Chemistry

Optimal Control of Spin Systems

with Newton-Raphson Methods

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Optimal Control - Gradient Ascent Pulse Engineering (GRAPE)

The evolution of a quantum system can be characterised by a Liouville equation with a vector representation of the density operator, $\frac{\partial}{\partial t}|\hat{\rho}(t)\rangle = -i\hat{\hat{\mathcal{L}}}(t)|\hat{\rho}(t)\rangle$, having the general solution,

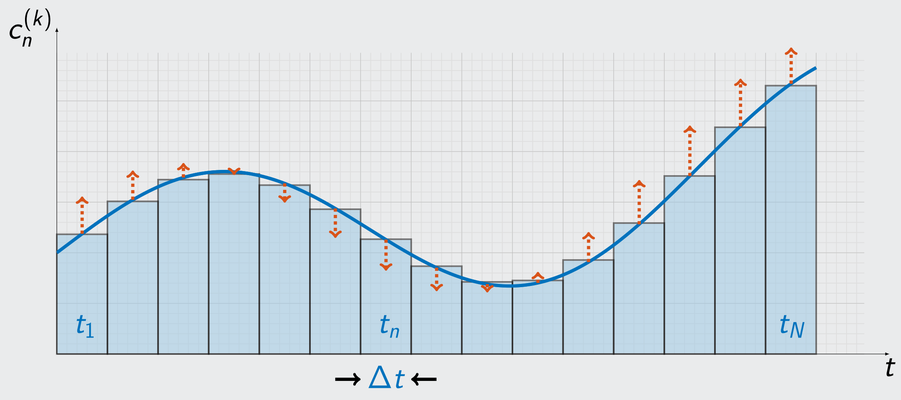
$$|\hat{\rho}(t)\rangle = \exp_{(0)}\left(-i\int_0^t \hat{\hat{\mathcal{L}}}(t)\,\mathrm{d}t\right)|\hat{\rho}(t)\rangle$$

A practical Magnetic Resonance system can be split into two parts; that is beyond experimental control, $\hat{\hat{\mathcal{L}}}_0$, and a set of controllable electromagnetic pulses $\left\{\hat{\hat{\mathcal{L}}}_k\right\}$:

$$\hat{\hat{\mathcal{L}}}(t) = \hat{\hat{\mathcal{L}}}_0 + \sum_k c^{(k)}(t)\hat{\hat{\mathcal{L}}}_k$$

The problem is simplified if the control sequences $\left\{c^{(k)}(t)\right\}$ are assumed to be piecewise constant. For a piecewise constant Hamiltonian, we sequentially multiply each of the, discrete in time, propagators into the initial conditions:

$$\hat{\hat{\mathcal{P}}}_n = \exp\left[-i\left(\hat{\hat{\mathcal{L}}}_0 + \sum_k \underbrace{c^{(k)}(t_n)}_{\| \; c_n^{(k)}}\hat{\hat{\mathcal{L}}}_k\right)\Delta t\right]$$



The expression for fidelity, the overlap between the current state of the system ρ_0 and the target state σ, is

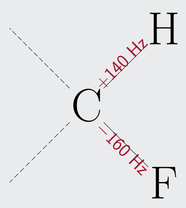
$$J = \mathrm{Re}\,\langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\hat{\hat{\mathcal{P}}}_{N-1}\ldots\hat{\hat{\mathcal{P}}}_2\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle$$

Since $\left\{c_n^{(k)}\right\}$ are vectors of finite dimension, we can use the standard non-linear numerical optimisation to find the maximum of J in their space (it is useful to note that the maximum of J is the same as the minimum of $1-J$).

Simulation System

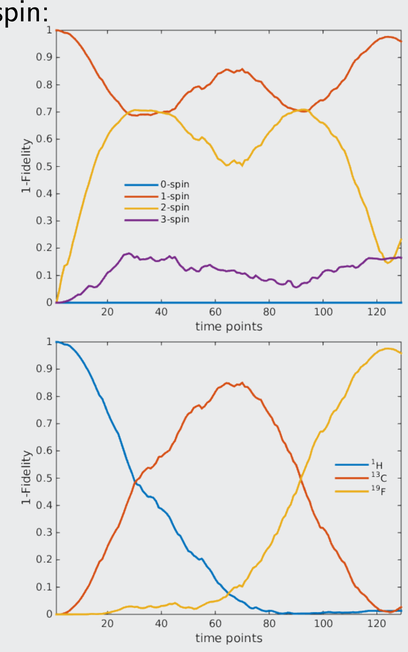
We prepare the *Spinach* software to find a pulse set to transfer magnetisation from ^{1}H atom to ^{19}F atom with the following molecule:

Interaction parameters of a molecular group used in state transfer simulations on a system characterising the fragment of a fluorohydrocarbon molecule (magnetic induction = 9.4 Tesla).

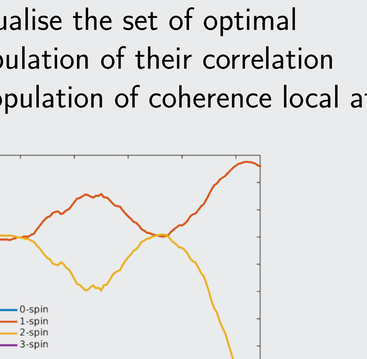


In this case the set of control channels operators are $\left\{\hat{L}_x^{(H)}, \hat{L}_y^{(H)}, \hat{L}_x^{(C)}, \hat{L}_y^{(C)}, \hat{L}_x^{(F)}, \hat{L}_y^{(F)}\right\}$.

It is useful to visualise the set of optimal pulses by the population of their correlation subspaces and population of coherence local at each spin:



The Hessian Matrix:



- Symmetric,
- Non-singular,
- Diagonally dominant.

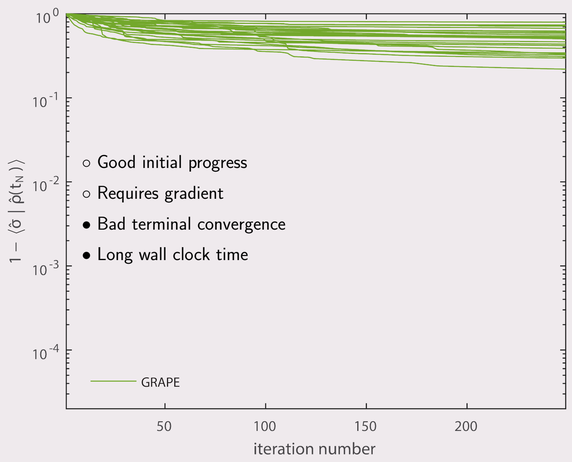
Regularise the Hessian, so it is non-singular and well conditioned; take the eigendecomposition of an augmented Hessian matrix:

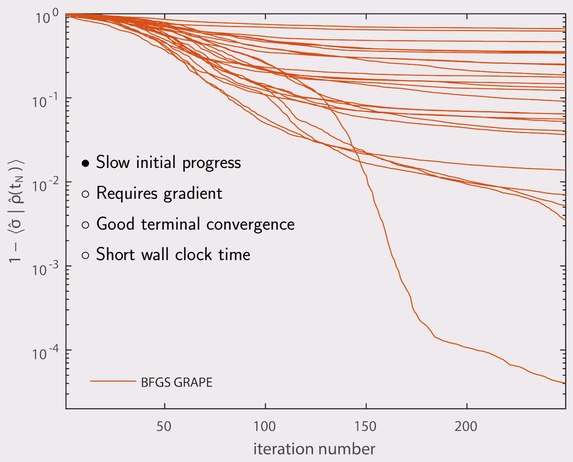
$$\mathbf{H}_{aug} = \begin{bmatrix}\delta^2\mathbf{H} & \delta\vec{g}\\ \delta\vec{g} & \mathbf{0}\end{bmatrix} = Q\Lambda Q^\dagger$$

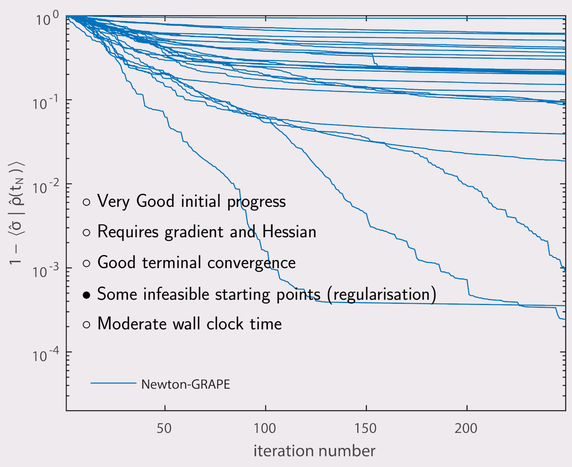
where $\vec{g}$ is the gradient, Λ is a diagonal matrix of eigenvalues and Q is a matrix of eigenvectors. We have introduced a constant δ, found iteratively; the region of a radius we trust to give a Hessian that is sufficiently positive definite.

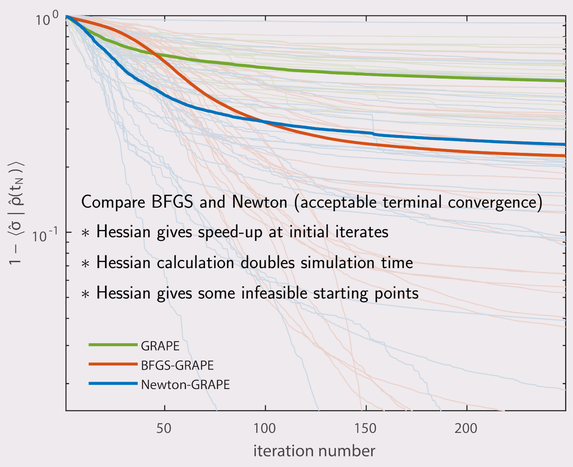
$$\mathbf{H}_{reg} = Q(\Lambda + \lambda_{min}\hat{I})Q^\dagger$$
$$\lambda_{min} = \max\left[0, -\min(\Lambda)\right]$$

Simulation Results









Efficient Propagator Derivative Calculations

The numerical optimisation method simulated in the results section above require a gradient calculation. This is reduced to:

$$J = \langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\hat{\hat{\mathcal{P}}}_{N-1}\hat{\hat{\mathcal{P}}}_{N-2}\hat{\hat{\mathcal{P}}}_{N-3}\underbrace{\hat{\hat{\mathcal{P}}}_{N-4}\ldots\hat{\hat{\mathcal{P}}}_3\hat{\hat{\mathcal{P}}}_2\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle}_{\text{(I) propagate forwards from source}}$$

$$\frac{\partial}{\partial c_{N-3}^{(k)}}\hat{\hat{\mathcal{P}}}_{N-3}$$

(III) compute expectation of the derivative

$$\overbrace{\langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\hat{\hat{\mathcal{P}}}_{N-1}\hat{\hat{\mathcal{P}}}_{N-2}}^{\text{(II) propagate backwards from target}}\hat{\hat{\mathcal{P}}}_{N-3}\hat{\hat{\mathcal{P}}}_{N-4}\ldots\hat{\hat{\mathcal{P}}}_3\hat{\hat{\mathcal{P}}}_2\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle$$

The total cost of the gradient of J is therefore one forward simulation, one backward simulation and (n steps) $\times$ (k controls) derivatives of matrix exponentials with respect to scalar parameters. The expectation of first order derivatives is

$$\left\langle\frac{\partial J}{\partial c_{n=t}^{(k)}}\right\rangle = \langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\hat{\hat{\mathcal{P}}}_{N-1}\cdots\frac{\partial}{\partial c_{n=t}^{(k)}}\hat{\hat{\mathcal{P}}}_{n=t}\cdots\hat{\hat{\mathcal{P}}}_2\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle$$

Efficient calculation of the expectation of first order derivatives can be made utilising the work of C.Van Loan; using an augmented exponential in the following form

$$\exp\begin{pmatrix}-i\hat{\hat{\mathcal{L}}}\Delta t & -i\hat{\hat{\mathcal{L}}}_n^{(k)}\Delta t\\ \mathbf{0} & -i\hat{\hat{\mathcal{L}}}\Delta t\end{pmatrix} = \begin{pmatrix}e^{-i\hat{\hat{\mathcal{L}}}\Delta t} & \frac{\partial}{\partial c_n^{(k)}}e^{-i\hat{\hat{\mathcal{L}}}\Delta t}\\ \mathbf{0} & e^{-i\hat{\hat{\mathcal{L}}}\Delta t}\end{pmatrix}$$

extracting the derivative from the upper right block. In practice, the exponential is calculated using a two-point finite difference stencil with Krylov propagation. The Newton-Raphson method is a second order method, additionally requiring the explicit calculation of the Hessian matrix. This requires the expectation of the second order derivatives:

$$\left\langle\frac{\partial^2 J}{\partial c_n^2}\right\rangle = \langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\cdots\hat{\hat{\mathcal{P}}}_{n+1}\frac{\partial^2\hat{\hat{\mathcal{P}}}_n}{\partial c_n^2}\hat{\hat{\mathcal{P}}}_{n-1}\cdots\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle$$

$$\left\langle\frac{\partial^2 J}{\partial c_n\partial c_{n+1}}\right\rangle = \langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\cdots\hat{\hat{\mathcal{P}}}_{n+2}\frac{\partial\hat{\hat{\mathcal{P}}}_{n+1}}{\partial c_{n+1}}\frac{\partial\hat{\hat{\mathcal{P}}}_n}{\partial c_n}\hat{\hat{\mathcal{P}}}_{n-1}\cdots\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle$$

$$\left\langle\frac{\partial^2 J}{\partial c_m\partial c_n}\right\rangle = \langle\sigma|\,\hat{\hat{\mathcal{P}}}_N\cdots\hat{\hat{\mathcal{P}}}_{n+1}\frac{\partial\hat{\hat{\mathcal{P}}}_n}{\partial c_n}\hat{\hat{\mathcal{P}}}_{n-1}\cdots\hat{\hat{\mathcal{P}}}_{m+1}\frac{\partial\hat{\hat{\mathcal{P}}}_m}{\partial c_m}\hat{\hat{\mathcal{P}}}_{m-1}\cdots\hat{\hat{\mathcal{P}}}_1\,|\rho_0\rangle$$

- Computation to scale with $O(n\times k)$ by storing propagators from gradient calculation.
- Problem now reduces to finding $n\times k$ second-order derivatives on the block diagonal of the Hessian with a 3×3 augmented exponential:

$$\exp\begin{pmatrix}-i\hat{\hat{\mathcal{L}}}\Delta t & -i\hat{\hat{\mathcal{L}}}_n^{(k)}\Delta t & \mathbf{0}\\ \mathbf{0} & -i\hat{\hat{\mathcal{L}}}\Delta t & -i\hat{\hat{\mathcal{L}}}_m^{(k)}\Delta t\\ \mathbf{0} & \mathbf{0} & -i\hat{\hat{\mathcal{L}}}\Delta t\end{pmatrix} = \begin{pmatrix}e^{-i\hat{\hat{\mathcal{L}}}\Delta t} & \frac{\partial}{\partial c_n^{(k)}}e^{-i\hat{\hat{\mathcal{L}}}\Delta t} & \frac{1}{2}\frac{\partial^2}{\partial c_n^{(k)}\partial c_m^{(k)}}e^{-i\hat{\hat{\mathcal{L}}}\Delta t}\\ \mathbf{0} & e^{-i\hat{\hat{\mathcal{L}}}\Delta t} & \frac{\partial}{\partial c_m^{(k)}}e^{-i\hat{\hat{\mathcal{L}}}\Delta t}\\ \mathbf{0} & \mathbf{0} & e^{-i\hat{\hat{\mathcal{L}}}\Delta t}\end{pmatrix}$$

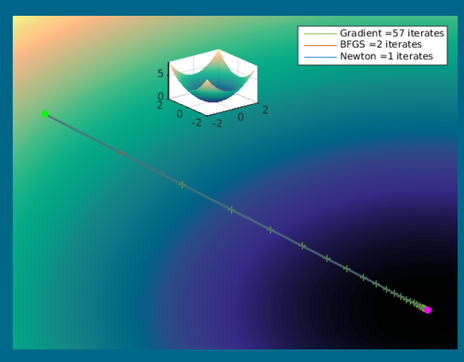
Numerical optimization is concerned with finding an extrema of an objective function. We consider two variables in finding the minimiser of a function:

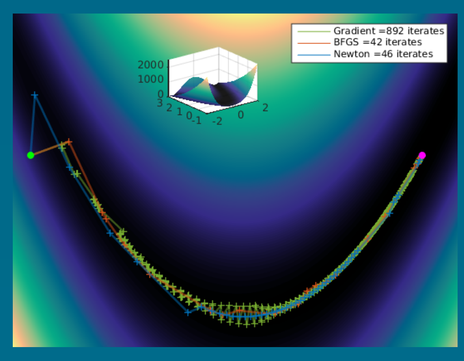
- Step length, α - the distance moved away from the point in the current iterate.
- Search direction, p_k - the direction to move away from the current point in the iterate.

For the line search method, we can find the minimizer considering the above two variables:

$$\min_{\alpha>0} f\left(x_k + \alpha p_k\right)$$

where we begin at some initial point, x_0, and generate a set of iterates using $x_{k+1} = x_k + \alpha_k p_k$, until a solution has been found to some defined level of accuracy. A well defined, convex objective function is best optimized with a Newton-Raphson method.





The Newton-Raphson Method expands the Taylor series to second order;

$$f\left(x_k + p\right) \approx f_k + p^T\nabla f_k + \tfrac{1}{2}p^T\nabla^2 f_k p$$

where the right hand side of the above formula is minimised by the search direction:

$$p_k = -\mathbf{H}_k^{-1}\nabla f_k$$

where $\mathbf{H}_k = \nabla^2 f_k$ is the Hessian matrix. Quasi-Newton methods use an approximation to the Hessian (using a formula such as the BFGS update). Gradient descent method approximates the Hessian matrix to be the unit matrix.

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