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Large Scale Parallel Simulation of EPR Lineshape Spectra

Abstract: *Electron Paramagnetic Resonance* is a spectroscopy method to examine systems of unpaired electron spins. *Spinach*[1] is a Matlab library to simulate different kinds of spin system experiemnts, including EPR. The aim of this work is to make use of Spinach and adopt parallel computing methods on Linux clusters to accelerate the calculation of EPR lineshape spectra.

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Contents

1 Basics

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

1.1 Fourier transorm

What happens during EPR from a quite general point of view? We excite a certain system with an electromagnetic signal and measure the system's response. In other words, the system Φ uses the time-resolved input $x(t)$ to generate output $y(t)$:

$$y(x) = \Phi\{x(t)\} \tag{1}$$

If we assume the system to be linear

$$\Phi\{\alpha x_1(t) + \beta x_2(t)\} = \alpha y_1(t) + \beta y_2(t) \tag{2}$$

and time-invariant

$$\Phi\{x(t - t_0)\} = y(t - t_0) \tag{3}$$

we can expand the input function in a series of some orthonormal basis set $g_k(t)$, or in some integral transform in the continuous limit with basis $g(\tau, t)$ and define the system completely by its set of responses to the basis functions:

$$x(t) = \sum_k \chi_k g_k(t) = \int_{-\infty}^{\infty} \chi(\tau) g(\tau, t) d\tau \tag{4}$$

$$\Rightarrow \Phi x(t) = \sum_k \chi_k \Phi\{g_k(t)\} = \int_{-\infty}^{\infty} \chi(\tau) \Phi\{g(\tau, t)\} d\tau \tag{5}$$

Using the definition of the Dirac delta function and applying our LTI (linear time-invariant) system

$$x(t) = \int_{-\infty}^{\infty} x(\tau)\delta(\tau - t) d\tau \tag{6}$$

$$\Rightarrow \Phi\{x(t)\} = \int_{-\infty}^{\infty} x(\tau)\Phi\{\delta(\tau - t)\} d\tau = \int_{-\infty}^{\infty} x(\tau) h(\tau - t) d\tau = x(t) * h(t) \tag{7}$$

we find the system's output to be the convolution of the input wit its *pulse response* or *free induction decay (FID)* $h(t) = \Phi\{\delta(t)\}$. Furthermore, harmonics are eigenfunctions of LTI systems, and the *frequency response* or *spectrum* $H(\omega)$ is just the Fourier transform of the system's FID:

$$\Phi\{e^{i\omega t}\} = \int_{-\infty}^{\infty} e^{i\omega t} h(\tau - t) d\tau = e^{i\omega t} \int_{-\infty}^{\infty} e^{i\omega(\tau - t)} h(\tau - t) d\tau = e^{i\omega t} \int_{-\infty}^{\infty} e^{i\omega(\tau)} h(\tau) d\tau = H(\omega) e^{i\omega t} \tag{8}$$

1.2 Matrix formalism

1.2.1 Diagonizable matrices

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

$$P^{-1}AP = \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ldots & \\ & & & \lambda_n \end{pmatrix} = D \tag{9}$$

If so, then

$$AP = P \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & ... & \\ & & & \lambda_n \end{pmatrix} = PD \tag{10}$$

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

$$A\vec{\alpha}_i = \lambda_i \vec{\alpha}_i \tag{11}$$

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:

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

while the power of a diagonal matrix is just

$$D^k = \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & ... & \\ & & & \lambda_n \end{pmatrix}^k = \begin{pmatrix} \lambda_1^k & & & \\ & \lambda_2^k & & \\ & & ...^k & \\ & & & \lambda_n^k \end{pmatrix} \tag{12}$$

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

1.2.2 Matrix exponentials

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

$$e^x = \sum_{k=0}^{\infty} \frac{x^k}{k!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + ... \tag{13}$$

can be easily applied to square matrices, eg.:

$$e^{i\phi A} = I + i\phi A - \frac{(\phi A)^2}{2!} - i\frac{(\phi A)^3}{3!} + \frac{(\phi A)^4}{4!} + i\frac{(\phi A)^5}{5!} - ... \tag{14}$$

1.3 Spin formalism

Though the basic mechanisms of EPR can be understood on the basis of a semi classical approach, a quantum mechanical approach is necessary to account for many more subtle features. Here one finds a short introduction to the quantum mechanical formalism involved in EPR theory.

1.3.1 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 an Hilbert vector space spanned by all allowed *azimuthal quantum number* states $|m\rangle$:

$$|\Psi\rangle = \sum_m a_m |m\rangle \tag{15}$$

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

$$S_z|m\rangle = m|m\rangle \tag{16}$$

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

$$\langle m|m'\rangle = \delta_{mm'} \tag{17}$$

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

$$\langle m|S_z|m\rangle = m \tag{18}$$

The measurement on a general superposition will yield

$$\langle\Psi|S_z|\Psi\rangle = \sum_{m,m'} a_m^* a_{m'} \langle m'|S_z|m\rangle \tag{19}$$

$$= \sum_{m,m'} a_m^* a_{m'} m \langle m'|m\rangle \tag{20}$$

$$= \sum_{m} |a_m|^2 m \tag{21}$$

due to the orthormality of the basis set.

1.3.2 Density operator and spin ensembles

Due to equation (15) the expectation value of an observable A can be expressed as

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \sum_{m,n} c_m^* c_n \langle m|A|n\rangle \tag{22}$$

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

$$\langle n|P|m\rangle = c_n c_m^* \tag{23}$$

Equation (22) becomes

$$\langle A\rangle = \sum_{m,n} \langle n|P|m\rangle\langle m|A|n\rangle \tag{24}$$

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:

$$P|m\rangle = \sum_l a_l|l\rangle = \sum_l \langle l|P|m\rangle|l\rangle \tag{25}$$

$$A|n\rangle = \sum_m a_m|m\rangle = \sum_m \langle m|A|n\rangle|m\rangle \tag{26}$$

$$\Rightarrow PA|n\rangle = \sum_m P|m\rangle\langle m|A|n\rangle \tag{27}$$

$$= \sum_{l,m} |l\rangle\langle l|P|m\rangle\langle m|A|n\rangle \tag{28}$$

$$\Rightarrow \langle n|PA|n\rangle = \sum_{l,m} \langle n|l\rangle\langle l|P|m\rangle\langle m|A|n\rangle \tag{29}$$

$$= \sum_{l,m} \delta_{ln}\langle l|P|m\rangle\langle m|A|n\rangle \tag{30}$$

$$= \sum_m \langle n|P|m\rangle\langle m|A|n\rangle \tag{31}$$

Comparing with equation (24) we find

$$\langle A\rangle = \sum_n \langle n|PA|n\rangle = Tr(PA) = Tr(AP) \tag{32}$$

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

$$\overline{\langle A\rangle} = \overline{\langle\psi|A|\psi\rangle} \tag{33}$$

$$= \sum_\psi p_\psi\langle\psi|A|\psi\rangle \tag{34}$$

$$= \sum_\psi p_\psi \left(\sum_{m,n} c_m^* c_n\langle m|A|n\rangle\right) \tag{35}$$

$$= \sum_{m,n} \left(\sum_\psi p_\psi c_m^* c_n\right)\langle m|A|n\rangle \tag{36}$$

$$= \sum_{m,n} \overline{c_m^* c_n}\langle m|A|n\rangle \tag{37}$$

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*

$$\langle n|\rho|m\rangle = \overline{c_m^* c_n} = \overline{\langle n|P|m\rangle} \tag{38}$$

whereby equation (37) can be expressed in analogy to equation (32) as

$$\overline{\langle A\rangle} = \sum_{n,m} \langle n|\rho|m\rangle\langle m|A|n\rangle = \sum_n \langle n|\rho A|n\rangle = Tr(\rho A) = Tr(A\rho) \tag{39}$$

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

$$\langle n|\psi\rangle\langle\psi|m\rangle = \langle n|\left(\sum_{n'} c_{n'}|n'\rangle\right)\left(\sum_{m'} c^*_{m'}\langle m'|\right)|m\rangle \tag{40}$$

$$= \sum_{n',m'} c_{n'}c^*_{m'}\langle n|n'\rangle\langle m'|m\rangle = c^*_n c_m = \langle n|P|m\rangle \tag{41}$$

$$\Rightarrow |\psi\rangle\langle\psi| = P \quad ; \quad \overline{|\psi\rangle\langle\psi|} = \rho \tag{42}$$

1.3.3 Liouville equation

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

$$\langle\psi|\frac{\partial}{\partial t}|\psi\rangle = -i\langle\psi|\mathcal{H}|\psi\rangle \tag{43}$$

$$\left(\frac{\partial}{\partial t}\langle\psi|\right)|\psi\rangle = \sum_{m,n}\frac{\partial c^*_m}{\partial t}c_n\langle m|n\rangle = \sum_m \frac{\partial c^*_m}{\partial t}c_m \tag{44}$$

$$= \left(\sum_m c^*_m \frac{\partial c_m}{\partial t}\right)^* = \left(\langle\psi|\frac{\partial}{\partial t}|\psi\rangle\right)^* = i\langle\psi|\mathcal{H}|\psi\rangle \tag{45}$$

the density matrix' equation of motion can be derived by differentiating equation (42) with respect to time:

$$\frac{\partial}{\partial t}\rho = \left(\frac{\partial}{\partial t}|\psi\rangle\right)\langle\psi| + |\psi\rangle\left(\frac{\partial}{\partial t}\langle\psi|\right) \tag{46}$$

$$= -i\mathcal{H}|\psi\rangle\langle\psi| + i|\psi\rangle\langle\psi|\mathcal{H} \tag{47}$$

$$= -i(\mathcal{H}\rho - \rho\mathcal{H}) = -i[\mathcal{H},\rho] \tag{48}$$

1.3.4 Dynamics

In case of a stationary Hamiltonian, the Schrödinger equation

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \mathcal{H}|\Psi(t)\rangle \tag{49}$$

has the solution

$$|\Psi(t)\rangle = U(t)|\Psi(0)\rangle \tag{50}$$

where

$$U(t) = e^{-i\mathcal{H}t} \tag{51}$$

is called the *evolution operator*.
In case of a time-dependent, but piecewise-constant Hamiltonian the solution has the form

$$|\Psi(t)\rangle = \left[\prod_k e^{-i\mathcal{H}_k\Delta t_k}\right]|\Psi(0)\rangle \tag{52}$$

2 $\frac{\pi}{2}$-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 magnetic dipole vanish, and enabling the system to be accessible by NMR, and according to [4, Chap. 4, p. 107], NMR technique offer two further "advantages" in comparison with EPR: First, relaxation time of spin electrons is very short compared with nuclei; second the nuclear spin Hamiltonian offers a broader diversity of interactions giving insight to the system's properties. Nevertheless, EPR experiments are only suitable to investigate systems with unpaired electrons, 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 the emitted radiation during the relaxation process. When we place a spin sytem 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 system. The pulse $\vec{B}_1 = B_1\hat{x}e^{i(\vec{k}\cdot\vec{r}-\omega_1 t} \cdot u(t_0 - t)$ linearly polarized in x-direction will tilt the electron spins and disturb the equilibrium in a way we are going to examine in the following:

2.1 Spin system Hamiltonian

The Hamiltonian of an unpaired spin electron system will exhibit several perturbation terms of different nature:

$$\mathcal{H} = [\mathcal{H}_{EZ} + \mathcal{H}_{ECS} + \mathcal{H}_{LS}] + [\mathcal{H}_{HF}] + [\mathcal{H}_{NZ} + \mathcal{H}_{NCS} + \text{weaker interactions}] \tag{53}$$

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 dependant 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

   $$E^1_{\pm} = \pm\mu_B\gamma_J B_0 m_J \tag{54}$$

   resulting from algebraic acrobatics with the Hamiltonian above [3, insert]. Boltzmann statistics yields the relation for the equilibrium occupancy of states

   $$\frac{N_+}{N_-} = e^{-\frac{\Delta E}{k_B T}} \tag{55}$$

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* $\sigma_S(t)$:

   $$\vec{B}_{\text{eff}}(t) = -\sigma_S(t)\cdot\vec{B}_0 \tag{56}$$

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 to 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.

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

   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 $\mathbf{I}$.
   $$\vec{B}_{\text{eff}}(t) = -\sigma_I(t) \cdot \vec{B}_0 \tag{57}$$

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 are neglected in this work.

2.2 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*:

$$\mathcal{H}_{\text{linear}} = \mu_B \mathbf{S} \cdot g \cdot \vec{B}_0 \tag{58}$$

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:

$$\mathcal{H}_{\text{bilinear}} = \mathbf{S} \cdot A \cdot \mathbf{I} \tag{59}$$

Those interaction tensors are diagonizable matrices. Assume the 3×3 g-tensor has three eigenvalues g_{xx}, g_{yy} and g_{zz} on his diagonal. g is called rhombic in the common case $g_{xx} \neq g_{yy} \neq g_{zz}$. In the special case $g_{xx} = g_{yy} = g_{zz}$ g is said to be *isotropic*. In EPR practice, g and other tensors are usually quantified by their isotropic part and the anisotropic deviation from it:

$$g_{\text{iso}} = \frac{1}{3} Tr(g) = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) \tag{60}$$
$$g_{\text{aniso}} = g - g_{\text{iso}} \cdot I \tag{61}$$

where I is the identity matrix.

2.2.1 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. Since the electron's magnetic moment is proportional to its angular momentum $\vec{\mu} = \gamma \vec{J}$ with the *Landé g-factor* γ, the interaction energy $E = -\vec{\mu} \cdot \vec{B}$ and thus the Hamiltonian, the evolution operator and the Schrödinger equation's solution can be expressed as

$$\mathcal{H} = -\gamma B_0 J_z, \quad U(t) = e^{i\gamma B_0 t J_z}, \quad \Psi(t) = e^{i\gamma B_0 t J_z}\Psi(0) = e^{i\omega_0 t J_z}\Psi(0) \quad \text{with} \quad \omega_0 = \gamma B_0 \tag{62}$$

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

$$R_z(\phi) = e^{-i\phi J_z} \tag{63}$$

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.
Suppose we are changing from the lab frame to a frame which is rotating anticlockwise with angular velocity ω_1 around the z-Axis. The passive clockwise rotation by $\omega_1 t$ converting from rotating frame to inertial frame is realized by the operator $R_z(\omega_1 t) = e^{-i\omega_1 t I_z}$, while an passive anticklockwise transition from lab frame to rotating frame is realized by the operator $R_z(-\omega_1 t) = e^{i\omega_1 t I_z}$. Thus we can apply any operator A we know in the inertial frame, packed in a sandwich of rotational operators $R(-\omega_1 t)AR(\omega_1 t)$, to receive the value of an observable in the rotating frame. Let's convert the Hamiltonian to our rotating frame:

$$\mathcal{H}_{\text{rot}} = e^{i\omega_1 t I_z}\mathcal{H}e^{-i\omega_1 t I_z} \tag{64}$$

We transform the Schrödinger equation for wave $|\Phi(t)\rangle$ to the rotating frame with the rotated wave function $|\Phi'(t)\rangle$:

$$i\frac{\partial}{\partial t}|\Phi'(t)\rangle = \mathcal{H}|\Phi'(t)\rangle \tag{65}$$

$$\Rightarrow i\frac{\partial}{\partial t}\left(e^{-i\omega_1 t I_z}|\Phi'(t)\rangle\right) = \left(e^{-i\omega_1 t I_z}\mathcal{H}_{\text{rot}}e^{i\omega_1 t I_z}\right)\left(e^{-i\omega_1 t I_z}|\Phi'(t)\rangle\right) \tag{66}$$

Differentiating the equation's left hand side and rearranging yields

$$i\frac{\partial}{\partial t}|\Phi'(t)\rangle = (\mathcal{H}_{\text{rot}} - \omega_1 I_z)|\Phi'(t)\rangle \tag{67}$$

$$= \mathcal{H}'|\Phi'(t)\rangle \quad \text{with} \quad \mathcal{H}' = e^{i\omega_1 t I_z}\mathcal{H}e^{-i\omega_1 t I_z} - \omega_1 I_z \tag{68}$$

2.3 Resonant frequency field

Suppose we observe the equilibrium system due to Zeeman interaction $\mathcal{H} = -\gamma B_0 I_z$ from a rotating frame. According to equation (68)

$$\mathcal{H}' = -\gamma(B_0 + \frac{\omega_1}{\gamma})I_z \tag{69}$$

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 it appear stationary.
Now switching on the pulse B_1 in x-direction modifies the lab frame Hamiltonian[2]

$$\mathcal{H} = -\gamma B_0 I_z - 2\gamma B_1 \cos(\omega_1 t)I_x \tag{70}$$

and the rotating frame Hamiltonian

$$\mathcal{H}' = -\gamma(B_0 + \frac{\omega_1}{\gamma}I_z) - \gamma B_1 I_x \tag{71}$$

At resonant frequency the field in z-direction vanishes and the field component in x-direction causes a simple precession of the system's spin around the magnetic field axis at frequency $\omega_2 = -\gamma B_1$ in the rotating frame. Choosing an appropriate duration of the pulse $\omega_2 t_p = \frac{\pi}{2}$, the equilibrium magnetisation of the sample will be disturbed, since the system's spins are all tilted by 90° around the x-axis into the x-y-plane.

[2]see [4, Chap. 4.2.2 The resonant radiofrequency field, p.111f]

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 ...
2. ... and calculates the evolution of the density matrix through the pulse secquence and afterwards by propagating the Liouville equation (48), ...
3. ...then determines the transversal magnetization deppending on S_+, a superposition of spin in x- and y-direction, at acquisition time using equation (??).

For the π-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.

```
15 % Set the sequence parameters
16 parameters.offset=0;
17 parameters.sweep=1e9;
18 parameters.npoints=512;
19 parameters.zerofill=1024;
20 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 $[0, \frac{\pi}{2}]$

$$\mathrm{FID}'(t) = \mathrm{FID}(t) \cdot \cos^8\left(\frac{\pi}{2} \cdot \frac{t}{L_{\mathrm{FID}}}\right) \tag{72}$$

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

$$L_y = \frac{1}{2i}(L_+ - L_-) = \frac{1}{2i}(L_+ - L_+^\dagger) \tag{73}$$

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 fore 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:

$$L = L_{\text{aniso}} + I \otimes L_{\text{iso}} = \begin{pmatrix} L_{\text{aniso},1} & & & \\ & L_{\text{aniso},2} & & \\ & & \dots & \\ & & & L_{\text{aniso},n} \end{pmatrix} + \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & \dots & \\ & & & 1 \end{pmatrix} \otimes L_{\text{iso}} \tag{74}$$

```
% 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 (51) 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

$$R_y(\tfrac{\pi}{2}) = e^{-i\frac{\pi}{2}L_y} \tag{75}$$

in analogy to equation (63). 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.

References

[1] Dr. Ilya Kuprov, *Spin Dynamics, Lecture 1 - 10*. University of Oxford, 2011.

[2] H.J. Hogben, M. Krzystyniak, G.T.P. Charnock, P.J. Hore, Ilya Kuprov, *Spinach - A software library for simulation of spin dynamics in large spin systems*. Journal of Magnetic Resonance, 208 (2011) 179-194.

[3] David J. Griffiths, *Introduction to Quantum Mechanics*. Pearson, 2nd Edition, 2005.

[4] Paul T. Callaghan, *Translational Dynamics & Magnetic Resonance. Principles of Pulsed Gradient Spin Echo NMR*. Oxford University Press, 2011.