optimal control theory module for both NMR and ESR. *Spinach* implements Krotov, Zhu-Rabitz, GRAPE and BFGS-GRAPE algorithms. The implementation of the GRAPE family in particular is very general and supports several propagator derivative calculation algorithms and several types of penalty functionals [11].
3. Trajectory visualization and analysis module. High-dimensional spin system trajectories are often hard to visualize and *Spinach* supports trajectory partitioning into various physically meaningful subspaces. It was the analysis module that generated Figure 1 [12].
4. Fokker-Planck module, supporting any type of spatial dynamics (diffusion, rotation, *etc.*) for NMR, EPR or any other type of spin dynamics in general.
5. Reduced state space infrastructure – *Spinach* was designed from the beginning to support low correlation order basis sets, to automatically detect and take advantage of hidden conservation laws and to aggressively reduce matrix dimensions at all simulation stages. At the time of writing, a 2D NOESY simulation of strychnine (22 protons) in Liouville space with full Redfield superoperator takes about a minute [9].
6. Simulation of all types of DNP spectroscopy. This is a result of a very fruitful collaboration with Walter Köckenberger and Alexander Karabanov at Nottingham University [13]. Restricted state spaces are supported. Waugh and Krylov-Bogolyubov average Hamiltonian theories are also available. Relaxation superoperator options include Redfield theory, Lindblad theory and a relaxation theory that Walter and Alexander specifically designed for DNP [14].

Spinach code is open, extensively commented and uses Matlab as the programming environment. It was our intention to make it easy to modify and re-use parts of the code, if necessary, outside *Spinach*. A collection of example simulations is intended to simplify the initial adoption – it is often easier to modify a generic example than to write a new simulation script from scratch. We continue growing the example set based on the practical simulation requests and queries that we are getting from the users.

An interesting by-product of creating *Spinach* is our Spin Dynamics lecture course (http://spindynamics.org/support.php) – programming something at a high level of efficiency and generality requires deep understanding of the topic, and we distilled that understanding into an online lecture course. That course supplements the manual. According to YouTube, it has scored over 14,000 views and over 120 regular subscribers in the last academic year.

Literature

1. I. Kuprov, N. Wagner-Rundell, P. J. Hore: Polynomially scaling spin dynamics simulation algorithm based on adaptive state-space restriction, J. Magn. Reson. 189 (2007) 241–250.
2. M. Krzystyniak, L. J. Edwards, I. Kuprov: Destination state screening of active spaces in spin dynamics simulations, J. Magn. Reson. 210 (2011) 228–232.
3. I. Kuprov: Polynomially scaling spin dynamics II: Further state-space compression using Krylov subspace techniques and zero track elimination, J. Magn. Reson. 195 (2008) 45–51.
4. I. Kuprov, Diagonalization-free implementation of spin relaxation theory for large spin systems: J. Magn. Reson. 209 (2011) 31–38.
5. M. E. Halse, J. N. Dumez, L. Emsley: Quasi-equilibria in reduced Liouville spaces, J. Chem. Phys. 136 (2012).
6. J. N. Dumez, M. C. Butler, L. Emsley: Numerical simulation of free evolution in solid-state nuclear magnetic resonance using low-order correlations in Liouville space, J. Chem. Phys. 133 (2010).
7. M. C. Butler, J. N. Dumez, L. Emsley: Dynamics of large nuclear-spin systems from low-order correlations in Liouville space, Chem. Phys. Lett. 477 (2009) 377–381.
8. A. Karabanov, I. Kuprov, G. T. P. Charnock, A. van der Drift, L. J. Edwards, W. Koeckenberger: On the accuracy of the state space restriction approximation for spin dynamics simulations, J. Chem. Phys. 135 (2011).
9. H. J. Hogben, M. Krzystyniak, G. T. P. Charnock, P. J. Hore, I. Kuprov: Spinach – A software library for simulation of spin dynamics in large spin systems, J. Magn. Reson. 208 (2011) 179–194.
10. H. J. Hogben, P. J. Hore, I. Kuprov: Multiple decoherence-free states in multi-spin systems, J. Magn. Reson. 211 (2011) 217–220.
11. P. de Fouquieres, S. G. Schirmer, S. J. Glaser, I. Kuprov: Second order gradient ascent pulse engineering, J. Magn. Reson. 212 (2011) 412–417.
12. I. Kuprov: Spin system trajectory analysis under optimal control pulses, J. Magn. Reson., in press.
13. A. Karabanov, A. van der Drift, L. J. Edwards, I. Kuprov, W. Kockenberger: Quantum mechanical simulation of solid effect dynamic nuclear polarisation using Krylov-Bogolyubov time averaging and a restricted state-space, Phys. Chem. Chem. Phys. 14 (2012) 2658–2668.
14. A. Karabanov, G. Kwiatkowski, W. Kockenberger: Quantum mechanical simulation of cross effect DNP using Krylov-Bogolyubov averaging, Appl. Magn. Reson. 43 (2012) 43–58.