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Large Scale Parallel Simulation of EPR Lineshape Spectra

Abstract: *Electron Paramagnetic Resonance* is a spectroscopy method to investigate systems of unpaired electron spins. *Spinach*[1] is a Matlab library to simulate different kinds of spin system experiemnts, including EPR. This paper aims to give an overview of the theoretical concepts involved in spin dynamics, especially those necessary to comprehend Spinach's way of numerical computation. After understanding the parameters determining Spinach's resources usage we adopt parallel computing methods on Linux clusters to accelerate the calculation of EPR lineshape spectra.

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1 $\frac{\pi}{2}$-pulsed EPR

The mechanisms of *EPR (Electron Paramegnetic Resonance)*, also called *ESR (Electron Spin Resonance)*, work analogous to the mechanisms of *NMR (Nuclear Magnetic Resonance)*. In *diamagnetic* materials, all electrons are spin-paired, making the elctron magnetic dipole vanish, and enabling the system to be accessible by NMR. EPR experiments are suitable to investigate *paramagnetic* systems with unpaired electron spins, which exhibit a non-zero electron spin. The basic idea is to perturb a spin system's equilibrium by a small pulsed oscillating magnetic field and record resulting time-dependent magnetization during the relaxation process.
When we place a sample of spin sytems inside a static magnetic field $\vec{B}_0 = B_0\hat{z}$ and let it settle to equilibrium, due to Zeeman effect more electron spins are goint to align parallel to $\vec{B}_0$ than antiparallel, resulting in a net magnetization of the sample. A magnetic pulse $\vec{B}_1(t) = B_1(t)\hat{x}$ linearly polarized in x-direction will tilt the electron spins and disturb the equilibrium in a way we are going to examine in the course of this article.

1.1 Spin system Hamiltonian

Like in any other quantum mechanical problem the starting point when treating an EPR experiment theoretically is the Schrödinger equation[2]

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \mathcal{H}|\psi\rangle \tag{1}$$

For a start we examine the Hamiltonion of an unpaired spin electron system in a static magnetic field. It will exhibit several perturbation terms of different nature:

$$\mathcal{H} = [\mathcal{H}_{EZ} + \mathcal{H}_{ECS} + \mathcal{H}_{LS}] + [\mathcal{H}_{HF}] + [\mathcal{H}_{NZ} + \mathcal{H}_{NCS} + \text{weaker interactions}] \tag{2}$$

1. <u>Electron Zeeman contribution</u> $\mathcal{H}_{EZ} = -\vec{\mu}\cdot\vec{B}_0 = -\hbar B_0(\gamma_L\mathbf{L}_z + \gamma_S\mathbf{S}_z)$

   The static magnetic field $\vec{B}_0 = B_0\hat{z}$ acts a torque on the electron's magnetic dipole moment μ, linearly dependent on its angular momentum and spin. Thus the *Zeeman effect* lifts the spin degeneracy of energy levels, reducing the energy of spins aligned parallel to the magnetic field (-), and increasing the energy of spins aligned antiparallel (+) by the correction term[3]

   $$E^1_{\pm} = \pm\mu_B\gamma_J B_0 m_J \tag{3}$$

2. <u>Electron chemical shift</u> $\mathcal{H}_{ECS} = \gamma_S\hbar\mathbf{S}\cdot\sigma_S(t)\cdot\vec{B}_0$

   The moving electron clouds change the effective magnetic field $\vec{B}_{\text{eff}}$ "seen" by the every electron spin. This "shielding" behaviour is desctribed by the *chemical shift tensor* $\sigma_S(t)$:

   $$\vec{B}_{\text{eff}}(t) = -\sigma_S(t)\cdot\vec{B}_0 \tag{4}$$

3. <u>Spin-orbit coupling</u> $\mathcal{H}_{LS} = \lambda\mathbf{L}\cdot\mathbf{S}$

   The electron's motion around the nucleus creates a magnetic field, with which the electron's spin will interact. Together with the Zeeman interaction, those two Hamiltonian contributions are due to the influence of a magnetic field. Furthermore, the externam Zeeman field causes $\vec{L}$ to change, thus also influencing the spin-orbit interaction.

4. <u>Hyperfine interaction</u> $\mathcal{H}_{HF} = \frac{\gamma_I\gamma_S\hbar^2}{r^3}\left[\frac{3(\mathbf{I}\cdot\vec{r}(t))(\mathbf{S}\cdot\vec{r}(t))}{r^2} - \mathbf{I}\cdot\mathbf{S}\right]$

   The nucleus interacts with the orbiting electron due to the electron's induced magnetic field acting on the nuclear magnetic dipole moment.

[2] Following spin dynamics conventions in the course of this article we set $\hbar = 1$
[3] for a thorought derivation of the energy correction term see [4, chap. 6.4 The Zeeman Effect, p. 277ff]

5. Nuclear Zeeman contribution $\mathcal{H}_{NZ} = -\hbar B_0 \gamma_I \mathbf{I}_z$

   Just like the electron, the nucleus posseses intrinsic spin and thus a nuclear magnetic moment, enabling it to interact with an external magnetic field.

6. Nuclear chemical shift $\mathcal{H}_{NCS} = \gamma_I \hbar \mathbf{I} \cdot \sigma_I(t) \cdot \vec{B}_0$

   Of course, the shielding by the electron clouds also applies to the nuclei's spins $\mathbf{I}$.

$$\vec{B}_{\text{eff}}(t) = -\sigma_I(t) \cdot \vec{B}_0 \tag{5}$$

7. Other weaker interactions like coupling of the nuclear quadrupole moment to the electron's electromagnetic field and the magnetic coupling of electrons with each other or nuclei with each other.

1.2 g-tensor and A-tensor

In the spin Hamiltonian above different interactions have been grouped with square brackets into three packages. The latter package $[\mathcal{H}_{NZ} + \mathcal{H}_{NCS} + \text{weaker interactions}]$ simply marks interactions which we are allowed to neglect in the case of high field EPR. When the external magnetic field $\vec{B}_0$ becomes sufficiently strong, their contribution diminishes in comparison with the interactions depending on $\vec{B}_0$.
The former package $[\mathcal{H}_{EZ} + \mathcal{H}_{ECS} + \mathcal{H}_{LS}]$ marks major interactions linear in spin. In EPR the overall behaviour of those interactions is summarized in the *g-tensor*:

$$\mathcal{H}_{\text{linear}} = \mu_B \, \mathbf{S} \cdot g \cdot \vec{B}_0 \tag{6}$$

The second package only including the hyperfine interaction characterizes the term bilinear in spin: the coupling between one spin and another. Though not evident from the sketch above, but those interactions are anisotropic in general and thus summarized by the A-tensor in the case of EPR:

$$\mathcal{H}_{\text{bilinear}} = \mathbf{S} \cdot A \cdot \mathbf{I} \tag{7}$$

One might wonder, why the spin-orbit interaction does not contribute to the bilinear part. In [6, chap 11.2, p. 505ff] one finds a dedicated explanation why spin-orbit coupling results in a changed effective magnetic field and thus rather contributes to the g-tensor, very much like the chemical shift. Another possible self-interaction $\mathcal{H}_{\text{quadratic}} = \mathbf{S} \cdot A \cdot \mathbf{S}$ we are not going to encounter in the case of high field EPR.

1.3 Matrix exponentials

In the following we shall make use of matrix exponentials to express some quantum mechanical operators. The defintion of the exponential

$$e^x = \sum_{k=0}^{\infty} \frac{x^k}{k!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + ... \tag{8}$$

can be easily applied to square matrices, eg.:

$$e^{i\phi A} = I + i\phi A - \frac{(\phi A)^2}{2!} - i\frac{(\phi A)^3}{3!} + \frac{(\phi A)^4}{4!} + i\frac{(\phi A)^5}{5!} - ... \tag{9}$$

such that exponentials are defined for matrices as well.

1.4 Rotating reference frame

A magnetic field B_0 applied along the z-axis causes a magnetic moment to precess around the z-axis at the Larmor frequency ω_0. With this classical approach as a starting point it is possible to explain a fair amount of EPR phenomena, but since we want to get used to spin formalism, we will explain a spin system's behaviour from the quantum mechanical perspective right from the beginning. Since the electron's magnetic moment is proportional to its angular momentum $\vec{\mu} = \gamma \mathbf{J}$ with the *Landé g-factor* γ, the interaction energy $E = -\vec{\mu} \cdot \vec{B}$ and thus the Hamiltonian, the evolution operator[4] and the Schrödinger equation's solution can be expressed as

$$\mathcal{H} = -\gamma B_0 \mathbf{J_z}, \quad U(t) = e^{i\gamma B_0 t \mathbf{J_z}}, \quad |\psi(t)\rangle = e^{i\gamma B_0 t \mathbf{J_z}} |\psi(0)\rangle = e^{i\omega_0 t \mathbf{J_z}} |\psi(0)\rangle \quad \text{with} \quad \omega_0 = \gamma B_0 \tag{10}$$

Analogous to the classical approach, the time dependent solution must be a rotation of the initial state by angle $\phi = -\omega_0 t$, and we can identify

$$\mathbf{R_z}(\phi) = e^{-i\phi \mathbf{J_z}} \tag{11}$$

as an rotation operator around the z-axis. $\phi > 0$ results in an *active* rotation of the state in "positive", anticlockwise direction, whereas $\phi < 0$ results in a rotation in "negative", clockwise direction. Likewise we can speak of $\phi > 0$ causing a *passive* rotation of the reference frame in negative, clockwise direction, whereas $\phi < 0$ rotates the reference frame in positive, anticlockwise direction.

If we want to determine an observable $\mathbf{A}$ of the rotated state $|\psi(t)\rangle$, we find

$$\langle \psi(\phi)|\mathbf{A}|\psi(\phi)\rangle = \langle \psi(0)| e^{-i\phi \mathbf{J_z}} \ \mathbf{A} \ e^{i\phi \mathbf{J_z}} |\psi(0)\rangle \tag{12}$$

$$= \langle \psi(0)|\mathbf{A}'(\phi)|\psi(0)\rangle \quad \text{with} \quad \mathbf{A}'(\phi) = e^{-i\phi \mathbf{J_z}} \ \mathbf{A} \ e^{i\phi \mathbf{J_z}} \tag{13}$$

it being the same as applying an rotated operator $\mathbf{A}'$ on the unrotated state $|\psi(0)\rangle$. Say $|\psi(\phi)$ is rotated in positive sense, then the operator $\mathbf{A}'$ must be rotated in the negative sense. The two perspectives must correspond to two different reference frames. In the first case we observe a rotated system from the unrotated lab frame, whereas in the second case the axis of our reference frame are aligned with the spin system, such that it appears unrotated in our frame. Hence we can convert back and forth between resting frame and rotating frame:

$$|\psi\rangle = e^{-i\omega_1 t \mathbf{J_z}} |\psi'\rangle \tag{14}$$

$$|\psi'\rangle = e^{i\omega_1 t \mathbf{J_z}} |\psi\rangle \tag{15}$$

And if we know the Hamiltonian $\mathcal{H}$ for $|\psi\rangle$ in one frame, we can find the rotating Hamiltonian $\mathcal{H}'$ in the frame of $|\psi'\rangle$ by plugging into the Schrödinger's equation:

$$\frac{\partial}{\partial t}|\psi\rangle = \frac{\partial}{\partial t}\left(e^{-i\omega_1 t \mathbf{J_z}}|\psi'\rangle\right) = -i\omega_1 t \mathbf{J_z} \ e^{-i\omega_1 t \mathbf{J_z}}|\psi'\rangle + e^{-i\omega_1 t \mathbf{J_z}} \frac{\partial}{\partial t}|\psi'\rangle \tag{16}$$

$$i\frac{\partial}{\partial t}|\psi\rangle = \mathcal{H}|\psi\rangle \tag{17}$$

$$\Rightarrow i\left(-i\omega_1 \mathbf{J_z} \ e^{-i\omega_1 t \mathbf{J_z}}|\psi'\rangle + e^{-i\omega_1 t \mathbf{J_z}} \frac{\partial}{\partial t}|\psi'\rangle\right) = \mathcal{H}\left(e^{-i\omega_1 t \mathbf{J_z}}|\psi'\rangle\right) \quad | \cdot e^{i\omega_1 t \mathbf{J_z}}, \ e^{i\omega_1 t \mathbf{J_z}} \mathbf{J_z} e^{-i\omega_1 t \mathbf{J_z}} = \mathbf{J_z} \tag{18}$$

$$\Leftrightarrow \omega_1 \mathbf{J_z}|\psi'\rangle + i\frac{\partial}{\partial t}|\psi'\rangle = \left(e^{i\omega_1 t \mathbf{J_z}} \mathcal{H} e^{-i\omega_1 t \mathbf{J_z}}\right)|\psi'\rangle \tag{19}$$

$$\Leftrightarrow i\frac{\partial}{\partial t}|\psi'\rangle = \left(e^{i\omega_1 t \mathbf{J_z}} \mathcal{H} e^{-i\omega_1 t \mathbf{J_z}} - \omega_1 \mathbf{J_z}\right)|\psi'\rangle \tag{20}$$

$$= \mathcal{H}'|\psi'\rangle \quad \text{with} \quad \mathcal{H}' = e^{i\omega_1 t \mathbf{J_z}} \mathcal{H} e^{-i\omega_1 t \mathbf{J_z}} - \omega_1 \mathbf{J_z}) \tag{21}$$

[4]this is a bit of a spoiler, see section (2.2.4)

1.5 Resonant frequency field

Suppose we observe the equilibrium system due to Zeeman interaction $\mathcal{H} = -\gamma B_0 J_z$ from frame rotating with ω_1. According to equation (21)

$$\mathcal{H}' = e^{i\omega_1 t \mathbf{J_z}} \mathcal{H} e^{-i\omega_1 t \mathbf{J_z}} - \phi \mathbf{J_z} = -\gamma (B_0 + \frac{\omega_1}{\gamma}) \mathbf{J_z} \tag{22}$$

The rotating frame introduces another term acting like an additional magnetic field. By choosing the angular velocity to equal the Zeeman effect's Larmor frequency $\omega_1 = -\gamma B_0$ we can make the net magnetic field vanish in the rotating frame. This is easy to imagine: The rotating frame just follows the system's Larmor precession, letting the system appear stationary.
Now it is easy to imagine what happens in the rotating frame, if we pulse the system by a transversal circularly polarized magnetic field $\vec{B_1} = B_1(\hat{x}\cos\omega_2 t + \hat{y}\sin\omega_2 t)$ and choose the frequency of B_1 to approximately equal the system's Larmor frequency around the static field $\omega_2 \approx \omega_1 = -\gamma B_0$. In this case of "resonance" the static magnetic field in the rotating frame disappears and the circularly polarized fiel appears to be static in x-direction. The static Hamiltonian[5]

$$\mathcal{H} = -\gamma \vec{B}_{\text{tot}} \cdot \mathbf{J} = -\gamma \left(B_0 \mathbf{J_z} + B_1 (\cos\omega_2 t \ \mathbf{J_x} + \sin\omega_2 t \ \mathbf{J_y}) \right) \tag{23}$$

$$= -\gamma \left(B_0 \mathbf{J_z} + B_1 e^{-i\omega_2 t \mathbf{J_z}} \mathbf{J_x} e^{i\omega_2 t \mathbf{J_z}} \right) \tag{24}$$

transforms to the rotating Hamiltonian

$$\mathcal{H}' = e^{i\omega_1 t \mathbf{J_z}} \mathcal{H} e^{-i\omega_1 t \mathbf{J_z}} \tag{25}$$

$$= -\gamma \left((B_0 + \frac{\omega_1}{\gamma}) \mathbf{J_z} + B_1 \mathbf{J_x} \right) \quad \text{with} \quad \omega_2 = \omega_1 \tag{26}$$

$$= -\gamma B_1 \mathbf{J_x} \quad \text{with} \quad \omega_1 = -\gamma B_0 \tag{27}$$

In case of using a linearly polarized instead of a circularly polarized pulse, it may be argued that the rotating Hamiltonian still looks the same, since a linearly polarized field may be decomposed into two circularly polarized components, rotating in opposite directions. In the rotating frame , one of those components just behaves like the B_1 field above, the other one oscillates so rapidly at $2\omega_2$, that the spins experience only the fluctuating field's average value of zero[6]. From the classical point of view, in the rotating frame the spins now precess around $B_1\hat{x}'$ as they do around $B_0\hat{z}$ in the resting frame. From the quantum mechanical point of view, spins are now inclined to undergoe quantized transitions from states aligned around B_0 into states aligned around B_1.
If the pulse is applied for a duration Δt such that $\omega_1 \Delta t = \frac{\pi}{2}$, the spin system aligned along the z-axis will be reorientated along the y'-axis of the rotating frame. After the pulse, the system will evolve in time and relax into its equilibrium under the spin Hamiltonian's interactions.

1.6 Experimental setup

When the spins are precessing around B_1 in the rotating frame, and undergoing a more complex motion resulting from a superposition of precession around the static B_0 and the rotating B_1, what physical quantity are we going to measure? As has been noticed, the system's magnetic moment is proportional to its spin orientation $\vec{\mu} \propto \mathbf{S}$, hence we want to record the system's total magnetization. For this purpose a detection coil is installed orthogonal to the static magnetic field B_0, which records the change of the spin system's oscillating magnetization via Faraday induction.

[5]for a prove of $e^{-i\omega_2 t \mathbf{J_z}} \mathbf{J_x} e^{i\omega_2 t \mathbf{J_z}} = \cos\omega_2 t \ \mathbf{J_x} + \sin\omega_2 t \ \mathbf{J_y}$ see [6, chap 2.6 Exponential Operators, p. 27f]
[6]this is argued in [?, chap. 4.2.2 The resonant frequency field, p.111f]

For $\frac{\pi}{2}$-pulse EPR, right after the pulse the spins lie in the x-y-plane of the lab frame, rotating around the z-axis, and together with them the magnetization $\vec{M}$. Say, the detection coil is aligned along the x-axis, then it will record the change of magnetization in x-direction M_x, and the coil's signal will oscillate with the spin system's Larmor frequency

$$S(t) = S_0(t)\cos\omega_1 t = S_0(t)\frac{e^{-i\omega_1 t} + e^{i\omega_1 t}}{2} \tag{28}$$

The signal is modulated with a complex oscillating signal $e^{i\omega t}$

$$S'(t) = S(t)e^{i\omega t} = \frac{1}{2}S_0(t)\left(e^{-i(\omega_1-\omega)t} + e^{i(\omega_1+\omega)t}\right) \tag{29}$$

and the sum frequency term is filtered out to yield

$$S'(t) = \frac{1}{2}S_0(t)e^{-i(\omega_1-\omega)t} \tag{30}$$

Neglecting any relaxation, the evolution of a density matrix titled into the x-y-plane by a $\frac{\pi}{2}$-pulse may be written as

$$\rho \propto \mathbf{J_y}\cos\omega_1 t + \mathbf{J_x}\sin\omega_1 t \tag{31}$$

and if we express the density matrix in a rotating frame of velocity ω

$$\rho \propto \mathbf{J_y}\cos(\omega_1-\omega)t + \mathbf{J_x}\sin(\omega_1-\omega)t \tag{32}$$

If we are able to evaluate $\mathbf{J}_+ = \mathbf{J_x} + i\mathbf{J_y}$ as a "complex observable" in the rotating frame, it would yield

$$\begin{aligned} Tr(\mathbf{J}_+\rho') &\propto i\ Tr(\mathbf{J_y}^2)\cos(\omega_1-\omega)t + Tr(\mathbf{J_x}^2)\sin(\omega_1-\omega)t & (33)\\ &\propto i(\cos(\omega_1-\omega)t - i\sin(\omega_1-\omega)t) \quad \text{since} \quad Tr(\mathbf{J_y}^2) = Tr(\mathbf{J_x}^2) & (34)\\ &\propto e^{-i(\omega_1-\omega)t} \propto S'(t) & (35)\end{aligned}$$

Hence we see that the detection coil's modulated signal is just proportional to the magnetization we would observe in a reference frame rotating with the modulation frequency ω. The signal oscillates at frequency $\Delta\omega = \omega_1 - \omega$, and the conclusion to draw is that the rotating frame does not only constitute a handy tool to visualize the effect of a magnetic pulse, but proves equally useful in the detection process as well. Thus any simulation might well be performed without ever leaving the rotating frame, yielding the FID in form of the complex observable $\mathbf{J}_+ = \mathbf{J_x} + \mathbf{J_y}$.

2 Mathematical methods

First of all, we are going to introduce several theoretical concepts necessary to understand the mechanisms of EPR and numerical spectra computation.

2.1 Matrix formalism

2.1.1 Diagonizable matrices

An $n \times n$ matrix A is said to be diagonizable if there exists an invertible matrix P such that

$$P^{-1}AP = \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ldots & \\ & & & \lambda_n \end{pmatrix} = D \tag{36}$$

If so, then

$$AP = P \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & ... & \\ & & & \lambda_n \end{pmatrix} = PD \tag{37}$$

and by writing P composed by its column vectors $P = (\vec{\alpha}_1 \vec{\alpha}_2 ... \vec{\alpha}_n)$ we find for every $i = 1, 2, ..., n$

$$A\vec{\alpha}_i = \lambda_i \vec{\alpha}_i \tag{38}$$

Obviously P is made up by the eigenvectors of A, while the entries of its diagonalized form D are its eigenvalues. Furthermore, for an $n \times n$ matrix A to possess exactly n distintc eigenvalues is a sufficient condition for diagonalizabilty.
Diagonizable matrices are of interest because once diagonalized their powers can be computet in a very efficient manner:

$$\begin{aligned} A^k &= (PDP^{-1})^k = (PDP^{-1}) \cdot (PDP^{-1}) \cdot ... \cdot (PDP^{-1}) \\ &= PD(P^{-1}P)D(P^{-1}P) \cdot ... \cdot (P^{-1}P)DP^{-1} \\ &= PD^k P^{-1} \end{aligned}$$

while the power of a diagonal matrix is just

$$D^k = \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & ... & \\ & & & \lambda_n \end{pmatrix}^k = \begin{pmatrix} \lambda_1^k & & & \\ & \lambda_2^k & & \\ & & ...^k & \\ & & & \lambda_n^k \end{pmatrix} \tag{39}$$

Also matrix exponentials can be computed in this way, since they can be expanded as power series such as below.

2.2 Spin formalism

Our aim is to understand the scaling of Spinach's memory and CPU time consumption. Hence we will examine the mathematical formalism underlying numerical computation.

2.2.1 Quantum states and measurments done on them

Any allowed spin state $|\Psi\rangle$ can be written as a linear superposition of an orthogonal basis set of a Hilbert space spanned by all allowed *azimuthal quantum number* states $|m\rangle$:

$$|\Psi\rangle = \sum_m a_m |m\rangle \tag{40}$$

where the amplitudes are complex $a_m = |a_m| e^{i\phi_m}$ with phase ϕ_m and magnitude $|a_m|$. The $|m\rangle$ can be represented by a proper scaled basis of choice, but the m lable offers a general independant representation.
All measurements to be done on a spin system yield eigenvalues of a linear operator associated with the particular measurement. The corresponding observed physical quantity is called *observable*. Measuring the spin component of a system in one of the basis states along the z-axis S_z thus yields

$$S_z|m\rangle = m|m\rangle \tag{41}$$

The orthogonal basis can be normalized by requiring the inner product of basis vectors to be

$$\langle m|m'\rangle = \delta_{mm'} \tag{42}$$

If a spin system exists in the eigenstate $|m\rangle$ of S_z, then the measurement of S_z will yield

$$\langle m|S_z|m\rangle = m \tag{43}$$

The measurement on a general superposition will yield

$$\langle\Psi|S_z|\Psi\rangle = \sum_{m,m'} a_m^* a_{m'} \langle m'|S_z|m\rangle \tag{44}$$

$$= \sum_{m,m'} a_m^* a_{m'} m \langle m'|m\rangle \tag{45}$$

$$= \sum_{m} |a_m|^2 m \tag{46}$$

due to the orthormality of the basis set.

2.2.2 Density operator and spin ensembles

Due to equation (40) the expectation value of an observable A can be expressed as

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \sum_{m,n} c_m^* c_n \langle m|A|n\rangle \tag{47}$$

Now, when the expectation value of a certain observable is required, we are always interested in the product $c_m^* c_n$ rather than the distinct c_n, thus we can think of a matrix representation of those probabilities and define an operator P with

$$\langle n|P|m\rangle = c_n c_m^* \tag{48}$$

Equation (47) becomes

$$\langle A\rangle = \sum_{m,n} \langle n|P|m\rangle\langle m|A|n\rangle \tag{49}$$

Since $|m\rangle$ form an orthonormal basis set, the results of A and P acting on a basis vector can be expanded in the basis:

$$P|m\rangle = \sum_l a_l |l\rangle = \sum_l \langle l|P|m\rangle|l\rangle \tag{50}$$

$$A|n\rangle = \sum_m a_m |m\rangle = \sum_m \langle m|A|n\rangle|m\rangle \tag{51}$$

$$\Rightarrow PA|n\rangle = \sum_m P|m\rangle\langle m|A|n\rangle \tag{52}$$

$$= \sum_{l,m} |l\rangle\langle l|P|m\rangle\langle m|A|n\rangle \tag{53}$$

$$\Rightarrow \langle n|PA|n\rangle = \sum_{l,m} \langle n|l\rangle\langle l|P|m\rangle\langle m|A|n\rangle \tag{54}$$

$$= \sum_{l,m} \delta_{ln}\langle l|P|m\rangle\langle m|A|n\rangle \tag{55}$$

$$= \sum_m \langle n|P|m\rangle\langle m|A|n\rangle \tag{56}$$

Comparing with equation (49) we find

$$\langle A\rangle = \sum_n \langle n|PA|n\rangle = Tr(PA) = Tr(AP) \tag{57}$$

where Tr is the trace – the total sum of the matrix' diagonal elements.
In EPR we pulse a powder sample. Theoretically this means a measurement on an ensemble of many spin systems with many (most generally different) spin states $|\psi\rangle$ instead of determining the state of a single system. The observable averaged about the whole statistical ensemble is written as

$$\begin{aligned}
\overline{\langle A\rangle} &= \overline{\langle\psi|A|\psi\rangle} && (58)\\
&= \sum_{\psi} p_{\psi}\langle\psi|A|\psi\rangle && (59)\\
&= \sum_{\psi} p_{\psi}\left(\sum_{m,n} c_m^* c_n \langle m|A|n\rangle\right) && (60)\\
&= \sum_{m,n}\left(\sum_{\psi} p_{\psi} c_m^* c_n\right)\langle m|A|n\rangle && (61)\\
&= \sum_{m,n}\overline{c_m^* c_n}\langle m|A|n\rangle && (62)
\end{aligned}$$

where p_{ψ} is an appropriate statistical averaging weight chosen according to the occupancy of $|\psi\rangle$. On this basis we introduce the *density matrix operator*

$$\langle n|\rho|m\rangle = \overline{c_m^* c_n} = \overline{\langle n|P|m\rangle} \tag{63}$$

whereby equation (62) can be expressed in analogy to equation (57) as

$$\overline{\langle A\rangle} = \sum_{n,m}\langle n|\rho|m\rangle\langle m|A|n\rangle = \sum_{n}\langle n|\rho A|n\rangle = Tr(\rho A) = Tr(A\rho) \tag{64}$$

Another beautiful expression for the density matrix can be derived by noticing that

$$\begin{aligned}
\langle n|\psi\rangle\langle\psi|m\rangle &= \langle n|\left(\sum_{n'} c_{n'}|n'\rangle\right)\left(\sum_{m'} c_{m'}^*\langle m'|\right)|m\rangle && (65)\\
&= \sum_{n',m'} c_{n'}c_{m'}^*\langle n|n'\rangle\langle m'|m\rangle = c_n^* c_m = \langle n|P|m\rangle && (66)\\
\Rightarrow |\psi\rangle\langle\psi| &= P \quad ; \quad \overline{|\psi\rangle\langle\psi|} = \rho && (67)
\end{aligned}$$

2.2.3 Liouville equation

Under comparison with the general Schrödinger equation and its complex conjugate below

$$\begin{aligned}
\langle\psi|\frac{\partial}{\partial t}|\psi\rangle &= -i\langle\psi|\mathcal{H}|\psi\rangle && (68)\\
\left(\frac{\partial}{\partial t}\langle\psi|\right)|\psi\rangle &= \sum_{m,n}\frac{\partial c_m^*}{\partial t}c_n\langle m|n\rangle = \sum_{m}\frac{\partial c_m^*}{\partial t}c_m && (69)\\
&= \left(\sum_{m} c_m^*\frac{\partial c_m}{\partial t}\right)^* = \left(\langle\psi|\frac{\partial}{\partial t}|\psi\rangle\right)^* = i\langle\psi|\mathcal{H}|\psi\rangle && (70)
\end{aligned}$$

the density matrix' equation of motion can be derived by differentiating equation (67) with respect to time:

$$\frac{\partial}{\partial t}\rho = \left(\frac{\partial}{\partial t}|\psi\rangle\right)\langle\psi| + |\psi\rangle\left(\frac{\partial}{\partial t}\langle\psi|\right) \tag{71}$$

$$= -i\mathcal{H}|\psi\rangle\langle\psi| + i|\psi\rangle\langle\psi|\mathcal{H} \tag{72}$$

$$= -i(\mathcal{H}\rho - \rho\mathcal{H}) = -i[\mathcal{H}, \rho] \tag{73}$$

2.2.4 Dynamics

In case of a stationary Hamiltonian, the Schrödinger equation

$$i\frac{\partial}{\partial t}|\psi(t)\rangle = \mathcal{H}|\psi(t)\rangle \tag{74}$$

has the solution

$$|\Psi(t)\rangle = U(t)|\psi(0)\rangle \tag{75}$$

where

$$U(t) = e^{-i\mathcal{H}t} \tag{76}$$

is called the *evolution operator*. Equivalently, the Liouville equation has the solution

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| = e^{-i\mathcal{H}t}|\psi(0)\rangle\langle\psi(0)|e^{i\mathcal{H}t} = e^{-i\mathcal{H}t}\rho(0)e^{i\mathcal{H}t} \tag{77}$$

In case of a time-dependent, but piecewise-constant Hamiltonian the solution has the form

$$|\Psi(t)\rangle = \left[\prod_k e^{-i\mathcal{H}_k \Delta t_k}\right]|\Psi(0)\rangle \tag{78}$$

This is the basis of numerical time propagation.

2.2.5 Superoperators, Liouville space

The Hamiltonian $\mathcal{H}$ is an operation defined on the space of vectors, similarly the commutation operator $\mathcal{L} = [\mathcal{H}, \cdot]$ is an operation defined on the space of operators. Thus it is called the *Liouvillian superoperator*. Therefore, the spaces one usually comes to deal with when treating spin dynamics are

- the space where all states live. States are represented as a vector (40) of dimension N, and with the scalar product $\langle\phi|\psi\rangle$ they fulfill every requirement to span an N-dimensional *Hilbert space*. This space is isomorph to $\mathbb{C}^N$.
- the space where all operators which act on spin states live. Operators such as $\mathcal{H}$ are represented by $N \times N$-matrices, thus the space spanned by those operators is N^2-dimensional and isomorph to $\mathbb{C}^{N^2}$. There exist many possible scalar products, so again we deal with a Hilbert space. The special operator space, where we choose $Tr(A^\dagger B)$ as the scalar product is known as the *Liouville space* in spin dynamics.
- the space where all *superoperators* which act on operators live. Superoperators such as $\mathcal{L} = [\mathcal{H}, \cdot]$ are represented by $N^2 \times N^2$ matrices, thus the space spanned by those superoperators is N^4-dimensional and isomorph to $\mathbb{C}^{N^4}$. Again, we chose the scalar product $Tr(A^\dagger B)$ for this Hilbert and call it *superoperator space*.

Now, if we represent states as vectors and operators as matrices, how come we do not have to represent superoperators as more complex objects like "three-dimensional matrices"? The mathematical trick is to stretch the original operator matrix ρ column-wise into a vertical vector:

$$\rho = \left(\vec{\rho}_1, \vec{\rho}_2, \ldots, \vec{\rho}_N\right) \to |\rho\rangle = \begin{pmatrix} \vec{\rho}_1 \\ \vec{\rho}_2 \\ \ldots \\ \vec{\rho}_N \end{pmatrix} \tag{79}$$

Of course, every single column vector of ρ has dimension N, so $|\rho\rangle$ has dimension N^2. The trace of two matrices A, B stretches into a vector scalar product:

$$Tr(A^\dagger B) = \sum_{n,k} A^*_{nk} B_{nk} = \sum_{n'} A^*_{n'} B_{n'} = \langle A|B\rangle \tag{80}$$

This allows the calculation of a matrix scalar product in $O(N^2)$ runtime.
With the operator stretched into a vector, the superoperator can accordingly be stretched into an $N^2 \times N^2$ matrix representation. The matrix version of the Liouvillian is the sum of two Kronecker products

$$\mathcal{L} = E \otimes \mathcal{H}^T - \mathcal{H} \otimes E \tag{81}$$

where E is the $N \times N$ unity matrix.
For visualization, a spin-$\frac{1}{2}$ system with the two-dimensional Hilbert space basis consisting of $|-\frac{1}{2}\rangle$ and $|\frac{1}{2}\rangle$ yields a four-dimensional Liouville space, and as its orthonormal basis we might choose $\frac{1}{2}E$, J_x, J_y and J_z, or E, I_z, $-\frac{1}{\sqrt{2}}J_+$ and $\frac{1}{\sqrt{2}}J_-$, which are all 2×2 matrices. Similarly a spin-1 system with the three-dimensional Hilbert space spanned by $|-1\rangle, |0\rangle$ and $|1\rangle$ requires a nine-dimensional Liouville basis, and in general a spin system of N possible states yields an N^2 dimensional Liouville space (and an N^4 dimensional superoperator space). To illustrate the explosion of dimensions, a spin system of 10 spin-$\frac{1}{2}$ particles allows $N = 2^{10} = 1024$ states, requring an $N^2 = 1,048,576$ dimensional Liouville basis. Thus in numerical computation this basis is reduced under loss of information to yield acceptable memory costs. The next section treats the question, how to choose an apropriate basis out of many orthonormal possibilities.

2.2.6 Choice of basis set and irreducible spherical tensors

When we are looking for a suitable basis of the Liouville space to conduct some spin dynamics simulation, the perfect choice would be *eigenoperators* S_k of the Liouvillian, since they are invariant under all interactions of the system:

$$\mathcal{L}S_k = l_k S_k \tag{82}$$

To find those eigenoperators in their vector form, one could diagonalize the Liouvillians matrix representation. Unfortunately the computation costs would be enourmous due to the N^4 dimensions of the Liouville space. A wise choice would be a set of eigenoperators invariant under commutation with J_z, since this operator characterizes the dominating Zeeman interaction in EPR. Or even better, a set of operators invariant under rotations, since we have to examine the spin system from many different angles to average the powder spectrum.
As we know, the angular momentum operators J_x, J_y and J_z generate rotations. It is possible to define a family of operators T_{lm} called *irreducible spherical tensors (IST)* of rank l and order m, which fulfill the commutation relations

$$[J_\pm, T_{lm}] = \sqrt{l(l+1) - m(m \pm 1)}\,T_{l(m\pm1)} \tag{83}$$

$$[J_z, T_{lm}] = mT_{lm} \tag{84}$$

In the space of operators they are the analogon to the spherical harmonics in the space of wavefunctions, for every l there exist $2l+1$ independent IST with $m = -l, -l+1, \ldots, l-1, l$ and any rotation transforms T_{lm} into a linear combination of $T_{lm'}$ with same l:

$$R(\alpha,\beta,\gamma)\ T_{lm} = \sum_{m'=-l}^{l} \mathfrak{D}^{(l)}_{m',m}(\alpha,\beta,\gamma)\ T_{lm'} \tag{85}$$

The matrix elements $\mathfrak{D}^{(l)}_{m,m'}(\alpha.\beta,\gamma)$ are called *Wigner functions* and make up the *Wigner rotation matrix* of rank l corresponding to a certain rotation $R(\alpha,\beta,\gamma)$. They can be evaluated with the spherical harmonics

$$\mathfrak{D}^{(l)}_{m,m'}(\alpha.\beta,\gamma) = \langle Y_{lm}|R(\alpha,\beta,\gamma)|Y_{lm'}\rangle \tag{86}$$

Just as the spherical harmonics Y_{lm} form an orthonormal basis on the unit sphere of the wave functions' Hilbert space, do all IST T_{lm} form an orthonormal basis on the Liouville space of operators, and thus any operator, e.g. the density matrix ρ of dimension N^2, may be expanded in a linear combination of IST:

$$\rho = \sum_{l=0}^{N-1} \sum_{m=-l}^{l} a_{lm} T_{lm} \tag{87}$$

Obviously, a spin-$\frac{1}{2}$ density matrix of dimension $N^2 = 4$ can be fully represented by the single zero-order IST and the three first-order IST, while for a $N^2 = 9$ Liouville space all IST of second rank are required as well.
The lowerst rank IST is the identity operator, the first rank IST are linear superpositions of J_x, J_y and J_z. All higher rank IST $T_{LM}(J_1, J_2)$ can be formed as products of lower rank IST following the rule for combining angular momenta:

$$T_{LM}(J_1, J_2) = \sum_{m_1,m_2} \langle l_1 m_1 l_2 m_2 | LM\rangle\ T_{l_1 m_1}(J_1)\ T_{l_2 m_2}(J_2) \tag{88}$$

where the *Clebsch-Gordan coefficients* $\langle l_1 m_1 l_2 m_2 | LM\rangle$ are zero except for $m_1 + m_2 = M$. K ranges from $|k_1 - k_2|$ to $k_1 + k_2$. The new IST again obey the rotational features above. Taking $k_1 = k_2 = 1$ we can produce the nine tensors below for $J_1 = J_2 = J$

$$\begin{array}{llllll} & & & & T_{2-2} & = \frac{1}{2}J_-^2 \\ & & T_{1-1} & = \frac{1}{\sqrt{2}}J_- & T_{2-1} & = \frac{1}{2}(J_zJ_- + J_-J_z) \\ T_{00} & = E & T_{10} & = J_z & T_{20} & = \frac{1}{\sqrt{6}}(3J_z^2 - 2E) \\ & & T_{11} & = -\frac{1}{\sqrt{2}}J_+ & T_{21} & = -\frac{1}{2}(J_zJ_+ + J_+J_z) \\ & & & & T_{22} & = \frac{1}{2}J_+^2 \end{array} \tag{89}$$

while for $J_1 \neq J_2$ we can produce 16 independent tensors, of which the second rank tensors read

$$\begin{aligned} T_{2-2} &= J_{1-}J_{2-} \\ T_{2-1} &= (J_{1z}J_{2-} + J_{1-}J_{2z}) \\ T_{20} &= \sqrt{\tfrac{2}{3}}(3J_{1z}J_{2z} - J_1 \cdot J_2) \\ T_{21} &= -(J_{1z}J_{2+} + J_{1+}J_{2z}) \\ T_{22} &= -J_{1+}J_{2+} \end{aligned} \tag{90}$$

From there on it would be possible to construct IST for an arbitrary number of spins, but looking at the most general interaction included in an EPR Hamiltonian, the maximum number of interacting spins amounts to two, e.g. $\vec{L}$ and $\vec{S}$ coupled by the interaction tensor A

$$\vec{L} \cdot A \cdot \vec{S} = \sum_{k,n} a_{kn} L_k S_n \quad \text{with} \quad k, n = x, y, z \tag{91}$$

of which linear and quadratic interactions form special cases. Having a linear superposition of $L_k S_n$ terms, the interaction must be expandeble in a basis consisting of rank two IST at maximum. In praxis, first rank terms' contribution diminishes and hence is ignored:

$$\vec{L} \cdot A \cdot \vec{S} = \sum_{l=0}^{2} \sum_{m=-l}^{l} \alpha_{lm} T_{lm}(L, S) \approx \alpha_{00} T_{00} + \sum_{m=-2}^{2} \alpha_{2m} T_{2m}(L, S) \tag{92}$$

Therefore the whole anisotropic Hamiltonian consisting of scalar-spin and spin-spin interactions of N spins may be expanded in second rank IST representation (ignoring quadratic self-interaction):

$$\mathcal{H} = \mathcal{H}_{\text{iso}} + \sum_{L} \sum_{m=-2}^{2} \alpha_{L,m}\ T_{2m}(L) + \sum_{L,S \neq L} \sum_{m=-2}^{2} \beta_{L,S,m}\ T_{2m}(L, S) \tag{93}$$

The special feature of this expansion is its behaviour under rotations $R(\alpha, \beta, \gamma)$ – the Hamiltonian inherits the IST's rotational transformation rule (85):

$$R\mathcal{H} = \mathcal{H}_{\text{iso}} + \sum_{L} \sum_{m=-2}^{2} \alpha_{L,m}\ RT_{2m}(L) + \sum_{L,S \neq L} \sum_{m=-2}^{2} \beta_{L,S,m}\ RT_{2m}(L, S) \tag{94}$$

$$= \mathcal{H}_{\text{iso}} + \sum_{L} \sum_{m=-2}^{2} \alpha_{L,m} \sum_{m'=-2}^{m'} \mathfrak{D}^{(2)}_{mm'} T_{2m'}(L) + \sum_{L,S \neq L} \sum_{m=-2}^{2} \beta_{L,S,m} \sum_{m'=-2}^{2} \mathfrak{D}^{(2)}_{mm'} T_{2m'}(L, S) \tag{95}$$

$$= \mathcal{H}_{\text{iso}} + \sum_{m=-2}^{2} \sum_{m'=-2}^{2} \mathfrak{D}^{(2)}_{mm'} \left(\sum_{L} \alpha_{L,m} T_{2m'}(L) + \sum_{L,S \neq L} \beta_{L,S,m} T_{2m'}(L, S) \right) \tag{96}$$

$$= \mathcal{H}_{\text{iso}} + \sum_{m,m'=-2}^{2} \mathfrak{D}^{(2)}_{mm'} Q_{mm'} \quad \text{with} \quad Q_{mm'} = \sum_{L} \alpha_{L,m} T_{2m'}(L) + \sum_{L,S \neq L} \beta_{L,S,m} T_{2m'}(L, S) \tag{97}$$

The 25 elements $Q_{mm'}$ of the 5×5 matrix Q are called *rotational basis operators*. They store the anisotropic part of any spin system's Hamiltonian such that any rotational orientation of the system yields a linear combination of this rotational basis with precomputable Wigner function coefficients. Notice that each $Q_{mm'}$ has dimensions $N \times N$.

3 Spinach

The Matlab library *Spinach* supplies efficient methods for large-scale spin dynamics simulations. It consists of the *kernel* with the implementation of general spin dynamics simulation techniques and the *user-land* with a collection of different experiements to perform. Basically, the user prepares the description of a spin system, which is then translated by the kernel into the most efficient basis sets, superoperators, etc. The user-land decides how to deal with those objects, whether to apply a pre-established experiment, or whether to perform the kernel's simulation

procedures manually. Though Spinach is able to simulate numerous kinds of experiments, in this work we are going to restrict ourselves to standard EPR experiments.
Using the theoretical basis introduced above, the procedure of an EPR simulation comes down to the following key steps:

1. Spinach constructs the isotropic and anisotropic part of the Liouvillian in the rotational basis ...
2. ... and propagates the evolution of the density matrix through the pulse secquence and afterwards by applying the Liouville equation (73), ...
3. ...then determines the transversal magnetization depending on S_+, a superposition of spin in x- and y-direction, at acquisition time using equation (**??**).

For the $\frac{\pi}{2}$-pulsed EPR, the user-land readily provides the method `pulse_acquire`.
In the following the preparation of input data and computation flow are summarized, such that the idea where to implement parallelization becomes obvious.

3.1 A Spinach EPR Simulation

3.1.1 Typical input file

This file prepares a typical spin system and conducts a π-pulsed EPR experiment on it. The data structure `sys` contains information about the spin system and the experimental setup, `inter` represents the linear and bilinear interactions of the spins, `bas` specifies the state basis set to be used and `parameters` specifies the enquired simulation results.

```
function jlh_3spins()

% Set the simulation parameters
sys.magnet=3.356;
sys.regime='powder';
bas.mode='ESR-1';
sys.tols.grid_rank=101;
```

Specifies $B_0 = 3.356T$ and tells Spinach to average the spectrum over uniformly distributed orientations in a “powder”. The mode “ESR-1” generates a complete state space for all electrons, but reduces the state space for all nuclei in a certain way to be efficient enough and still yield reasonable EPR results. The grid rank 101 chooses a certain Lebedev grid of orientations to average about.

```
% Interactions
sys.isotopes={'E','14N', '1H'};
inter.zeeman.matrix=cell(3,1);
inter.zeeman.matrix{1,1}=[ 2.0056023 -0.0013775 -0.0004019; -0.0008185 2.0038816 0.0002087;
    -0.0002747 0.0001729 2.0062982];
inter.coupling.matrix=cell(3,3);
inter.coupling.matrix{1,2}=1e6*[29.4479  3.9997  -0.4979;   3.9997  76.1445  -14.8367;  -0.4979
    -14.8367  38.4285]; %92.815191
inter.coupling.matrix{1,3}=1e6*[-1.2922  2.0819  -1.9943;  2.0819  -1.407  -1.7023;  -1.9943
    -1.7023  -1.5011]; %5.3217912
```

Advises Spinach to prepare a spin system of an unpaired electron, a nitrogen nucleus and a proton spin. The Zeeman matrix states the 3×3 g-Tensor, while the coupling matrices state the 3×3 A-tensors accounting for the hyperfine interactions between electron spin and all other spins.

```
% Set the sequence parameters
parameters.offset=0;
parameters.sweep=1e9;
parameters.npoints=512;
parameters.zerofill=1024;
parameters.spins='E';
```

```
21 parameters.axis_units='Gauss';
22 parameters.derivative=0;
```

Sets parameters for the experiment to simulate: `npoints` determines the number of time steps in the simulation, `sweep` chooses the spectral window's width, and thus the duration of one time step, *zerofill* sets the FID zero-filling and `spins` selects the spins to be pulsed and detected – the electron spin in our case.

```
23 % Run Spinach
24 spin_system=create(sys,inter);
25 spin_system=basis(spin_system,bas);
26 fid=pulse_acquire(spin_system,parameters);
```

The first kernel functions to be called are `create(sys,inter)` and `basis(spin_system,bas)`. Former returns the data structure `spin_system`, which can be handed to the kernel lateron to reference to our spin system, e.g. to fetch the Liouvillian in question. `pulse_acquire(spin_system, para` finally conducts the π-pulsed EPR and returns the time-resolved FID.

```
27 % Apodization
28 fid=apodization(fid,'crisp-1d');
29
30 % Perform Fourier transform
31 spectrum=fftshift(fft(fid,parameters.zerofill));
32
33 % ...
34
35 end
```

The "crisp" apodization modulates the FID by a declining cosine window function in the interval $[0, \frac{\pi}{2}]$

$$\mathrm{FID}'(t) = \mathrm{FID}(t) \cdot \cos^8\left(\frac{\pi}{2} \cdot \frac{t}{L_{\mathrm{FID}}}\right) \tag{98}$$

Line 31 finally performs Fast Fourier Transform to generate the frequency domain spectrum.

3.1.2 pulse_acquire

```
function fid=pulse_acquire(spin_system,parameters,L,rho)

%...

% Compute the digitization parameters.
timestep=1/parameters.sweep;

% Generate the basic operators
Lp=operator(spin_system,'L+',parameters.spins);
Ly=(Lp-Lp')/2i;
```

The function `operator` prepares the raising operator L_+ and then constructs

$$L_y = \frac{1}{2i}(L_+ - L_-) = \frac{1}{2i}(L_+ - L_+^\dagger) \tag{99}$$

The apostrophe in the Matlab code marks the complex conjugate transposition $L_+^\dagger$ of L_+. The relation above can be easily found by realizing that the raising and the lowering operator form a Hermitian conjugate pair $L_- = L_+^\dagger$

```
% Set the secularity assumptions
spin_system=secularity(spin_system,'nmr');

% Start from thermal equilibrium
rho=equilibrium(spin_system);
```

The `secularity` function decides about the importance of interactions. In high field EPR and NMR, only the electrons' states are accounted for fully, whereas the nuclei's spins are only evaluated in z-direction. Density matrix `rho` is initialized with the termal equilibrium state of the spin system.

```
[Iso,Q]=h_superop(spin_system);
```

The isotropic part of the Liouvillian is stored in `Iso`, while `Q` is the set of five rank-2 *irreducible spherical tensors* representing the Liouvillian's anisotropic part in the rotational basis. The dimensions of those two matrices determine Spinach's memory consumption.

```
% Get the spherical averaging grid
grid=load([spin_system.sys.root_dir spin_system.sys.slash 'exp' ...
           spin_system.sys.slash 'grids' ...
           spin_system.sys.slash 'lebedev_rank_' num2str(spin_system.tols.grid_rank) '.dat'],
              'ASCII');
grid_size=size(grid,1); phi=pi*grid(:,1)/180; theta=pi*grid(:,2)/180; weight=grid(:,3);
```

The Lebedev grid is read from a file holding all precomputed orientations on the unit sphere. The number of points for a Lebedev grid of certain rank can be found in table (??).

```
% Get the orientation array
L_aniso=orientation(Q,[phi theta zeros(size(theta))]);
L=blkdiag(L_aniso{:})+kron(speye(grid_size),Iso);
L=clean_up(spin_system,L,spin_system.tols.liouv_zero);
```

`orientation` rotates the anisotropic part of the Liouvillian in the rotational basis by the specified Euler angles and creates a cell array of operators, one for each orientation. The Liouvillian block matrix `L` has a diagonal element for every Lebedev orientation n:

$$L = L_{\text{aniso}} + I \otimes L_{\text{iso}} = \begin{pmatrix} L_{\text{aniso},1} & & & \\ & L_{\text{aniso},2} & & \\ & & \dots & \\ & & & L_{\text{aniso},n} \end{pmatrix} + \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & \dots & \\ & & & 1 \end{pmatrix} \otimes L_{\text{iso}} \tag{100}$$

```
% Get the initial and the detection states
rho=kron(ones(grid_size,1),rho);
coil=kron(weight,state(spin_system,'L+',parameters.spins));
```

The density matrix is duplicated n times in a column vector to propagate one for each orientation, and similarly the observable to be detected is duplicated and the Lebedev weights are applied in a column vector `coil`. In the experimental setup the detection coil measures independently the magnetization in x- and y-direction, which correspond to the horizontal spin state $S_+ = S_x + iS_y$, `'L+'` in Spinach notation.

```
% Apply the pulse
rho=step(spin_system,kron(speye(grid_size),Ly),rho,pi/2);

fid=evolution(spin_system,L,coil,rho,timestep,parameters.npoints-1,'observable');

end
```

Generally, `step(spin_system,L,rho,dt)` propagates the density matrix `rho` under the influence of a certain Liouvillian `L` by a time step `dt`. Because `step` makes uses of the evolution operator (76) internally, it can conduct a 90° rotation around the y-axis by replacing the time step by an angle $\frac{\pi}{2}$ and the Liouvillian by the spin operator L_y, letting it construct the rotation operator

$$R_y(\tfrac{\pi}{2}) = e^{-i\frac{\pi}{2}L_y} \tag{101}$$

in analogy to equation (11). This just rotates all spins into the x-y-plane, just as a $\frac{\pi}{2}$-pulse will do. Sequently, `evolution` can be regarded as a sequence of `npoints` `step`-functions propagating the density matrix through the whole time interval by steps of duration `timestep` by applying Liouvillian `L`. In addition, the observable `coil` is evaluated for every single step, recording the time resolved FID with magnetization in x-direction as its real part and magnetization in y-direction as its imaginary part.

4 Parallelization

4.1 Clusters and platforms

4.1.1 Sheldon

4.1.2 Soroban

4.2 Matlab parallel computing toolbox

4.2.1 Matlab licences

4.2.2 Matlab - Linux interaction

4.3 Spinach modification

4.3.1 Master process

4.3.2 Child processes

4.3.3 Finalization process

4.4 Benchmarking

5 Conclusion and outlook

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