C5320 Physical Principles of NMR

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Chapter 1

No spin

1.1 Wave function and state of the system

We postulate that the state of the system is completely described by a *wave function*.

- *Newton mechanics*: coordinates and moments of all particles describe all properties of the current state and all future states
- *Quantum mechanics*: wave function describes all properties of the current state and all future states

Quantum mechanics is postulated, not derived. It can be only tested experimentally. Introduced because Newton mechanics did not described experiments correctly.

Example – two-slit (Young) experiment:

- *Question*: Particles or waves?
- *Answer*: Particles, but with probabilities added like waves

(Complex) probability amplitude: $\Psi = C\mathrm{e}^{\mathrm{i}\phi}$

(Real) probability density: $\rho = \Psi^*\Psi = |\Psi|^2 = |C|^2$

Probability of finding single particle in volume L^3: $\int\limits_0^L\int\limits_0^L\int\limits_0^L \Psi^*\Psi \mathrm{d}x\mathrm{d}y\mathrm{d}z$

Wave function of a free particle moving in direction x (coordinate frame can be always chosen so that x is the direction of motion of a free particle):

$$\Psi = C\mathrm{e}^{\mathrm{i}2\pi(\frac{x}{\lambda}-\frac{t}{T})} = C\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px-Et)}, \tag{1.1}$$

where $h = 2\pi\hbar$ is the Planck's constant, $p = mv$ is momentum (along x), and E is (kinetic) energy.

Note that Ψ corresponds to a *monochromatic wave* with period equal to h/E, wavelength equal to h/p, and a complex amplitude (it may contain a phase factor $\mathrm{e}^{\mathrm{i}\phi}$).

Calculating "square": real number $c^2 = cc$, complex number $|c|^2 = cc^*$, real vector $|v|^2 = \vec{v}\cdot\vec{v} = v_1v_1 + v_2v_2 + \cdots$, complex vector $|v|^2 = \vec{v}^\dagger\cdot\vec{v} = v_1^*v_1 + v_2^*v_2 + \cdots$, (continuous) function $\int_a^b f^*(x)f(x)\mathrm{d}x$ (function can be viewed as a vector of infinite number of infinitely "dense" elements – summation $\rightarrow$ integration).

Dirac's notation: $|v\rangle$, $|f\rangle$ is a vector v or function f, respectively:

$$\langle v|v\rangle = \vec{v}^\dagger \cdot \vec{v} = \sum_{j=1}^{N} v_j^* v_j \tag{1.2}$$

$$\langle f|f\rangle = \int_{-\infty}^{\infty} f^*(x) f(x) \mathrm{d}x \tag{1.3}$$

1.2 Superposition and localization in space

Note that a monochromatic wave function describes exactly what is p of the particle, but does not say anything about *position* of the particle because $\rho = \Psi^*\Psi = |C|$ is the same for any x (distribution of probability is constant from $x = -\infty$ to $x = \infty$). Wave function describing a particle (more) localized in space can be obtained by *superposition* of monochromatic waves.

$$\Psi(x,t) = c_1 \mathcal{A} \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 x - E_1 t)} + c_2 \mathcal{A} \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x - E_2 t)} + \cdots \tag{1.4}$$

We postulate that if possible states of our system are described by wave functions $\psi_1, \psi_2, \ldots$, their linear combination also describes a possible state of the system.

Note that monochromatic waves are *orthogonal*:

$$\int_{-\infty}^{\infty} \mathcal{A}^* \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1 x - E_1 t)} \mathcal{A} \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x - E_2 t)} \mathrm{d}x = |\mathcal{A}|^2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_1 - E_2)t} \int_{-\infty}^{\infty} \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 - p_2)x} \mathrm{d}x =$$

$$|\mathcal{A}|^2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_1 - E_2)t} \int_{-\infty}^{\infty} \cos \frac{(p_1 - p_2)x}{\hbar} \mathrm{d}x + \mathrm{i}|\mathcal{A}|^2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_1 - E_2)t} \int_{-\infty}^{\infty} \sin \frac{(p_1 - p_2)x}{\hbar} \mathrm{d}x = 0 \tag{1.5}$$

unless $p_1 = p_2$ (positive and negative parts of sine and cosine functions cancel each other during integration, with the exception of $\cos 0 = 1$).

Values of $\mathcal{A}$ can be also *normalized* to give the result of Eq. 1.5 equal to 1 if $p_1 = p_2$ and $E_1 = E_2$. It follows from the property of the Fourier transform that in such a case $|\mathcal{A}|^2 = 1/h$ if we integrate over a single coordinate (or $|\mathcal{A}|^2 = 1/h^3$ if we integrate over three coordinates etc.).

In the language of algebra, the complete set of normalized monochromatic waves constitutes *orthonormal basis* for wave functions, in a similar way as unit vectors $\vec{\imath}, \vec{\jmath}, \vec{k}$ are the orthonormal basis for all vectors in the Cartesian coordinate system x, y, z.

Also, Ψ can be normalized based on the condition

$$\int_{-\infty}^{\infty} \Psi^* \Psi \mathrm{d}x = P = 1 \tag{1.6}$$

(if a particle exists, it must be somewhere). It requires

$$\int_{-\infty}^{\infty} (c_1^* c_1 + c_2^* c_2 + \cdots) \mathrm{d}x = 1. \tag{1.7}$$

1.3 Operators and possible results of measurement

We postulated that the wave function contains a complete information about the system, but how can we extract this information from the wave function? For example, how can we get the value of a momentum of a free particle described by Eq. 1.4? Calculation of $\partial\Psi/\partial x$ gives us a clue:

$$\frac{\partial\Psi}{\partial x} = c_1\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + c_2\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots = \frac{\mathrm{i}}{\hbar}p_1c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + \frac{\mathrm{i}}{\hbar}p_2c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots \tag{1.8}$$

It implies that

$$-\mathrm{i}\hbar\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} = p_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}, \quad -\mathrm{i}\hbar\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} = p_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)}, \ldots \tag{1.9}$$

We see that

1. calculation of the partial derivative of any monochromatic wave and multiplying the result by $-\mathrm{i}\hbar$ gives us the same wave just multiplied by a constant. In general, the instruction to calculate the partial derivative and multiply the result by $-\mathrm{i}\hbar$ is known as *operator*. If application of the operator to a function gives the same function, only multiplied by a constant, the function is called *eigenfunction* of the operator and the constant is called *eigenvalue* of the operator.

2. the eigenvalues are well-defined, measurable physical quantities – possible values of the momentum along x.

3. the eigenvalues can be obtained by applying the operator to the eigenfunction and multiplying the result by the complex conjugate of the eigenfunction:

$$p_1 = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\left(-\mathrm{i}\hbar\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\right) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}p_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} = p_1\underbrace{\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}}_{=1} \tag{1.10}$$

We postulate that any measurable property is represented by an operator (acting on the wave function) and that result of a measurement must be one of eigenvalues of the operator.

Here, we usually write operators with "hats", like $\hat{A}$. Writing $\hat{A}\Psi$ means "take function Ψ and modify it as described by $\hat{A}$. It is *not* a multiplication: $\hat{A}\Psi \neq \hat{A}\cdot\Psi$, $\hat{A}$ is not a number but an instruction what to do with Ψ!

Recipe to calculate *possible results of a measurement*:

1. Identify the operator representing what you measure ($\hat{A}$)

2. Find all eigenfunctions $|\psi_1\rangle, |\psi_2\rangle, \ldots$ of the operator and use them as an orthonormal basis for Ψ: $\Psi = c_1|\psi_1\rangle + c_2|\psi_2\rangle, \ldots$

3. Calculate individual eigenvalues A_j as

$$\langle\psi_j|\hat{A}\psi_j\rangle = \langle\psi_j|A_j\cdot\psi_j\rangle = A_j\underbrace{\langle\psi_j|\psi_j\rangle}_{=1} = A_j. \tag{1.11}$$

The first equality in step 3 follows from the definition of eigenfunctions, then A_j is just a (real) number and can be factored out of the brackets (representing integration or summation) as described by the second equality, and the last equality reflects orthonormality of $|\psi_j\rangle$.

1.4 Matrix representation and expected result of measurement

Eq. 1.11 tells us what are the *possible* results of a measurement, but it does not say which value *is actually measured*. We can only calculate probabilities of getting individual eigenvalues and predict the expected result of the measurement.

We postulate that the expected result of measuring a quantity A represented by an operator $\hat{A}$ in a state of the system described by a wave function Ψ is

$$\langle A \rangle = \langle \Psi | \hat{A} | \Psi \rangle. \tag{1.12}$$

There are three ways how to do the calculation described by Eq. 1.12:

1. Express Ψ, calculate its complex conjugate $\Psi^* \equiv \langle \Psi |$, calculate $\hat{A}\Psi \equiv |\hat{A}\Psi\rangle$, and in the manner of Eq. 1.3

$$\langle A \rangle = \langle \Psi | \hat{A} | \Psi \rangle \equiv \langle \Psi | (\hat{A}\Psi) \rangle = \int_{-\infty}^{\infty} \cdots \Big(\Psi^*(x, \ldots) \hat{A} \Psi(x, \ldots) \mathrm{d}x \ldots \Big). \tag{1.13}$$

   Three dots in Eq. 1.13 tell us that for anything else that a single free particle (with zero spin) we integrate over all degrees of freedom, not just over x.

2. Find eigenfunctions $\psi_1, \psi_2, \ldots$ of $\hat{A}$ and write Ψ as their linear combination $\Psi = c_1\psi_1 + c_2\psi_2 + \cdots$ (use the eigenfunctions as an *orthonormal basis* for Ψ). Due to the orthonormality of the basis functions, the result of Eq. 1.13 is $\langle A \rangle = c_1^* c_1 A_1 + c_2^* c_2 A_2 + \cdots$, where $A_1, A_2, \ldots$ are eigenvalues of $\hat{A}$. We see that $\langle A \rangle$ is a *weighted average* of eigenvalues A_j with the weights equal to the squares of the coefficients ($c_j^* c_j = |c_j|^2$). The same result is obtained if we calculate

$$\langle A \rangle = \begin{pmatrix} c_1^* & c_2^* & \cdots \end{pmatrix} \begin{pmatrix} A_1 & 0 & \cdots \\ 0 & A_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \tag{1.14}$$

   We see that we can replace (i) operators by two-dimensional diagonal matrices, with eigenvalues forming the diagonal, and (ii) wave functions by one-dimensional matrices (known as *state vectors*) composed of the coefficients c_j. Eq. 1.14 shows calculation of the expected results of the measurement of A using *matrix representation* of operators and wave functions. Matrix representation is a big simplification because it allows us to calculate $\langle A \rangle$ without knowing how the operator $\hat{A}$ and its eigenfunctions look like! We just need the eigenvalues and coefficients c_j. This simplification is paid by the fact that the right coefficients are defined by the right choice of the basis.

3. Write Ψ as a linear combination of basis functions $\psi_1', \psi_1', \ldots$ (not necessarily eigenfunctions of $\hat{A}$)

$$\Psi = c_1'\psi_1' + c_2'\psi_2' + \cdots \tag{1.15}$$

   Build a two-dimensional matrix $\hat{P}'$ from the products of coefficients $c_j'^* c_k'$:

$$\hat{P}' = \begin{pmatrix} c_1' c_1'^* & c_1' c_2'^* & \cdots \\ c_2' c_1'^* & c_2' c_2'^* & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{1.16}$$

Multiply the matrix $\hat{P}'$ by a matrix[1] $\hat{A}'$ representing the operator $\hat{A}$ in the basis $\psi_1', \psi_1', \ldots$. The sum of the diagonal elements (called *trace*) of the resulting matrix $\hat{P}'\hat{A}'$ is equal to the expected value $\langle A \rangle$

$$\langle A \rangle = \mathrm{Tr}\{\hat{P}'\hat{A}'\} \tag{1.17}$$

Why should we use such a bizarre way of calculating the expected value of A when it can be calculated easily from Eq. 1.14? The answer is that Eq. 1.17 is *more general*. We can use the same basis for operators with different sets of eigenfunctions.

1.5 Operators of position and momentum

We need to find operators in order to describe measurable quantities. Let's start with the most fundamental quantities, *position* of a particle x and *momentum* $p = mv$.

1.5.1 Operator of momentum

We have already obtained the operator of momentum of a particle moving in the x direction when calculating $\partial\Psi/\partial x$ (Eq. 1.9). If a particle moves in a general direction, operators of components of the momentum tensor are derived in the same manner.

$$\hat{p}_x \equiv \frac{\partial}{\partial x} \tag{1.18}$$

$$\hat{p}_y \equiv \frac{\partial}{\partial y} \tag{1.19}$$

$$\hat{p}_z \equiv \frac{\partial}{\partial z} \tag{1.20}$$

1.5.2 Operator of position

The wave function $\Psi(x,t)$ defined by Eq. 1.4 is a function of the position of the particle, not of the momentum (it is a sum of contributions of *all* possible momenta). If we define basis as a set of functions $\psi_j = \Psi(x_j, t)$ for all possible positions x_j, operator of position is simply *multiplication by the value of the coordinate* describing the given position. Operators of the y and z are defined in the same manner.

$$\hat{x} \equiv x \cdot \tag{1.21}$$

To see how the operator acts, write $\Psi^*(x,t)$ and $x\Psi(x,t)$ as the set of functions $\Psi(x_j,t)$ for all possible positions x_j:

$$x\Psi(x,t) = \begin{pmatrix} x_1 c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 x_1 - E_1 t)} + x_1 c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x_1 - E_2 t)} + x_1 c_3 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3 x_1 - E_3 t)} + \cdots \\ x_2 c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 x_2 - E_1 t)} + x_2 c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x_2 - E_2 t)} + x_2 c_3 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3 x_2 - E_3 t)} + \cdots \\ x_3 c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 x_3 - E_1 t)} + x_3 c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x_3 - E_2 t)} + x_3 c_3 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3 x_3 - E_3 t)} + \cdots \\ \vdots \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \end{pmatrix} \tag{1.22}$$

[1] How can we get a matrix representation of an operator with eigenfunctions different from the basis? The complete set of N functions defines an abstract N-dimensional space ($N = \infty$ for free particles!). The wave function Ψ is represented by a vector in this space built from coefficients $c_1', c_2', \ldots$, as described by Eq. 1.15, and a change of the basis is described as a rotation in this space. The same rotation describes how the matrix representing the operator $\hat{A}$ changes upon changing the basis. Note that the matrix is not diagonal if the basis functions are not eigenfunctions of $\hat{A}$.

If the position of the particle is e.g. x_2,

$$\Psi(x_2,t) = \begin{pmatrix} 0 \\ c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 x_2 - E_1 t)} + c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x_2 - E_2 t)} + c_3 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3 x_2 - E_3 t)} + \cdots \\ 0 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ \psi_2 \\ 0 \\ \vdots \end{pmatrix} \tag{1.23}$$

and $x \cdot \Psi(x,t)$ for $x = x_2$ is

$$x_2 \Psi(x_2,t) = \begin{pmatrix} 0 \\ x_2 \left(c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1 x_2 - E_1 t)} + c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2 x_2 - E_2 t)} + c_3 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3 x_2 - E_3 t)} + \cdots \right) \\ 0 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ x_2 \psi_2 \\ 0 \\ \vdots \end{pmatrix}. \tag{1.24}$$

We see that multiplication of $\Psi(x_2,t) = \psi_2$ by x_2 results in $x_2\psi_2$, i.e., ψ_2 is an eigenfunction of the operator $\hat{x} = x\cdot$ and x_2 is the corresponding eigenvalue.

Note that multiplication by p_j does not work in the same way! We could multiply ψ_2 by x_2 because ψ_2 does not depend on any other value of the x coordinate. However, ψ_2 depends on all possible values of p. On the other hand, partial derivative gave us each monochromatic wave multiplied by its value of p and ensured that the monochromatic waves acted as eigenfunctions.

1.5.3 Commutators

If we apply two operators subsequently to the same wave function, order of the operators sometimes does not matter. E.g., $\hat{x}\hat{p}_y\Psi = \hat{p}_y\hat{x}\Psi$ ($\hat{x}$ and $\hat{p}_y$ commute). It means that x and p_y can be measured independently at the same time. However, sometimes the order of operators makes a difference. For example

$$\hat{x}\hat{p}_x\Psi = -\mathrm{i}\hbar x \frac{\partial \Psi}{\partial x} \tag{1.25}$$

but

$$\hat{p}_x\hat{x}\Psi = -\mathrm{i}\hbar \frac{\partial (x\Psi)}{\partial x} = -\mathrm{i}\hbar\Psi - \mathrm{i}\hbar x \frac{\partial \Psi}{\partial x} \tag{1.26}$$

The difference is known as the *commutator* and is written as $\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = [\hat{x}, \hat{p}_x]$. A non-zero commutator tells us that $\hat{x}$ and $\hat{p}_x$ are not independent and cannot be measured exactly at the same time. Analysis of the action of the operators shows that

- commutators of operators of a coordinate and the momentum component in the same direction are equal to $-\mathrm{i}\hbar$ (i.e., multiplication of Ψ by the factor $-\mathrm{i}\hbar$)
- all other position and coordinate operators commute.

Written in a mathematically compact form,

$$[\hat{r}_j, \hat{p}_k] = -\mathrm{i}\hbar\delta_{j,k} \qquad [\hat{r}_j, \hat{r}_k] = [\hat{r}_j, \hat{p}_k] = 0, \tag{1.27}$$

where j and k are x, y, or z, r_j is the x, y, or z component of the position vector $\vec{r} = (r_x, r_y, r_z) \equiv (x, y, z)$, p_k is the x, y, or z component of the momentum vector $\vec{p} = (p_x, p_y, p_z)$, and $\delta_{j,k} = 1$ for $j = k$ and $\delta_{j,k} = 0$ for $j \neq k$.

The described commutator relations follow from the way how we defined Ψ in Eq. 1.4. However, we can also use Eq. 1.27 as the fundamental definition and Eq. 1.4 as its consequence:

We postulate that operators of position and momentum obey the relations

$$[\hat{r}_j, \hat{p}_k] = -\mathrm{i}\hbar\delta_{j,k} \qquad [\hat{r}_j, \hat{r}_k] = [\hat{p}_j, \hat{p}_k] = 0. \tag{1.28}$$

Note that we only postulate relations between operators. Other choices are possible and correct as long as Eq. 1.27 holds.

1.6 Operator of energy and equation of motion

We obtained the operator of momentum by calculating $\partial\Psi/\partial x$. What happens if we calculate $\partial\Psi/\partial t$?

$$\frac{\partial\Psi}{\partial t} = c_1\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + c_2\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots = -\frac{\mathrm{i}}{\hbar}E_1c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} - \frac{\mathrm{i}}{\hbar}E_2c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} - \cdots \tag{1.29}$$

and consequently

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} = E_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}, \quad \mathrm{i}\hbar\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} = E_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)}, \ldots \tag{1.30}$$

1. First, we obtain the *operator of energy* from Eq. 1.30, in analogy to Eq. 1.9.
2. The second achievement is Eq. 1.29 itself. Energy of free particles is just the kinetic energy (by definition). Therefore, all energies E_j in the right-hand side of Eq. 1.29 can be written as

$$E_j = \frac{mv_j^2}{2} = \frac{p_j^2}{2m}, \tag{1.31}$$

resulting in

$$\frac{\partial\Psi}{\partial t} = -\frac{\mathrm{i}}{\hbar}\left(\frac{p_1^2}{2m}c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + \frac{p_2^2}{2m}c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots\right) \tag{1.32}$$

But an equation with the p_j^2 terms can be also obtained by calculating

$$\frac{1}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{2m}\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial x} = -\frac{1}{\hbar^2}\left(\frac{p_1^2}{2m}c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + \frac{p_2^2}{2m}c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots\right) \tag{1.33}$$

Comparison of Eqs. 1.32 and 1.33 gives us the *equation of motion*

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \tag{1.34}$$

If we extend our analysis to particles experiencing a time-independent potential energy $V(x, y, z)$, the energy will be given by

$$E_j = \frac{p_j^2}{2m} + V, \tag{1.35}$$

where p_j is now the absolute value of a momentum vector $\vec{p}_j$ (we have to consider all three direction x, y, z because particles change direction of motion in the presence of a potential). The time derivative of Ψ is now

$$\frac{\partial \Psi}{\partial t} = -\frac{\mathrm{i}}{\hbar}\left(\frac{p_1^2}{2m}c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_1\vec{r}-E_1 t)} + \frac{p_2^2}{2m}c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_2\vec{r}-E_2 t)} + \cdots\right) - \frac{\mathrm{i}}{\hbar}V(\vec{r})\Psi \tag{1.36}$$

and

$$\left(\frac{p_1^2}{2m}c_1 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_1\vec{r}-E_1 t)} + \frac{p_2^2}{2m}c_2 \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_2\vec{r}-E_2 t)} + \cdots\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial x^2}\right) \tag{1.37}$$

Substituting Eq. 1.37 into Eq. 1.36 gives us the famous Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = \underbrace{\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2}\right) + V(x,y,z)\right)}_{\hat{H}}\Psi \tag{1.38}$$

The sum of kinetic and potential energy is known as Hamiltonian in the classical mechanics and the same term is used for the operator $\hat{H}$.

The association of Hamiltonian (energy operator) with the time derivative makes it essential for analysis of dynamics of systems in quantum mechanics:

We postulate that evolution of a system in time is given by the Hamiltonian:

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{1.39}$$

1.6.1 Schrödinger equation in matrix representation and stationary states

Eq.1.39 can be also written for matrix representation of Ψ and $\hat{H}$. If eigenfunctions of $\hat{H}$ are used as a basis

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} c_1^* \\ c_2^* \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1 & 0 & \cdots \\ 0 & E_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} c_1^* \\ c_2^* \\ \vdots \end{pmatrix}, \tag{1.40}$$

which is simply a set of independent differential equations

$$\frac{\mathrm{d}c_j}{\mathrm{d}t} = -\mathrm{i}\frac{E_j}{\hbar}c_j \quad \Rightarrow \quad c_j = a_j \mathrm{e}^{-\mathrm{i}\frac{E_j}{\hbar}t}, \tag{1.41}$$

where the (possibly complex) integration constant a_j is given by the value of c_j at $t = 0$.

Note that the coefficients c_j evolve, but the products $c_j^* c_j = |a_j|^2$ do not change in time. Each product $c_j^* c_j$ describes the probability that the system is in the state with the energy equal to the eigenvalue E_j, described by an eigenfunction ψ_j. We see that states corresponding to the eigenfunctions of the Hamiltonian are *stationary* (do not vary in time). Only such states can be described by the *energy level diagram*.

1.7 Operator of angular momentum and rotation in space

In a search for operators needed to describe NMR experiment, we start from what we know, position and momentum operators. We use classical physics and just replace the values of coordinates and momentum components by their operators.

1.7.1 Operator of angular momentum

Classical definition of the vector of angular momentum $\vec{L}$ is

$$\vec{L} = \vec{r} \times \vec{p} \tag{1.42}$$

The sign "$\times$" denotes the vector product:

$$L_x = r_y p_z - r_z p_y \tag{1.43}$$
$$L_y = r_z p_x - r_x p_z \tag{1.44}$$
$$L_z = r_x p_y - r_y p_x \tag{1.45}$$

Going to the operators

$$\hat{L}_x = \hat{r}_y \hat{p}_z - \hat{r}_z \hat{p}_y = -\mathrm{i}\hbar y \frac{\partial}{\partial z} + \mathrm{i}\hbar z \frac{\partial}{\partial y} \tag{1.46}$$
$$\hat{L}_y = \hat{r}_z \hat{p}_x - \hat{r}_x \hat{p}_z = -\mathrm{i}\hbar z \frac{\partial}{\partial x} + \mathrm{i}\hbar x \frac{\partial}{\partial z} \tag{1.47}$$
$$\hat{L}_z = \hat{r}_x \hat{p}_y - \hat{r}_y \hat{p}_x = -\mathrm{i}\hbar x \frac{\partial}{\partial y} + \mathrm{i}\hbar y \frac{\partial}{\partial x} \tag{1.48}$$
$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{1.49}$$

It follows from Eq. 1.27 that

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar \hat{L}_z \tag{1.50}$$
$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar \hat{L}_x \tag{1.51}$$
$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar \hat{L}_y \tag{1.52}$$

but

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \tag{1.53}$$

- Two components of angular momentum cannot be measured exactly at the same time
- Eqs. 1.50–1.53 can be used as a definition of angular momentum operators if the position and momentum operators are not available.

1.7.2 Eigenvalues of angular momentum

Let's find eigenvalues $L_{z,j}$ and eigenfunctions ψ_j of $\hat{L}_z$. In spherical coordinates $(r,\ \vartheta,\ \varphi)$, $\psi_j = Q(r,\vartheta)R_j(\varphi)$ and $\hat{L}_z = -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}$

Eigenvalues and eigenfunctions are defined by

$$\hat{L}_z \psi_j = L_{z,j}\psi_j \tag{1.54}$$
$$-\mathrm{i}\hbar \frac{\partial(QR_j)}{\partial\varphi} = L_{z,j}(QR_j) \tag{1.55}$$
$$-\mathrm{i}\hbar Q \frac{\mathrm{d}R_j}{\mathrm{d}\varphi} = L_{z,j} Q R_j \tag{1.56}$$

$$-\mathrm{i}\hbar\frac{\mathrm{d}\ln R_j}{\mathrm{d}\varphi} = L_{z,j} \tag{1.57}$$

$$R_j = \mathrm{e}^{\mathrm{i}\frac{L_{z,j}}{\hbar}\varphi} \tag{1.58}$$

Since $\psi_j(\varphi) = \psi_j(\varphi + 2\pi)$,

- Value of the z-component of the angular momentum must be an integer multiple of $\hbar$

1.7.3 Angular momentum and rotation

Rotation about an axis given by the angular frequency vector $\vec{\omega}$

$$\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} = \vec{\omega} \times \vec{r} \tag{1.59}$$

$$\frac{\mathrm{d}r_x}{\mathrm{d}t} = \omega_y r_z - \omega_z r_y \tag{1.60}$$

$$\frac{\mathrm{d}r_y}{\mathrm{d}t} = \omega_z r_x - \omega_x r_z \tag{1.61}$$

$$\frac{\mathrm{d}r_z}{\mathrm{d}t} = \omega_x r_y - \omega_y r_x \tag{1.62}$$

If a coordinate frame is chosen so that $\vec{\omega} = (0, 0, \omega)$

$$\frac{\mathrm{d}r_x}{\mathrm{d}t} = -\omega r_y \tag{1.63}$$

$$\frac{\mathrm{d}r_y}{\mathrm{d}t} = \omega r_x \tag{1.64}$$

$$\frac{\mathrm{d}r_z}{\mathrm{d}t} = 0 \tag{1.65}$$

Solution: multiply the second equation by i and add it to the first equation or subtract it from the first equation.

$$\frac{\mathrm{d}(r_x + \mathrm{i}r_y)}{\mathrm{d}t} = \omega(-r_y + \mathrm{i}r_x) = +\mathrm{i}\omega(r_x + \mathrm{i}r_y) \tag{1.66}$$

$$\frac{\mathrm{d}(r_x - \mathrm{i}r_y)}{\mathrm{d}t} = \omega(-r_y - \mathrm{i}r_x) = -\mathrm{i}\omega(r_x - \mathrm{i}r_y) \tag{1.67}$$

$$r_x + \mathrm{i}r_y = C_+\mathrm{e}^{+\mathrm{i}\omega t} \tag{1.68}$$

$$r_x - \mathrm{i}r_y = C_-\mathrm{e}^{-\mathrm{i}\omega t} \tag{1.69}$$

where the integration constants $C_+ = r_x(0) + \mathrm{i}r_y(0) = r\mathrm{e}^{\phi_0}$ and $C_+ = r_x(0) - \mathrm{i}r_y(0) = r\mathrm{e}^{-\phi_0}$ are given by the initial phase ϕ_0 of $\vec{r}$ in the coordinate system:

$$r_x + \mathrm{i}r_y = r\mathrm{e}^{+(\mathrm{i}\omega t + \phi_0)} = r(\cos(\omega t + \phi_0) + \mathrm{i}(\sin(\omega t + \phi_0)) \tag{1.70}$$

$$r_x - \mathrm{i}r_y = r\mathrm{e}^{-(\mathrm{i}\omega t + \phi_0)} = r(\cos(\omega t + \phi_0) - \mathrm{i}(\sin(\omega t + \phi_0)), \tag{1.71}$$

- Comparison with Eq. 1.58 shows that the eigenfunction of $\hat{L}_z$ describes rotation about z.

For zero initial phase, $r_x(t=0) = r$, and evolution of r_x and r_y is obtained by adding and subtracting Eqs. 1.70 and 1.71:

$$r_x = r\cos(\omega t) \tag{1.72}$$
$$r_y = r\sin(\omega t) \tag{1.73}$$

1.8 Operator of orbital magnetic moment

A moving charged particle can be viewed as an electric current. Classical definition of the magnetic moment of a charged particle travelling in a circular path (orbit) is

$$\vec{\mu} = \frac{Q}{2}(\vec{r}\times\vec{v}) = \frac{Q}{2m}(\vec{r}\times\vec{p}) = \frac{Q}{2m}\vec{L} = \gamma\vec{L}, \tag{1.74}$$

where Q is the charge of the particle, m is the mass of the particle, $\vec{v}$ is the velocity of the particle, and γ is known as the *magnetogyric ratio (constant)*.[2]

Therefore, we can write the operators

$$\hat{\mu}_x = \gamma\hat{L}_x \qquad \hat{\mu}_y = \gamma\hat{L}_y \qquad \hat{\mu}_z = \gamma\hat{L}_z \qquad \hat{\mu}^2 = \gamma^2\hat{L}^2. \tag{1.75}$$

1.9 Hamiltonian of orbital magnetic moment in magnetic field

Classically, the energy of a magnetic moment $\vec{\mu}$ in a magnetic field of induction $\vec{B}$ is $E = -\vec{\mu}\cdot\vec{B}$. Accordingly, the Hamiltonian of the interactions of an orbital magnetic moment with a magnetic field is

$$\hat{H} = -B_x\hat{\mu}_x - B_y\hat{\mu}_y - B_z\hat{\mu}_z = -\gamma\left(B_x\hat{\mu}_x + B_y\hat{\mu}_y + B_z\hat{\mu}_z\right) = -\frac{Q}{2m}\left(B_x\hat{I}_x + B_y\hat{I}_y + B_z\hat{I}_z\right). \tag{1.76}$$

[2] The term *gyromagnetic ratio* is also used.

Chapter 2

Single spin

2.1 Relativistic quantum mechanics

The angular momentum discussed in Section 1.7.1 is associated with the change of direction of a moving particle. However, the theory discussed so-far does not explain the experimental observation that even point-like particles moving along straight lines posses a well defined angular momentum, so-called *spin*.

The origin of the spin is relativistic. The Schrödinger equation is not relativistic and does not describe the spin. According to the special theory of relativity, time is slower and mass increases at a speed v close to the speed of light (in vacuum) c, and energy is closely related to the mass:

$$t = \frac{t_0}{\sqrt{1 - v^2/c^2}} \qquad m = \frac{m_0}{\sqrt{1 - v^2/c^2}} \qquad E_t = mc^2 = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}}, \tag{2.1}$$

where m_0 is the rest mass, m_0 is the rest energy, t_0 is the proper time (i.e., mass, energy, and time in the coordinate frame moving with the particle), and E_t is the total energy. The metrical properties of space and time are given by

$$c^2 \mathrm{d}t_0^2 = c^2 \mathrm{d}t^2 - \mathrm{d}x^2 - \mathrm{d}y^2 - \mathrm{d}z^2. \tag{2.2}$$

Multiplied by m^2 and divided by $\mathrm{d}t^2$,

$$\left(mc^2 \frac{\mathrm{d}t_0}{\mathrm{d}t}\right)^2 = (mc^2)^2 - \left(mc\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 - \left(mc\frac{\mathrm{d}y}{\mathrm{d}t}\right)^2 - \left(mc\frac{\mathrm{d}z}{\mathrm{d}t}\right)^2. \tag{2.3}$$

Using Eqs. 2.2,

$$(m_0 c^2)^2 = (mc^2) - (mcv_x)^2 - (mcv_y)^2 - (mcv_z)^2 \tag{2.4}$$

$$m_0^2 c^4 = E_t^2 - c^2 p_x^2 - c^2 p_y^2 - c^2 p_z^2 \tag{2.5}$$

Let us look for an equation of motion that fulfills Eq. 2.5 for a monochromatic wave function. As the answer is not intuitive, we will proceed step by step.

Monochromatic wave function ψ can be viewed as a continuous series of values of $\psi(x, y, z, t)$ for each time and place:

$$\psi = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_x x + p_y y + p_z z - E_t t)} \tag{2.6}$$

Partial derivatives of ψ serve as operators of energy and momentum:

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial x} = -p_x\psi \qquad \mathrm{i}\hbar\frac{\partial\psi}{\partial y} = -p_y\psi \qquad \mathrm{i}\hbar\frac{\partial\psi}{\partial z} = -p_z\psi \qquad \mathrm{i}\hbar\frac{\partial\psi}{\partial t} = E_t\psi \tag{2.7}$$

Zero spin, zero mass

If a free particle does not have spin, it has only momentum in the direction of motion ($p_x = p$ if the direction of motion defines the x axis). If the particle has a zero rest mass ($m_0 = 0$), we can write the following equations:

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial t} = -\mathrm{i}c\hbar\frac{\partial\psi}{\partial x} \tag{2.8}$$

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial t} = +\mathrm{i}c\hbar\frac{\partial\psi}{\partial x} \tag{2.9}$$

and write them in an operator form

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\right)\psi = \hat{O}^+\psi = 0 \tag{2.10}$$

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - \mathrm{i}c\hbar\frac{\partial}{\partial x}\right)\psi = \hat{O}^-\psi = 0. \tag{2.11}$$

Expressing the partial derivatives for a monochromatic wave function,

$$\hat{O}^+\psi = (E_t - cp)\psi \tag{2.12}$$

Acting by $\hat{O}^-$ on the result

$$\hat{O}^-\hat{O}^+\psi = \hat{O}^2\psi = \hat{O}^-((E_t - cp)\psi) = (E_t + cp)(E_t - cp)\psi = (E_t^2 - c^2p^2)\psi = 0 \tag{2.13}$$

We see that the Eqs. 2.10–2.11 satisfy Eq. 2.5, the desired value of $E_t^2 - c^2p^2$ s an eigenvalue of the operator $\hat{O}^2$, and ψ is its eigenfuction. The operators $\hat{O}^-$ and $\hat{O}^+$ can be viewed as "square roots" of $\hat{O}^2$:

$$\left(\hbar^2\frac{\partial^2}{\partial t^2} - c^2\hbar^2\frac{\partial^2}{\partial x^2}\right)\Psi = -\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - \mathrm{i}c\hbar\frac{\partial}{\partial x}\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial t} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\right)\Psi = 0. \tag{2.14}$$

In general, the operator $\hat{O}^2$ should look like

$$(m_0c^2)^2\Psi + \hbar^2\frac{\partial^2\Psi}{\partial t^2} - c^2\hbar^2\frac{\partial^2\Psi}{\partial z^2} - c^2\hbar^2\frac{\partial^2\Psi}{\partial x^2} - c^2\hbar^2\frac{\partial^2\Psi}{\partial y^2} \tag{2.15}$$

Such an operator cannot be decomposed into "sqare roots" as in the case of zero spin and zero rest mass. If we try to calculate product of some (more complex) operators $\hat{O}^+$ and $\hat{O}^-$, we never get $\hat{O}^2$ from Eq. 2.15: we always obtain some additional terms that do not cancel each other. No monochromatic wave function can serve as an eigenfuction for such operator if the particle has a spin or mass.

However, the solution can be found if we write the equation of motions for *more* monochromatic functions, coupled in such a way that they cancel unwanted terms of the product $\hat{O}^-\hat{O}^+$.

Non-zero spin, zero mass

Let us try to solve the problem for a particle with a spin, but with a zero rest mass. This is a good approximation of neutrinos. We can write the following equations of motions:

$$\mathrm{i}\hbar\frac{\partial(u_1\psi)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(u_1\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u_2\psi)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}u_2\psi)}{\partial y} \tag{2.16}$$

$$\mathrm{i}\hbar\frac{\partial(u_2\psi)}{\partial t} = +\mathrm{i}c\hbar\frac{\partial(u_2\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u_1\psi)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(\mathrm{i}u_1\psi)}{\partial y}, \tag{2.17}$$

where $u_1\psi$ and $u_2\psi$ are monochromatic functions. We can group them into vectors

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} u_1\psi \\ -u_2\psi \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} u_2\psi \\ u_1\psi \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} -\mathrm{i}u_2\psi \\ \mathrm{i}u_1\psi \end{pmatrix} = 0 \tag{2.18}$$

and write the equations in an operator form

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\right)\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix} = \hat{O}^+\Psi = 0 \tag{2.19}$$

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\right)\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix} = \hat{O}^-\Psi = 0. \tag{2.20}$$

Now,

$$\hat{O}^+\Psi = \begin{pmatrix} E_t u_1\psi - cp_z u_1\psi - cp_x u_2\psi + \mathrm{i}cp_y u_2\psi \\ E_t u_2\psi + cp_z u_2\psi - cp_x u_1\psi - \mathrm{i}cp_y u_1\psi \end{pmatrix} \tag{2.21}$$

and

$$\hat{O}^2\Psi = \hat{O}^-\hat{O}^+\Psi = \begin{pmatrix} E_t^2 - c^2p_z^2 - c^2p_x^2 - c^2p_y^2 \\ E_t^2 - c^2p_z^2 - c^2p_x^2 - c^2p_y^2 \end{pmatrix}\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix} = (E_t^2 - c^2p_z^2 - c^2p_x^2 - c^2p_y^2)\Psi \tag{2.22}$$

$E_t^2 - c^2p_z^2 - c^2p_x^2 - c^2p_y^2$ is an eigenvalue of $\hat{O}^2$, and the vector Ψ is an eigenfunction. This success is paid by the fact that we need two functions $u_1\psi, u_2\psi$ instead of one. The series of values constituting the wave function Ψ is twice as long compared to ψ of the spin-less particle because we have two values for each x, y, z, t. It means that the wave function is not unambiguously defined by x, y, z, t – it has one more degree of freedom, represented by the new "coordinate" u.

Zero spin, non-zero mass

To test the effect of mass, we now find a solution for a particle without spin but with a non-zero rest mass. The following equations of motion work in this case:

$$\mathrm{i}\hbar\frac{\partial(u\psi)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(v\psi^*)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(v\psi^*)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}v\psi^*)}{\partial y} + m_0c^2u\psi \tag{2.23}$$

$$\mathrm{i}\hbar\frac{\partial(v\psi^*)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(u\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u\psi)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}u\psi)}{\partial y} - m_0c^2u\psi^*. \tag{2.24}$$

The red partial derivatives are equal to zero if the particle moves in the x direction and $p_y = p_z = 0$ where $u_1\psi$ and $u_2\psi$ are monochromatic functions. We can group them into vectors

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} u\psi \\ -v\psi^* \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} u\psi \\ -v\psi^* \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} v\psi^* \\ -u\psi \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} -\mathrm{i}v\psi^* \\ \mathrm{i}u\psi \end{pmatrix} - m_0c^2\begin{pmatrix} u\psi \\ v\psi^* \end{pmatrix} = 0 \tag{2.25}$$

and write the equations in an operator form

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} - m_0c^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right)\begin{pmatrix} u\psi \\ v\psi^* \end{pmatrix} = \hat{O}^+\Psi = 0 \tag{2.26}$$

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} + m_0c^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right)\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix} = \hat{O}^-\Psi = 0. \tag{2.27}$$

$$\hat{O}^+\Psi = \begin{pmatrix} E_t u\psi + cpv\psi^* - m_0c^2u\psi \\ E_t v\psi^* + cpu\psi - m_0c^2v\psi^* \end{pmatrix} \tag{2.28}$$

and

$$\hat{O}^2\Psi = \hat{O}^-\hat{O}^+\Psi = \begin{pmatrix} E_t^2 - c^2p^2 - (m_0c^2)^2 \\ E_t^2 - c^2p^2 - (m_0c^2)^2 \end{pmatrix}\begin{pmatrix} u\psi \\ v\psi^* \end{pmatrix} = (E_t^2 - c^2p^2 - (m_0c^2)^2)\Psi \tag{2.29}$$

Again, we achieved the desired result using two monochromatic functions. This time, one contained complex conjugate to ψ – it represents an *antiparticle*.

Non-zero spin, non-zero mass

Finally we describe the solution for the most interesting particles as electron or quarks. If the particle has a spin and a non-zero rest mass, effects of discussed in the previous sections combine. We need four equations of motions with four components of the wave function:

$$\mathrm{i}\hbar\frac{\partial(u_1\psi)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(v_1\psi^*)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(v_2\psi^*)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}v_2\psi^*)}{\partial y} + m_0c^2u_1\psi \tag{2.30}$$

$$\mathrm{i}\hbar\frac{\partial(u_2\psi)}{\partial t} = +\mathrm{i}c\hbar\frac{\partial(v_2\psi^*)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(v_1\psi^*)}{\partial x} + \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}v_1\psi^*)}{\partial y} + m_0c^2u_2\psi \tag{2.31}$$

$$\mathrm{i}\hbar\frac{\partial(v_1\psi^*)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(u_1\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u_2\psi)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(\mathrm{i}u_2\psi)}{\partial y} - m_0c^2v_1\psi^* \tag{2.32}$$

$$\mathrm{i}\hbar\frac{\partial(v_2\psi^*)}{\partial t} = +\mathrm{i}c\hbar\frac{\partial(u_2\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u_1\psi)}{\partial x} + \mathrm{i}c\hbar\frac{\partial(\mathrm{i}u_1\psi)}{\partial y} - m_0c^2v_2\psi^*. \tag{2.33}$$

We can group the monochromatic functions into vectors

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} u_1\psi \\ u_2\psi \\ -v_1\psi^* \\ -v_2\psi^* \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix} v_1\psi^* \\ -v_2\psi^* \\ -u_1\psi \\ u_2\psi \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix} v_2\psi^* \\ v_1\psi^* \\ -u_2\psi \\ -u_1\psi \end{pmatrix} + \mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix} -\mathrm{i}v_2\psi^* \\ \mathrm{i}v_1\psi^* \\ \mathrm{i}u_2\psi \\ -\mathrm{i}u_1\psi \end{pmatrix} - m_0c^2\begin{pmatrix} u_1\psi \\ u_2\psi \\ v_1\psi^* \\ v_2\psi^* \end{pmatrix} = 0 \tag{2.34}$$

and write the equations in an operator form

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix}0&0&1&0\\0&0&0&-1\\-1&0&0&0\\0&1&0&0\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix}0&0&0&-\mathrm{i}\\0&0&\mathrm{i}&0\\0&\mathrm{i}&0&0\\-\mathrm{i}&0&0&0\end{pmatrix}\right.$$
$$\left.-m_0c^2\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^+\Psi=0 \tag{2.35}$$

$$\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix}0&0&1&0\\0&0&0&-1\\-1&0&0&0\\0&1&0&0\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix}0&0&0&-\mathrm{i}\\0&0&\mathrm{i}&0\\0&\mathrm{i}&0&0\\-\mathrm{i}&0&0&0\end{pmatrix}\right.$$
$$\left.-m_0c^2\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^-\Psi=0. \tag{2.36}$$

or shortly

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0+\mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1+\mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2+\mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3-m_0c^2\hat{1}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^+\Psi=0 \tag{2.37}$$

$$\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0-\mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1-\mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2-\mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3-m_0c^2\hat{1}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^-\Psi=0. \tag{2.38}$$

$$\hat{O}^+\Psi=\begin{pmatrix}E_tu_1\psi+cp_xv_2\psi^*-\mathrm{i}cp_yv_2\psi^*+cp_zv_1\psi^*-m_0c^2u_1\psi\\E_tu_2\psi+cp_xv_1\psi^*+\mathrm{i}cp_yv_1\psi^*-cp_zv_2\psi^*-m_0c^2u_2\psi\\E_tv_1\psi^*+cp_xu_2\psi^*-\mathrm{i}cp_yu_2\psi^*+cp_zu_1\psi^*-m_0c^2v_1\psi^*\\E_tv_2\psi^*+cp_xu_1\psi^*+\mathrm{i}cp_yu_1\psi^*-cp_zu_2\psi^*-m_0c^2v_2\psi^*\end{pmatrix} \tag{2.39}$$

and

$$\hat{O}^2\Psi=\hat{O}^-\hat{O}^+\Psi=\begin{pmatrix}E_t^2-c^2p^2-(m_0c^2)^2\\E_t^2-c^2p^2-(m_0c^2)^2\\E_t^2-c^2p^2-(m_0c^2)^2\\E_t^2-c^2p^2-(m_0c^2)^2\end{pmatrix}\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=(E_t^2-c^2p^2-(m_0c^2)^2)\Psi \tag{2.40}$$

2.2 Dirac equation

Eqs. 2.37 and 2.38 are known as the *Dirac equation*. When postulated by Dirac, they naturally explained the behavior of particles with spin number 1/2 and predicted existence of antiparticles, discovered a few years later.

Dirac equations are valid generally, not just for monochromatic ψ describing free particles. $\hat{O}^-\hat{O}^+$ always gives $\hat{O}^2$ with the eigenvalue $(E_t^2 - c^2p^2 - (m_0c^2)^2)$ and eigenfunction Ψ. The unwanted matrix products of $\hat{O}^-\hat{O}^+$ cancel due to the properties of the 4×4 matrices $\hat{\gamma}^j$:

$$\hat{\gamma}^0 \cdot \hat{\gamma}^0 = 1 \qquad \hat{\gamma}^1 \cdot \hat{\gamma}^1 = -1 \qquad \hat{\gamma}^2 \cdot \hat{\gamma}^2 = -1 \qquad \hat{\gamma}^3 \cdot \hat{\gamma}^3 = -1 \tag{2.41}$$

and

$$\hat{\gamma}^j \cdot \hat{\gamma}^k + \hat{\gamma}^k \cdot \hat{\gamma}^j = 0 \tag{2.42}$$

for $j \neq k$.

2.3 Relation to Schrödinger equation

We came to the Schrödinger equation using the relation $E = p^2/2m$ (energy of a free particle, i.e., kinetic energy), which is only an approximation for low speeds, obtained by neglecting the E^2 term ($E^2 \ll (m_0c^2)^2$ for $v^2 \ll c^2$) in Eq. 2.5:

$$\begin{aligned}
&(m_0c^2)^2 = (m_0c^2 + E)^2 - c^2p^2 = (m_0c^2)^2 + 2E(m_0c^2) + E^2 - c^2p^2 \approx (m_0c^2)^2 + 2E(m_0c^2) - c^2p^2 \\
&\Rightarrow \qquad E = \frac{p^2}{2m_0}
\end{aligned} \tag{2.43}$$

2.4 Operators of spin angular momentum

The 2×2 matrices in the operator Eqs. 2.20 and 2.20 and constituting the 4×4 matrices in Eqs. 2.37 and 2.38 are known as *Pauli matrices*. When we calculate their commutators, we find that

$$\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\right] = \mathrm{i}2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.44}$$

$$\left[\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] = \mathrm{i}2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{2.45}$$

$$\left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] = \mathrm{i}2 \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{2.46}$$

If we multiply the Pauli matrices by $\hbar/2$, we obtain the relations presented in Eqs. 1.50–1.53 as a definition of angular momentum operators. Therefore, Pauli matrices provide a basis for *operators of spin angular momentum*, a strange physical quantity describing intrinsic angular momentum of a point-like particle and not associated with its motion:

$$\hat{I}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{I}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad \hat{I}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \hat{I}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{2.47}$$

2.5 Eigenfunctions and eigenvalues of $\hat{I}_z$

The fact that $\hat{I}_z$ is diagonal tells us that we have written the matrix representations of the operators of the spin angular momentum in the basis formed by the eigenfunctions of $\hat{I}_z$:

$$\hat{I}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{I}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad \hat{I}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \hat{I}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{2.48}$$

This basis is a good choice if the matrix representing Hamiltonian is also diagonal in this basis and eigenfunctions of $\hat{I}_z$ are the same as eigenfunctions of the Hamiltonian, representing stationary states.

Traditionally, eigenfunctions of $\hat{I}_z$ are written as $|\alpha\rangle$ or $|\uparrow\rangle$ and $|\beta\rangle$ or $|\downarrow\rangle$.

$$\hat{I}_z|\alpha\rangle = +\frac{\hbar}{2}|\alpha\rangle \qquad \hat{I}_z|\uparrow\rangle = +\frac{\hbar}{2}|\uparrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = +\frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.49}$$

$$\hat{I}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle \qquad \hat{I}_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{2.50}$$

Note that the vectors used to represent $|\alpha\rangle$ and $|\beta\rangle$ in Eqs. 2.49 and 2.50 are not the only choice. Vectors in Eqs. 2.49 and 2.50 have a phase set to zero (they are made of real numbers). Any other phase ϕ would work as well, e.g.

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \to \begin{pmatrix} \mathrm{e}^{\mathrm{i}\phi} \\ 0 \end{pmatrix}. \tag{2.51}$$

- If the particle is in state $|\alpha\rangle$, the result of measuring I_z is *always* $+\hbar/2$. The expected value is

$$\langle I_z\rangle = \langle\alpha|I_z|\alpha\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = +\frac{\hbar}{2}. \tag{2.52}$$

- If the particle is in state $|\beta\rangle$, the result of measuring I_z is *always* $-\hbar/2$. The expected value is

$$\langle I_z\rangle = \langle\beta|I_z|\beta\rangle = \begin{pmatrix} 0 & 1 \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}. \tag{2.53}$$

- Any state $c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$ is possible, but the result of a single measurement of I_z is *always* $+\hbar/2$ or $-\hbar/2$. However, the expected value of I_z is

$$\langle I_z\rangle = \langle\alpha|I_z|\beta\rangle = \begin{pmatrix} c_\alpha^* & c_\beta^* \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = (|c_\alpha|^2 - |c_\beta|^2)\frac{\hbar}{2}. \tag{2.54}$$

Wave functions $|\alpha\rangle$ and $|\beta\rangle$ are *not* eigenfunctions of $\hat{I}_x$ or $\hat{I}_y$.

The eigenvalues $\pm\hbar/2$ are closely related to the fact that spin is a relativistic effect. Special relativity requires that the Dirac equation must not change if we rotate the coordinate frame or if it moves with a constant speed (Lorentz transformation). This requirement allows us to determine eigenvalues of the operators represented by the Pauli matrices:

- We know that the matrices in the Dirac equation do not change if we rotate the coordinate system.
- We know how $\partial/\partial t$, $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$ change if we change the coordinate system by a rotation (or by a boost to a different speed).
- We can calculate how the set of eigenfunctions Ψ change by the rotation (and boost)

- We obtain the following function describing rotation about z:

$$R_j = \mathrm{e}^{\mathrm{i}\frac{I_{z,j}}{\hbar}\frac{\varphi}{2}}. \tag{2.55}$$

  This looks very similar to Eq. 1.58, but with one important difference: rotation by 2π ($360\,^\circ$) does not give the same eigenfunction R_j as no rotation ($\varphi = 0$), but changes its sign. Only rotation by 4π ($720\,^\circ$) reverts the system to the initial state!

- Eq. 1.58 tells us that the eigenvalues of the operator of the spin angular momentum are half-integer multiples of $\hbar$:

$$I_{z,1} = \frac{\hbar}{2} \qquad I_{z,2} = -\frac{\hbar}{2}. \tag{2.56}$$

2.6 Eigenfunctions of $\hat{I}_x$ and $\hat{I}_y$

Eigenfunctions of $\hat{I}_x$ are the following linear combinations of $|\alpha\rangle$ and $|\beta\rangle$:

$$\frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \equiv |\rightarrow\rangle \tag{2.57}$$

$$-\frac{\mathrm{i}}{\sqrt{2}}|\alpha\rangle + \frac{\mathrm{i}}{\sqrt{2}}|\beta\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\\mathrm{i}\end{pmatrix} \equiv |\leftarrow\rangle \tag{2.58}$$

or these linear combinations multiplied by a phase factor $\mathrm{e}^{\mathrm{i}\phi}$. E.g., $|\leftarrow\rangle$ can be represented by

$$\mathrm{e}^{\mathrm{i}\pi/2}\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\\mathrm{i}\end{pmatrix} = \mathrm{i}\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\\mathrm{i}\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}. \tag{2.59}$$

Eigenvalues are again $\hbar/2$ and $-\hbar/2$:

$$\hat{I}_x|\rightarrow\rangle = +\frac{\hbar}{2}|\rightarrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = -\frac{\hbar}{2}\cdot\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \tag{2.60}$$

$$\hat{I}_x|\leftarrow\rangle = +\frac{\hbar}{2}|\leftarrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\\mathrm{i}\end{pmatrix} = -\frac{\hbar}{2}\cdot\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\\mathrm{i}\end{pmatrix} \tag{2.61}$$

Eigenfunctions of $\hat{I}_y$ are the following linear combinations of $|\alpha\rangle$ and $|\beta\rangle$:

$$\frac{1-\mathrm{i}}{2}|\alpha\rangle + \frac{1+\mathrm{i}}{2}|\beta\rangle = \frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\1+\mathrm{i}\end{pmatrix} \equiv |\otimes\rangle \tag{2.62}$$

$$-\frac{1+\mathrm{i}}{2}|\alpha\rangle + \frac{1-\mathrm{i}}{2}|\beta\rangle = \frac{1}{2}\begin{pmatrix}1+\mathrm{i}\\1-\mathrm{i}\end{pmatrix} \equiv |\odot\rangle \tag{2.63}$$

or these linear combinations multiplied by a phase factor $\mathrm{e}^{\mathrm{i}\phi}$. E.g., $|\otimes\rangle$ can be represented by

$$\mathrm{e}^{\mathrm{i}\pi/4}\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\1+\mathrm{i}\end{pmatrix} = \frac{1+\mathrm{i}}{\sqrt{2}}\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\1+\mathrm{i}\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\\mathrm{i}\end{pmatrix}. \tag{2.64}$$

Eigenvalues are again $\hbar/2$ and $-\hbar/2$:

$$\hat{I}_y|\otimes\rangle = +\frac{\hbar}{2}|\otimes\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\1+\mathrm{i}\end{pmatrix} = +\frac{\hbar}{2}\cdot\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\1+\mathrm{i}\end{pmatrix} \tag{2.65}$$

$$\hat{I}_y|\odot\rangle = -\frac{\hbar}{2}|\odot\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\frac{1}{2}\begin{pmatrix}1+\mathrm{i}\\1-\mathrm{i}\end{pmatrix} = -\frac{\hbar}{2}\cdot\frac{1}{2}\begin{pmatrix}1+\mathrm{i}\\1-\mathrm{i}\end{pmatrix} \tag{2.66}$$

2.7 Operators of spin magnetic moment

Similarly to the orbital magnetic moment, the magnetic moment associated with the spin is directly proportional to the spin angular momentum $\mu = \gamma \vec{I}$. Therefore, we can write the operators

$$\hat{\mu}_x = \gamma \hat{I}_x \qquad \hat{\mu}_y = \gamma \hat{I}_y \qquad \hat{\mu}_z = \gamma \hat{I}_z \qquad \hat{\mu}^2 = \gamma^2 \hat{I}^2. \tag{2.67}$$

However, the value of $\gamma = Q/2m$ derived for the orbital magnetic moment gives wrong values of the spin magnetic moment. The correct γ for spin magnetic moment must be derived from relativistic quantum mechanics (more precisely, from quantum electrodynamics), as shown in the next section.

2.8 Hamiltonian of spin magnetic moment

The classical theory of electromagnetism (Maxwell equations) show that energy and momentum of a particle in en electromagnetic field must be transformed as follows

$$E \to E - QV \qquad \vec{p} \to \vec{p} - Q\vec{A}, \tag{2.68}$$

where V is the electric potential and $\vec{A}$ is a so-called vector potential, related to the magnetic induction $\vec{B}$:

$$\vec{B} = \vec{\nabla} \times \vec{A}, \tag{2.69}$$

$\vec{\nabla} = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$.

Accordingly, the operators of energy and momentum change to

$$\mathrm{i}\hbar\frac{\partial}{\partial t} \to \mathrm{i}\hbar\frac{\partial}{\partial t} - QV \qquad -\mathrm{i}\hbar\frac{\partial}{\partial x} \to -\mathrm{i}\hbar\frac{\partial}{\partial x} - QA_x \qquad -\mathrm{i}\hbar\frac{\partial}{\partial y} \to -\mathrm{i}\hbar\frac{\partial}{\partial y} - QA_y \qquad -\mathrm{i}\hbar\frac{\partial}{\partial z} \to -\mathrm{i}\hbar\frac{\partial}{\partial z} - QA_z \tag{2.70}$$

This modifies the $\hat{O}^+$ and $\hat{O}^-$ in the Dirac equation so that the first two rows of the operator $\hat{O}^2$ become

$$\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - QV\right)^2 - c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 - c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 - c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2 - m_0^2c^4\right)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$
$$-Qc^2\hbar B_x\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} - Qc^2\hbar B_y\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix} - Qc^2\hbar B_z\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \tag{2.71}$$

$\mathrm{i}\hbar\partial/\partial t$ is the operator of the total energy $E_t = E + m_0c^2$. Therefore, we can express it as a sum of the Hamiltonian of the Schrödinger equation and the mass term: $\mathrm{i}\hbar\partial/\partial t = \hat{H} + m_0c^2$. Also, we can replace the Pauli matrices in the second line by the operators of the spin angular momentum:

$$\left(\left(\hat{H} + m_0c^2 - QV\right)^2 - c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 - c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 - c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2 - m_0^2c^4\right)\hat{1}$$
$$-2Qc^2\hbar B_x\hat{I}_x - 2Qc^2\hbar B_y\hat{I}_y - 2Qc^2\hbar B_z\hat{I}_z \tag{2.72}$$

The $\left(\hat{H} + m_0c^2 - QV\right)^2$ term can be expressed as

$$\left(\hat{H} + m_0c^2 - QV\right)^2 = m_0^2c^4 + c^2\left(\frac{(\hat{H} - QV)^2}{c^2} + 2m_0(\hat{H} - QV)\right). \tag{2.73}$$

If the speed of the particle is much lower than the speed of light, $m_0c^2 \gg \hat{H} - QV$, and the term divided by c^2 can be neglected. Then, the $m_0^2c^4$ terms in the expression 2.74 cancel each other and c^2 can be factored out:

$$\begin{aligned} &c^2\left(2m_0(\hat{H} - QV) - \left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 - \left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 - \left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2\right)\hat{1} \\ &-2Qc^2B_x\hat{I}_x - 2Qc^2B_y\hat{I}_y - 2Qc^2B_z\hat{I}_z \end{aligned} \tag{2.74}$$

Since $\hat{O}^2\Psi = 0$, the Hamiltonian $\hat{H}$ is equal to

$$\begin{aligned} \hat{H} = &-\frac{1}{2m}\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 + \left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 + \left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2\right)\hat{1} + QV\hat{1} \\ &+ \underbrace{2\frac{Q}{2m}B_x\hat{I}_x + 2\frac{Q}{2m}B_y\hat{I}_y + 2\frac{Q}{2m}B_z\hat{I}_z}_{\hat{H}_I} \end{aligned} \tag{2.75}$$

The second line describes the contribution to the Hamiltonian due to the interactions of the spin magnetic moment with the magnetic field. Comparison with 1.76 shows that

$$\hat{H}_I = -\gamma B_x\hat{I}_x + B_y\hat{I}_y + B_z\hat{I}_z, \tag{2.76}$$

where

$$\gamma = 2\frac{Q}{2m}. \tag{2.77}$$

2.9 Spin and magnetogyric ratio of real particles

Eq. 2.75, used to derive the value of γ, describes interaction of a particle with an external electromagnetic field. However, charged particles are themselves sources of magnetic fields. Therefore, γ is not exactly twice $Q/2m$. In general, the value of γ is

$$\gamma = g\frac{Q}{2m}, \tag{2.78}$$

where the constant g include corrections for interactions of the particle with its own field (and other effects). For electron, the corrections are small and easy to calculate. The current theoretical prediction of $g = 2.0023318361(10)$, compared to a recent experimental measured value of $g = 2.0023318416(13)$. On the other hand, "corrections" for the constituents of atomic nuclei, quarks, are two orders of magnitude higher than the basic value of 2! It is because quarks are not "naked" as electrons, they are confined in protons and nucleons, "dressed" by interactions, not only electromagnetic, but mostly strong nuclear with gluon. Therefore, the magnetogyric ratio of proton is difficult to calculate and we rely on its experimental value. Everything is even more complicated when we go to higher nuclei, consisting of multiple protons and neutrons. In such cases, adding spin angular momenta represents another level of complexity. Fortunately, all equations derived for electron also apply to nuclei with the same eigenvalues

of spin magnetic moments (spin-1/2 nuclei), if the value of γ is replaced by the correct value for the given nucleus.[1]

2.10 Stationary states and energy level diagram

In the presence of a homogeneous magnetic field $\vec{B}_0 = (0, 0, B_0)$, the evolution of the system is given by the Hamiltonian $\hat{H} = -\gamma B_0 \hat{I}_z$. The Schrödinger equation is then

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = -\gamma B_0 \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}, \tag{2.79}$$

which is a set of two equations with separated variables

$$\frac{\mathrm{d}c_\alpha}{\mathrm{d}t} = +\mathrm{i}\frac{\gamma B_0}{2} c_\alpha \tag{2.80}$$

$$\frac{\mathrm{d}c_\beta}{\mathrm{d}t} = -\mathrm{i}\frac{\gamma B_0}{2} c_\beta \tag{2.81}$$

with the solution

$$c_\alpha = c_\alpha(t=0)\mathrm{e}^{+\mathrm{i}\frac{\gamma B_0}{2}t} = c_\alpha(t=0)\mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t} \tag{2.82}$$

$$c_\beta = c_\beta(t=0)\mathrm{e}^{-\mathrm{i}\frac{\gamma B_0}{2}t} = c_\beta(t=0)\mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t}. \tag{2.83}$$

If the initial state is $|\alpha\rangle$, $c_\alpha(t=0) = 1$, $c_\beta(t=0) = 0$, and

$$c_\alpha = \mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t} \tag{2.84}$$

$$c_\beta = 0. \tag{2.85}$$

Note that the evolution changes only the phase factor, but the system stays in state $|\alpha\rangle$ (all vectors described by Eq. 2.51 correspond to state $|\alpha\rangle$). It can be shown by calculating the probability that the system is in the $|\alpha\rangle$ or $|\beta\rangle$ state.

$$P_\alpha = c_\alpha^* c_\alpha = \mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t}\mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t} = 1 \tag{2.86}$$

$$P_\beta = c_\beta^* c_\beta = 0 \tag{2.87}$$

If the initial state is $|\beta\rangle$, $c_\alpha(t=0) = 0$, $c_\beta(t=0) = 1$, and

$$c_\alpha = 0 \tag{2.88}$$

$$c_\beta = \mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t}. \tag{2.89}$$

Again, the evolution changes only the phase factor, but the system stays in state $|\beta\rangle$. The probability that the system is in the $|\alpha\rangle$ or $|\beta\rangle$ state is

$$P_\alpha = c_\alpha^* c_\alpha = 0 \tag{2.90}$$

$$P_\beta = c_\beta^* c_\beta = \mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t}\mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t} = 1 \tag{2.91}$$

[1] NMR in organic chemistry and biochemistry is usually limited to spin-1/2 nuclei because signal decays too fast if the spin number is grater than 1/2.

- The states described by basis functions which are eigenfunctions of the Hamiltonian do not evolve (are stationary). It makes sense to draw *energy level diagram* for such states, with energy of each state given by the corresponding eigenvalue of the Hamiltonian. Energy of the $|\alpha\rangle$ state is $-\hbar\omega_0/2 =$ and energy of the $|\beta\rangle$ state is $+\hbar\omega_0/2 =$. The measurable quantity is the energy difference $\hbar\omega_0$, corresponding to the angular frequency ω_0.

2.11 Oscillatory states

In the presence of a homogeneous magnetic field $\vec{B}_1 = (B_1, 0, 0)$, the evolution of the system is given by the Hamiltonian $\hat{H} = -\gamma B_0 \hat{I}_x$. The Schrödinger equation is then

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = -\gamma B_1 \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}, \tag{2.92}$$

which is a set of two equations

$$\frac{\mathrm{d}c_\alpha}{\mathrm{d}t} = \mathrm{i}\frac{\gamma B_1}{2} c_\beta \tag{2.93}$$

$$\frac{\mathrm{d}c_\beta}{\mathrm{d}t} = \mathrm{i}\frac{\gamma B_1}{2} c_\alpha \tag{2.94}$$

These equations have similar structure as Eqs. 1.63 and 1.64. Adding and subtracting them leads to the solution

$$c_\alpha + c_\beta = C_+ \mathrm{e}^{+\mathrm{i}\frac{\gamma B_1}{2}t} = C_+ \mathrm{e}^{-\mathrm{i}\frac{\omega_1}{2}t} \tag{2.95}$$

$$c_\alpha - c_\beta = C_- \mathrm{e}^{-\mathrm{i}\frac{\gamma B_1}{2}t} = C_- \mathrm{e}^{+\mathrm{i}\frac{\omega_1}{2}t}. \tag{2.96}$$

If the initial state is $|\alpha\rangle$, $c_\alpha(t=0) = 1$, $c_\beta(t=0) = 0$, $C_+ = C_- = 1$, and

$$c_\alpha = \cos\left(\frac{\omega_1}{2}t\right) \tag{2.97}$$

$$c_\beta = -\mathrm{i}\sin\left(\frac{\omega_1}{2}t\right). \tag{2.98}$$

Probability that the system is in the $|\alpha\rangle$ or $|\beta\rangle$ state is calculated as

$$P_\alpha = c_\alpha^* c_\alpha = \cos^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} + \frac{1}{2}\cos(\omega_1 t) \tag{2.99}$$

$$P_\beta = c_\beta^* c_\beta = \sin^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} - \frac{1}{2}\cos(\omega_1 t) \tag{2.100}$$

If the initial state is $|\beta\rangle$, $c_\alpha(t=0) = 0$, $c_\beta(t=0) = 1$, $C_+ = 1$, $C_- = -1$, and

$$c_\alpha = -\mathrm{i}\sin\left(\frac{\omega_1}{2}t\right) \tag{2.101}$$

$$c_\beta = \cos\left(\frac{\omega_1}{2}t\right). \tag{2.102}$$

Probability that the system is in the $|\alpha\rangle$ or $|\beta\rangle$ state is calculated as

$$P_\alpha = c_\alpha^* c_\alpha = \sin^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} + \frac{1}{2}\cos(\omega_1 t) \tag{2.103}$$

$$P_\beta = c_\beta^* c_\beta = \cos^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} - \frac{1}{2}\cos(\omega_1 t) \tag{2.104}$$

In both cases, the system oscillates between the $|\alpha\rangle$ and $|\beta\rangle$ states.

- The states described by basis functions different from eigenfunctions of the Hamiltonian are not stationary but oscillate between $|\alpha\rangle$ and $|\beta\rangle$ with the angular frequency ω_1, given by the difference of the eigenvalues of the Hamiltonian ($-\hbar\omega_1/2$ and $\hbar\omega_1/2$).

Chapter 3

Ensembles of spins not interacting with other spins

3.1 Mixed state

So far, we worked with systems in so-called *pure states*, when we described the whole studied system by its complete wave function. It is fine if the system consists of one particle or a small number of particles. However, the complete wave function of whole molecules (or ensembles of whole molecules) is very complicated, represented by multidimensional vectors and in properties described by operators represented by multidimensional matrices. In NMR spectroscopy, we are interested only with properties of molecules associated with spins of the observed nuclei. If we assume motions of the whole molecule, of its atoms, and of electrons and nuclei in the atoms, do not depend on the spin, we can divide the complete wave function into spin wave functions and wave function describing all the other degrees of freedom. The result of this division is that spin wave functions for different molecules are not identical. Therefore, the spin wave function describing the whole set of nuclei in different molecules is represented by multidimensional vectors and with properties described by operators represented by multidimensional matrices. This can be simplified dramatically if

1. the measured quantity does not depend on other coordinates that spin coordinates α or β – true for magnetization in homogeneous magnetic fields (contributions of individual nuclei to the magnetization then do not depend on their positions is space)
2. the interactions of the observed magnetic moments change only eigenvalues, not eigenfunctions – true for interactions with fields which can be described without using spin eigenfunctions

Using the same basis for different nuclei $\Rightarrow$ multidimensional operator matrices $\rightarrow$ two-dimensional operator matrices (for spin-1/2 nuclei).

Expected value $\langle A \rangle$ of a quantity A for a single nucleus can be calculated using Eq.1.17 as a trace of the following product of matrices:

$$\langle A \rangle = \begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \tag{3.1}$$

Expected value $\langle A \rangle$ of a quantity A for *multiple nuclei with the same basis* is

$$\langle A \rangle = \begin{pmatrix} c_{\alpha,1} c_{\alpha,1}^* & c_{\alpha,1} c_{\beta,1}^* \\ c_{\beta,1} c_{\alpha,1}^* & c_{\beta,1} c_{\beta,1}^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} + \begin{pmatrix} c_{\alpha,2} c_{\alpha,2}^* & c_{\alpha,2} c_{\beta,2}^* \\ c_{\beta,2} c_{\alpha,2}^* & c_{\beta,2} c_{\beta,2}^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} + \cdots$$

$$
\begin{aligned}
&= \left(\begin{pmatrix} c_{\alpha,1}c^*_{\alpha,1} & c_{\alpha,1}c^*_{\beta,1} \\ c_{\beta,1}c^*_{\alpha,1} & c_{\beta,1}c^*_{\beta,1} \end{pmatrix} + \begin{pmatrix} c_{\alpha,2}c^*_{\alpha,2} & c_{\alpha,2}c^*_{\beta,2} \\ c_{\beta,2}c^*_{\alpha,2} & c_{\beta,2}c^*_{\beta,2} \end{pmatrix} + \cdots \right) \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \\
&= \mathcal{N} \underbrace{\begin{pmatrix} \overline{c_\alpha c^*_\alpha} & \overline{c_\alpha c^*_\beta} \\ \overline{c_\beta c^*_\alpha} & \overline{c_\beta c^*_\beta} \end{pmatrix}}_{\hat{\rho}} \underbrace{\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}}_{\hat{A}} = \mathcal{N}\hat{\rho}\hat{A}
\end{aligned} \tag{3.2}
$$

The matrix $\hat{\rho}$ is the *(probability) density matrix*, the horizontal bar indicates average over the whole ensemble of nuclei in the sample.

Why probability density? Because the probability $P = \langle\Psi|\Psi\rangle \Rightarrow$ the operator of probability is the unit matrix $\hat{1}$: $\langle\Psi|\Psi\rangle \equiv \langle\Psi|\hat{1}|\Psi\rangle$. Therefore, the expectation value of probability can be also calculated using Eq.1.17 as $\mathrm{Tr}\{\hat{\rho}\hat{1}\} = \mathrm{Tr}\{\hat{\rho}\}$.

- Two-dimensional basis is sufficient for the whole set of $\mathcal{N}$ nuclei (if they do not interact with each other).
- Statistical approach: the possibility to use a 2D basis is paid by loosing the information about the *microscopic state*. The same density matrix can describe an astronomic number of possible combinations of individual angular momenta which give the same *macroscopic* result. What is described by the density matrix is called the *mixed state*.
- Choice of the basis is encoded in the definition of $\hat{\rho}$ (eigenfunctions of $\hat{I}_z$).
- The state is described not by a vector, but by a matrix, $\hat{\rho}$ is a matrix like operators.
- Any 2×2 matrix can be written as a linear combination of four 2×2 matrices. Such four matrices can be used as a *basis* of all 2×2 matrices, including operators (in the same manner as two selected 2-component vectors serve as a basis for all 2-component vectors).
- Good choice of a basis is a set of *orthonormal* matrices.[1]
- *Diagonal elements* of $\hat{\rho}$ (or matrices with diagonal elements only) are known as *populations*. They tell what populations of pure α and β states would give the same *polarization* along z.
- *Off-diagonal elements* (or matrices with diagonal elements only) are known as *coherences*. They tell what combinations of coefficients c_α and c_β would give the same coherence of phases of the rotation about z.

3.2 Coherence

- *Coherence* is a very important issue in NMR
- In a *pure state*, $c_\alpha c^*_\beta$ is given by amplitudes and by the difference of phases of c_α and c_β: $c_\alpha c^*_\beta = |c_\alpha||c_\beta|\mathrm{e}^{-\mathrm{i}(\phi_\alpha-\phi_\beta)}$.
- In a *mixed state*, $c_{\alpha,j}$ and $c_{\beta,j}$ is different for the observed nucleus in each molecule j. If $c_{\alpha,j}$ and $c_{\beta,j}$ describe stationary states, only phases of $c_{\alpha,j}$ and $c_{\beta,j}$ change as the system evolves. Therefore, $\overline{c_\alpha c^*_\beta} = \overline{|c_\alpha||c_\beta|}\cdot\overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha-\phi_\beta)}}$. The phase of $\overline{c_\alpha c^*_\beta}$ is given by $\overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha-\phi_\beta)}}$. If the evolution of phases is

[1] Orthonormality for a set of four matrices $\hat{A}_1, \hat{A}_2, \hat{A}_3, \hat{A}_4$ can be defined as $\mathrm{Tr}\{\hat{A}^\dagger_j\hat{A}_k\} = \delta_{j,k}$, where j and $k \in \{1,2,3,4\}$, $\delta_{j,k} = 1$ for $j = k$ and $\delta_{j,k} = 0$ for $j \neq k$, and $\hat{A}^\dagger_j$ is an *adjoint* matrix of $\hat{A}_j$, i.e., matrix obtained from $\hat{A}_j$ by exchanging rows and columns and replacing all numbers with their complex conjugates.

coherent, $\phi_{\alpha,j}$ and $\phi_{\beta,j}$ vary but $\phi_{\alpha,j} - \phi_{\beta,j}$ is constant. In such a case, $\overline{c_\alpha c_\beta^*} = \overline{|c_\alpha||c_\beta|}\mathrm{e}^{\mathrm{i}(\phi_\alpha - \phi_\beta)}$. However, if the phases $\phi_{\alpha,j}$ and $\phi_{\beta,j}$ evolve independently, $\overline{\mathrm{e}^{-\mathrm{i}(\phi_\alpha - \phi_\beta)}} = \overline{\mathrm{e}^{-\mathrm{i}\phi_\alpha}} \cdot \overline{\mathrm{e}^{\mathrm{i}\phi_\beta}} = 0 \cdot 0$ (because $\phi_{\alpha,j}$ and $\phi_{\beta,j}$ can be anywhere between 0 and 2π and the average value of both real component $\cos(\phi_{\alpha,j})$ and imaginary component $\sin(\phi_{\alpha,j})$ of $\mathrm{e}^{\mathrm{i}\phi_{\alpha,j}}$ in the interval $(0, 2\pi)$ is zero). Obviously, $\overline{c_\alpha c_\beta^*} = 0$ in such a case.

3.3 Basis sets

Usual choices of basis matrices are:

- *Cartesian operators*, equal to the operators of spin angular momentum divided by $\hbar$. In this text, these matrices are written as $\mathcal{I}_x$, $\mathcal{I}_y$, etc. In a similar fashion, we write $\mathcal{H} = \hat{H}/\hbar$ for Hamiltonians with eigenvalues expressed in units of (angular) frequency, not energy. The normalization factor $\sqrt{2}$ is often omitted (then the basis is still orthogonal, but not orthonormal).

$$\sqrt{2}\mathcal{I}_t = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \sqrt{2}\mathcal{I}_z = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sqrt{2}\mathcal{I}_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sqrt{2}\mathcal{I}_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{3.3}$$

- Single-element *population*

$$\mathcal{I}_\alpha = \mathcal{I}_t + \mathcal{I}_z = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \qquad \mathcal{I}_\beta = \mathcal{I}_t - \mathcal{I}_z = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{3.4}$$

  and *transition* operators

$$\mathcal{I}_+ = \mathcal{I}_x + \mathrm{i}\mathcal{I}_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \mathcal{I}_- = \mathcal{I}_x - \mathrm{i}\mathcal{I}_y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{3.5}$$

- $$\sqrt{2}\mathcal{I}_t = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sqrt{2}\mathcal{I}_z = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \mathcal{I}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \mathcal{I}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{3.6}$$

3.4 Equation of motion: Liouville-von Neumann equation

In order to describe the evolution of mixed states in time, we must find an equation describing how elements of the density matrix change in time.

We start with the Schrödinger equation for a single spin in matrix representation:

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = \begin{pmatrix} H_{\alpha,\alpha} & H_{\alpha,\beta} \\ H_{\beta,\alpha} & H_{\beta,\beta} \end{pmatrix}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = \begin{pmatrix} H_{\alpha,\alpha}c_\alpha + H_{\alpha,\beta}c_\beta \\ H_{\beta,\alpha}c_\alpha + H_{\beta,\beta}c_\beta \end{pmatrix}. \tag{3.7}$$

Note that the Hamiltonian matrix is written in a general form, the basis functions are not necessarily eigenfunctions of the operator. However, the matrix must be *Hermitian*, i.e., $H_{j,k} = H_{k,j}^*$:

$$H_{\alpha,\beta} = H_{\beta,\alpha}^* \qquad H_{\beta,\alpha} = H_{\alpha,\beta}^*. \tag{3.8}$$

If we multiply Eq. 3.7 by the basis functions from left, we obtained the differential equations for c_α and c_β (because the basis functions are orthonormal):

$$(1\ 0)\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}c_\alpha\\c_\beta\end{pmatrix}=\mathrm{i}\hbar\frac{\mathrm{d}c_\alpha}{\mathrm{d}t}=H_{\alpha,\alpha}c_\alpha+H_{\alpha,\beta}c_\beta \tag{3.9}$$

$$(0\ 1)\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}c_\alpha\\c_\beta\end{pmatrix}=\mathrm{i}\hbar\frac{\mathrm{d}c_\beta}{\mathrm{d}t}=H_{\beta,\alpha}c_\alpha+H_{\beta,\beta}c_\beta. \tag{3.10}$$

In general,

$$\frac{\mathrm{d}c_k}{\mathrm{d}t}=-\frac{\mathrm{i}}{\hbar}\sum_l H_{k,l}c_l \tag{3.11}$$

and its complex conjugate (using Eq. 3.8) is

$$\frac{\mathrm{d}c_k^*}{\mathrm{d}t}=+\frac{\mathrm{i}}{\hbar}\sum_l H_{k,l}^*c_l^*=+\frac{\mathrm{i}}{\hbar}\sum_l H_{l,k}c_l^*. \tag{3.12}$$

Elements of the density matrix consist of the products $c_jc_k^*$. Therefore, we must calculate

$$\frac{\mathrm{d}c_jc_k^*}{\mathrm{d}t}=c_j\frac{\mathrm{d}c_k^*}{\mathrm{d}t}+c_k^*\frac{\mathrm{d}c_j}{\mathrm{d}t}=\frac{\mathrm{i}}{\hbar}\sum_l H_{l,k}c_jc_l^*-\frac{\mathrm{i}}{\hbar}\sum_l H_{j,l}c_lc_k^* \tag{3.13}$$

For multiple nuclei with the same basis,

$$\frac{\mathrm{d}(c_{j,1}c_{k,1}^*+c_{j,2}c_{k,2}^*+\cdots)}{\mathrm{d}t}=c_{j,1}\frac{\mathrm{d}c_{k,1}^*}{\mathrm{d}t}+c_{k,1}^*\frac{\mathrm{d}c_{j,1}}{\mathrm{d}t}+c_{j,2}\frac{\mathrm{d}c_{k,2}^*}{\mathrm{d}t}+c_{k,2}^*\frac{\mathrm{d}c_{j,2}}{\mathrm{d}t}+\cdots \tag{3.14}$$

$$=\frac{\mathrm{i}}{\hbar}\sum_l H_{l,k}(c_{j,1}c_{l,1}^*+c_{j,2}c_{l,2}^*+\cdots)-\frac{\mathrm{i}}{\hbar}\sum_l H_{j,l}(c_{l,1}c_{k,1}^*+c_{l,2}c_{k,2}^*+\cdots) \tag{3.15}$$

Note that

$$\sum_l(c_{j,1}c_{l,1}^*+c_{j,2}c_{l,2}^*+\cdots)H_{l,k}=\mathcal{N}\sum_l\rho_{j,l}H_{l,k} \tag{3.16}$$

is the j,k element of the product $\mathcal{N}\hat{\rho}\hat{H}$, and

$$\sum_l H_{j,l}(c_{l,1}c_{k,1}^*+c_{l,2}c_{k,2}^*+\cdots)=\mathcal{N}\sum_l H_{j,l}\rho_{l,k} \tag{3.17}$$

is the j,k element of the product $\mathcal{N}\hat{H}\hat{\rho}$. Therefore, we can write the equation of motion for the whole density matrix as

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t}=\frac{\mathrm{i}}{\hbar}(\hat{\rho}\hat{H}-\hat{H}\hat{\rho})=\frac{\mathrm{i}}{\hbar}[\hat{\rho},\hat{H}]=-\frac{\mathrm{i}}{\hbar}[\hat{H},\hat{\rho}] \tag{3.18}$$

or in the units of (angular) frequency

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t}=\mathrm{i}(\hat{\rho}\mathcal{H}-\mathcal{H}\hat{\rho})=\mathrm{i}[\hat{\rho},\mathcal{H}]=-\mathrm{i}[\mathcal{H},\hat{\rho}] \tag{3.19}$$

Eqs. 3.18 and 3.19 are known as the *Liouville-von Neumann eqaution.*

3.5 Rotation in operator space

Liouville-von Neumann equation can be solved using techniques of linear algebra. However, a very simple geometric solution is possible, if the Hamiltonian does not change in time and consists solely of matrices which commute (e.g., $\mathcal{I}_t$ and $\mathcal{I}_z$, but not $\mathcal{I}_x$ and $\mathcal{I}_z$).

Example for $\mathcal{H} = \varepsilon\mathcal{I}_t + \omega_0\mathcal{I}_z$ and $\hat{\rho} = c_x\mathcal{I}_x + c_y\mathcal{I}_y + c_z\mathcal{I}_z + c_t\mathcal{I}_t$:

Let's first evaluate the commutators from the Liouville-von Neumann equation:

$\mathcal{I}_t$ is proportional to a unit matrix $\Rightarrow$ it must commute with all matrices:

$$[\mathcal{I}_t, \mathcal{I}_j] = 0 \qquad (j = x, y, z, t). \tag{3.20}$$

Commutators of $\mathcal{I}_z$ are given by the definition of angular momentum operators:

$$[\mathcal{I}_z, \mathcal{I}_z] = [\mathcal{I}_z, \mathcal{I}_t] = 0 \qquad [\mathcal{I}_z, \mathcal{I}_x] = \mathrm{i}\mathcal{I}_y \qquad [\mathcal{I}_z, \mathcal{I}_y] = -\mathrm{i}\mathcal{I}_x. \tag{3.21}$$

Let's write the Liouville-von Neumann equation with the evaluated commutators:

$$\frac{\mathrm{d}c_x}{\mathrm{d}t}\mathcal{I}_x + \frac{\mathrm{d}c_y}{\mathrm{d}t}\mathcal{I}_y + \frac{\mathrm{d}c_z}{\mathrm{d}t}\mathcal{I}_z + \frac{\mathrm{d}c_t}{\mathrm{d}t}\mathcal{I}_t = -\mathrm{i}\omega_0 c_x\mathcal{I}_y + \mathrm{i}\omega_0 c_y\mathcal{I}_x. \tag{3.22}$$

Written in a matrix representation (noticing that c_z and c_t do not evolve because the $c_z\mathcal{I}_z$ and $c_t\mathcal{I}_t$ components of the density matrix commute with both matrices constituting the Hamiltonian),

$$\frac{1}{2}\begin{pmatrix} 0 & \frac{\mathrm{d}c_x}{\mathrm{d}t} \\ \frac{\mathrm{d}c_x}{\mathrm{d}t} & 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i}\frac{\mathrm{d}c_y}{\mathrm{d}t} \\ \mathrm{i}\frac{\mathrm{d}c_y}{\mathrm{d}t} & 0 \end{pmatrix} + 0 + 0 = \frac{1}{2}\begin{pmatrix} 0 & -\omega_0 c_x \\ \omega_0 c_x & 0 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 0 & \mathrm{i}\omega_0 c_y \\ \mathrm{i}\omega_0 c_y & 0 \end{pmatrix}. \tag{3.23}$$

This corresponds to a set of two differential equations

$$\frac{\mathrm{d}c_x}{\mathrm{d}t} = -\mathrm{i}\omega_0 c_y \tag{3.24}$$

$$\frac{\mathrm{d}c_y}{\mathrm{d}t} = +\mathrm{i}\omega_0 c_x \tag{3.25}$$

with the same structure as Eqs. 1.63 and 1.64. The solution is

$$c_x = c_0 \cos(\omega_0 t + \phi_0) \tag{3.26}$$

$$c_y = c_0 \sin(\omega_0 t + \phi_0) \tag{3.27}$$

with the amplitude c_0 and phase ϕ_0 given by the initial conditions.

We see that coefficients c_x, c_y, c_z play the same roles as coordinates r_x, r_y, r_z in Eqs. 1.63–1.65, respectively, and operators $\mathcal{I}_x$, $\mathcal{I}_y$, $\mathcal{I}_z$ play the same role as unit vectors $\vec{\imath}, \vec{\jmath}, \vec{k}$, defining directions of the axes of the Cartesian coordinate system. Therefore, the evolution of $\hat{\rho}$ can be described as a *rotation in an abstract three-dimensional operator space* with the dimensions given by $\mathcal{I}_x$, $\mathcal{I}_y$, and $\mathcal{I}_z$.

3.6 General strategy of analyzing NMR experiments

The Liouville-von Neumann equation is the most important tool in the analysis of evolution of the spin system during the NMR experiment. The general strategy consists of three steps:

1. Define $\hat{\rho}$ at $t = 0$

2. Describe evolution of $\hat{\rho}$ using the relevant Hamiltonians – this is usually done in several steps
3. Calculate the expectation value $\langle M \rangle$ of the measured quantity according to Eq. 1.17

Obviously, the procedure requires knowledge of

1. relation(s) describing the initial state of the system ($\hat{\rho}(0)$)
2. all Hamiltonians
3. the operator representing the measurable quantity

Here, we start from the end and define first the operator of the measurable quantity. Then we spend a lot of time defining all necessary Hamiltonians. Finally, we use the knowledge of the Hamiltonians and basic thermodynamics to describe the initial state.

3.7 Operator of the observed quantity

The quantity observed in the NMR experiment is the *total magnetization*, i.e., the sum of magnetic moments of all nuclei. Technically, we observe oscillations in the plane perpendicular to the homogeneous field of the magnet $\vec{B}_0$. The associated oscillations of the magnetic fields of nuclei induce *electromotive force* in the detector coil. Since a complex signal is usually recorded, the operator of complex magnetization $M_+ = M_x + \mathrm{i}M_y$ is used ($M_- = M_x - \mathrm{i}M_y$ can be used as well).

$$\hat{M}_+ = \mathcal{N} \sum_n \gamma_n (\hat{I}_{x,n} - \mathrm{i}\hat{I}_{x,n}) = \mathcal{N} \sum_n \gamma_n \hat{I}_{+,n}, \tag{3.28}$$

where the index n distinguishes different types of nuclei and $\mathcal{N}$ is the number of nuclei of each type in the sample.

3.8 Static field $\vec{B}_0$

We already defined the Hamiltonian of the static homogeneous magnetic field $\vec{B}_0$, following the classical description of energy of a magnetic moment in a magnetic field. Since $\vec{B}_0$ defines direction of the z axis,

$$\hat{H}_{0,\mathrm{lab}} = -\gamma B_0 \hat{I}_z. \tag{3.29}$$

3.9 Radio-frequency field $\vec{B}_1$

The oscillating magnetic field of radio waves irradiating the sample is formally decomposed into two rotating magnetic fields (with the same speed given by the frequency of the radio waves ω_{radio}, but with opposite sense of rotation). The component resonating (approximately) with the precession frequency of the observed nuclei usually defines the x axis of the rotating coordinate frame used most often in NMR spectroscopy. In this system, frequency of the resonating component[2] is subtracted from the precession frequency and the difference $\Omega = \omega_0 - \omega_{\mathrm{rot}} = -\gamma B_0 - \omega_{\mathrm{rot}}$ is the frequency offset defining the evolution in the rotating frame in the absence of other fields:

In the absence of other fields than $\vec{B}_0$:

$$\hat{H}_{0,\mathrm{rot}} = (-\gamma B_0 - \omega_{\mathrm{rot}})\hat{I}_z = \Omega \hat{I}_z. \tag{3.30}$$

[2] Formally opposite to ω_{radio}

During irradiation by waves with the phase defining x

$$\hat{H}_{1,\mathrm{rot}} = (-\gamma B_0 - \omega_{\mathrm{rot}})\hat{I}_z - \gamma B_1 \hat{I}_x = \Omega \hat{I}_z + \omega_1 \hat{I}_y. \tag{3.31}$$

During irradiation by waves shifted by $\pi/2$ from the phase defining x

$$\hat{H}_{1,\mathrm{rot}} = (-\gamma B_0 - \omega_{\mathrm{rot}})\hat{I}_z - \gamma B_1 \hat{I}_y = \Omega \hat{I}_z + \omega_1 \hat{I}_y. \tag{3.32}$$

If the radio frequency is close to resonance, $-\gamma B_0 \approx \omega_{\mathrm{rot}}$, $\Omega \ll \omega_1$, and the $\hat{I}_z$ component of the Hamiltonian can be neglected.

3.10 Phenomenology of chemical shift

The energy of the magnetic moment of the observed nucleus is influenced by magnetic fields associated with motions of nearby electrons. Before we write the Hamiltonian describing this contribution to the energy of the system, we describe the magnetic fields of moving electrons.

If a moving electron enters a homogeneous magnetic field, it experiences a Lorentz force and moves in a circle in a plane perpendicular to the field (cyclotron motions). Such an electron represents an electric current in a circular loop, and is a source of a magnetic field induced by the homogeneous magnetic field. The homogeneous magnetic field $\vec{B}_0$ in NMR spectrometers induces a similar motion of electrons in atoms, which generates microscopic magnetic fields.

The observed nucleus feels the external magnetic field $\vec{B}_0$ slightly modified by the microscopic fields of electrons.

If the electron distribution is spherically symmetric, with the observed nucleus in the center (e.g. electrons in the 1s orbital of the hydrogen atom), the induced field of the electrons decreases the effective magnetic field felt by the nucleus in the center. Since the induced field of electrons is proportional to the inducing external field $\vec{B}_0$, the effective field can be described as

$$\vec{B} = \vec{B}_0 + \vec{B}_{\mathrm{e}} = (1+\delta)\vec{B}_0. \tag{3.33}$$

The constant δ is known as *chemical shift* and does not depend on the orientation of the molecule in such a case. The precession frequency of the nucleus is equal to $(1+\delta)\omega_0$

Electron distribution is not spherically symmetric in most molecules. As a consequence, the effective field depends on the orientation of the whole molecule and on mutual orientations of atoms, defining the shapes of molecular orbitals. Therefore, the effective field fluctuates as a result of rotational diffusion of the molecule and of internal motions changing mutual positions of atoms. The induced field of electrons is still proportional to the inducing external field $\vec{B}_0$, but the proportionality constants are different for each combination of components of $\vec{B}_{\mathrm{e}}$ and $\vec{B}_0$ in the coordination frame used. Therefore, we need six[3] constants δ_{jk} to describe the effect of electrons:

$$B_{\mathrm{e},x} = \delta_{xx}B_{0,x} + \delta_{xy}B_{0,y} + \delta_{xz}B_{0,z} \tag{3.34}$$

$$B_{\mathrm{e},y} = \delta_{yx}B_{0,x} + \delta_{yy}B_{0,y} + \delta_{yz}B_{0,z} \tag{3.35}$$

$$B_{\mathrm{e},z} = \delta_{zx}B_{0,x} + \delta_{zy}B_{0,y} + \delta_{zz}B_{0,z} \tag{3.36}$$

Eqs. 3.34–3.36 can be written in more compact forms

$$\begin{pmatrix} B_{\mathrm{e},x} \\ B_{\mathrm{e},y} \\ B_{\mathrm{e},z} \end{pmatrix} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix} \cdot \begin{pmatrix} B_{0,x} \\ B_{0,y} \\ B_{0,z} \end{pmatrix} \tag{3.37}$$

[3]There are nine constants in Eqs. 3.34–3.36, but $\delta_{xy} = \delta_{yx}$, $\delta_{xz} = \delta_{zx}$, and $\delta_{yz} = \delta_{zy}$.

or

$$\vec{B}_{\mathrm{e}} = \underline{\delta} \cdot \vec{B}_0, \tag{3.38}$$

where $\underline{\delta}$ is the *chemical shift tensor*.

It is always possible to find a coordinate system X, Y, Z known as the *principal frame*, where $\underline{\delta}$ is represented by a diagonal matrix. In such a system, we need only three constants (principal values of the chemical shift tensor): $\delta_{XX}, \delta_{YY}, \delta_{ZZ}$. However, three more parameters must be specified: three *Euler angles* (written as φ, ϑ, and ψ in this text) defining orientation of the coordinate system X, Y, Z in the laboratory coordinate system x, y, z. Note that $\delta_{XX}, \delta_{YY}, \delta_{ZZ}$ are true constants because they do not change as the molecule tumbles in solution (but they may change due to internal motions or chemical changes of the molecule). The orientation is completely described by the Euler angles.

The chemical shift tensor in its principal frame can be also written as a sum of three simple matrices, each multiplied by one characteristic constant:

$$\begin{pmatrix} \delta_{XX} & 0 & 0 \\ 0 & \delta_{YY} & 0 \\ 0 & 0 & \delta_{ZZ} \end{pmatrix} = \delta_{\mathrm{i}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \delta_{\mathrm{a}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \delta_{\mathrm{r}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{3.39}$$

where

$$\delta_{\mathrm{i}} = \frac{1}{3}\mathrm{Tr}\{\underline{\delta}\} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ}) \tag{3.40}$$

is the *isotropic component* of the chemical shift tensor,

$$\delta_{\mathrm{a}} = \frac{1}{3}\Delta_\delta = \frac{1}{6}\left(2\delta_{ZZ} - (\delta_{XX} + \delta_{YY})\right) \tag{3.41}$$

is the *axial component* of the chemical shift tensor (Δ_δ is the *chemical shift anisotropy*), and

$$\delta_{\mathrm{r}} = \frac{1}{3}\eta_\delta \Delta_\delta \frac{1}{2}(\delta_{XX} - \delta_{YY}) \tag{3.42}$$

is the *rhombic component* of the chemical shift tensor (η_δ is the *asymmetry of the chemical shift tensor*).

The chemical shift tensor written in its principle frame is relatively simple, but we need its description in the laboratory coordinate frame. Changing the coordinate systems represents a rotation in a three-dimensional space. Equations describing such a simple operation are relatively complicated. On the other hand, the equations simplify if $\vec{B}_0$ defines the z axis of the coordinate frame:

$$\vec{B}_{\mathrm{e}} = \delta_{\mathrm{i}} B_0 \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} + \delta_{\mathrm{a}} B_0 \begin{pmatrix} 3\sin\vartheta\cos\vartheta\cos\varphi \\ 3\sin\vartheta\cos\vartheta\sin\varphi \\ 3\cos^2\vartheta - 1 \end{pmatrix} + \delta_{\mathrm{r}} B_0 \begin{pmatrix} -(2\cos^2\psi - 1)\sin\vartheta\cos\vartheta\cos\varphi + 2\sin\psi\cos\psi\sin\vartheta\sin\varphi \\ -(2\cos^2\psi - 1)\sin\vartheta\cos\vartheta\sin\varphi - 2\sin\psi\cos\psi\sin\vartheta\cos\varphi \\ +(2\cos^2\psi - 1)\sin^2\vartheta \end{pmatrix}. \tag{3.43}$$

The first, isotropic contribution does not change upon rotation (it is a scalar). The second, axial contribution, is insensitive to the rotation about the symmetry axis $\vec{a}$, described by ψ. Rotation of the chemical shift anisotropy tensor from its principal frame to the laboratory frame can be also described by orientation of $\vec{a}$ in the laboratory frame:

$$\delta_{\mathrm{a}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \longrightarrow \begin{pmatrix} 3a_x^2 - a^2 & 3a_x a_y & 3a_x a_z \\ 3a_x a_y & 3a_y^2 - a^2 & 3a_y a_z \\ 3a_x a_z & 3a_y a_z & 3a_z^2 - a^2 \end{pmatrix}, \tag{3.44}$$

where $a_x = \delta_{\mathrm{a}} \sin\vartheta\cos\varphi$, $a_y = \delta_{\mathrm{a}} \sin\vartheta\sin\varphi$, and $a_z = \delta_{\mathrm{a}} \cos\vartheta$.

3.11 Hamiltonian of chemical shift

Once the magnetic fields of moving electrons are described, definition of the chemical shift Hamiltonian is straightforward:

$$\begin{aligned}\hat{H}_\delta &= -\gamma(\hat{I}_x B_{\mathrm{e},x} + \hat{I}_y B_{\mathrm{e},y} + \hat{I}_z B_{\mathrm{e},z}) = -\gamma(\,\hat{I}_x\ \hat{I}_y\ \hat{I}_z\,)\begin{pmatrix} B_{\mathrm{e},x} \\ B_{\mathrm{e},y} \\ B_{\mathrm{e},z}\end{pmatrix} = \\ &= -\gamma(\,\hat{I}_x\ \hat{I}_y\ \hat{I}_z\,)\begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz}\end{pmatrix}\begin{pmatrix} B_{0,x} \\ B_{0,y} \\ B_{0,z}\end{pmatrix} = -\gamma\hat{\vec{I}}\cdot\underline{\delta}\cdot\vec{B}\end{aligned} \tag{3.45}$$

The Hamiltonian can be decomposed into

- isotropic contribution, independent of rotation in space:

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma\delta_{\mathrm{i}} B_0(\hat{I}_x + \hat{I}_y + \hat{I}_z) \tag{3.46}$$

- axial component, dependent on φ and ϑ:

$$\begin{aligned}\hat{H}_{\delta,\mathrm{a}} &= -\gamma\delta_{\mathrm{a}} B_0(3\sin\vartheta\cos\vartheta\cos\varphi\hat{I}_x + 3\sin\vartheta\cos\vartheta\sin\varphi\hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z) \\ &= -\gamma B_0(3a_x a_z\hat{I}_x + 3a_y a_z\hat{I}_y + (3a_z^2 - a^2)\hat{I}_z)\end{aligned} \tag{3.47}$$

- rhombic component, dependent on φ, ϑ, and ψ:

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma\delta_{\mathrm{r}} B_0(\ & (-(2\cos^2\psi - 1)\sin\vartheta\cos\vartheta\cos\varphi + 2\sin\psi\cos\psi\sin\vartheta\sin\varphi)\hat{I}_x + \\ & (-(2\cos^2\psi - 1)\sin\vartheta\cos\vartheta\sin\varphi - 2\sin\psi\cos\psi\sin\vartheta\cos\varphi)\hat{I}_y + \\ & ((2\cos^2\psi - 1)\sin^2\vartheta)\hat{I}_z) = \\ \gamma B_0(\ & (\cos(2\psi)a_x - \sin(2\psi)a_y)a_z\hat{I}_x + (\cos(2\psi)a_y + \sin(2\psi)a_x)a_z\hat{I}_y + \cos(2\psi)(a_z^2 - a^2)\hat{I}_z)\end{aligned} \tag{3.48}$$

The complete Hamiltonian of a magnetic moment of a nucleus not interacting with magnetic moments of other nuclei in the presence of the static field $\vec{B}_0$ but in the absence of the radio waves is given by

$$\hat{H} = \hat{H}_{0,\mathrm{lab}} + \hat{H}_{\delta,\mathrm{i}} + \hat{H}_{\delta,\mathrm{a}} + \hat{H}_{\delta,\mathrm{r}}. \tag{3.49}$$

3.12 Secular approximation and averaging

The Hamiltonian $\hat{H}_{0,\mathrm{lab}} + \hat{H}_{\delta,\mathrm{i}} + \hat{H}_{\delta,\mathrm{a}} + \hat{H}_{\delta,\mathrm{r}}$ is complicated, but can be simplified in many cases.

- The components of the induced fields $B_{\mathrm{e},x}$ and $B_{\mathrm{e},y}$ are perpendicular to $\vec{B}_0$. The contributions of $\hat{H}_{\delta,\mathrm{i}}$ are constant and the contributions of $\hat{H}_{\delta,\mathrm{a}}$ and $\hat{H}_{\delta,\mathrm{r}}$ fluctuate with the molecular motions changing values of φ, ϑ, and ψ. Since the molecular motions do not resonate (in general) with the precession frequency $-\gamma B_0$, the components $\hat{I}_x B_{\mathrm{e},x}$ and $\hat{I}_y B_{\mathrm{e},y}$ of the Hamiltonian oscillate rapidly with a frequency close to $-\gamma B_0$. These oscillations are much faster than the precession about $B_{\mathrm{e},x}$ and $B_{\mathrm{e},y}$ (because the field B_{e} is much smaller than $\vec{B}_0$) and effectively average to

zero on the timescale given by $1/(\gamma B_0)$ (typically nanoseconds). Therefore, the $\hat{I}_x B_{\mathrm{e},x}$ and $\hat{I}_y B_{\mathrm{e},y}$ terms can be neglected if the effects on longer timescales are studied. Such a simplification is known as *secular approximation*.[4] The secular approximation simplifies the Hamiltonian to

$$H = -\gamma B_0(1 + \delta_\mathrm{i} + (3\cos^2\vartheta - 1)\delta_\mathrm{a} + \cos(2\psi)\sin^2\vartheta\delta_\mathrm{r})\hat{I}_z \tag{3.50}$$

- If the sample is an isotropic liquid, averaging over all molecules of the sample further simplifies the Hamiltonian. As no orientation of the molecule is preferred, all values of ψ are equally probable and independent of ϑ. Therefore, the last term in Eq. 3.50 is averaged to zero. Moreover, average values of $a_x^2 = \cos^2\varphi\sin^2\vartheta$, of $a_y^2 = \sin^2\varphi\sin^2\vartheta$, and of $a_z^2 = \cos^2\vartheta$ must be the same because none of the directions x, y, z is preferred:

$$\overline{a_x^2} = \overline{a_y^2} = \overline{a_z^2}. \tag{3.51}$$

Finally,

$$a_x^2 + a_y^2 + a_z^2 = a^2 \Rightarrow \overline{a_x^2 + a_y^2 + a_z^2} = \overline{3a_z^2} \Rightarrow \overline{3a_z^2 - a^2} = \overline{(3\cos^2\vartheta - 1)}\delta_\mathrm{a} = 0, \tag{3.52}$$

and Eq. 3.50 reduces to

$$H = -\gamma B_0(1 + \delta_\mathrm{i})\hat{I}_z. \tag{3.53}$$

Note that the described simplifications can be used only if they are applicable. Eq. 3.53 is valid only in isotropic liquids, not in liquid crystals, stretched gels, polycrystalline powders, monocrystals, etc.!

3.13 Thermal equilibrium as the initial state

Knowledge of the Hamiltonian allows us to derive the density matrix at the beginning of the experiment. Usually, we start from the thermal equilibrium. If the equilibrium is achieved, phases of individual magnetic moments are random and the magnetic moments precess incoherently. Therefore, the off-diagonal elements of the equilibrium density matrix (proportional to $\mathcal{I}_x$ and $\mathcal{I}_y$) are equal to zero.

Populations of the states can be evaluated using statistical arguments similar to the Boltzmann law in the classical molecular statistics:

$$P_\alpha^\mathrm{eq} = \frac{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T}}{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T} + \mathrm{e}^{-E_\beta/k_\mathrm{B}T}} \tag{3.54}$$

$$P_\beta^\mathrm{eq} = \frac{\mathrm{e}^{-E_\beta/k_\mathrm{B}T}}{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T} + \mathrm{e}^{-E_\beta/k_\mathrm{B}T}}, \tag{3.55}$$

where $k_\mathrm{B} = 1.38064852 \times 10^{-23}\,\mathrm{m^2\,kg\,s^{-2}\,K^{-1}}$ is the Boltzmann constant.

The energies E_α and E_β are the eigenvalues of the energy operator, the Hamiltonian. Since we use eigenfunctions of $\hat{I}_z$ as the basis, eigenfunctions of $H = -\gamma B_0(1 + \delta_\mathrm{i})\hat{I}_z$ are the diagonal elements of the matrix representation of $\hat{H}$:

[4] In terms of quantum mechanics, eigenfunctions of $\hat{I}_x B_{\mathrm{e},x}$ and $\hat{I}_y B_{\mathrm{e},y}$ differ from the eigenfunctions of $\hat{H}_{0,\mathrm{lab}}$ ($|\alpha\rangle$ and $|\beta\rangle$). Therefore, the matrix representation of $\hat{I}_x B_{\mathrm{e},x}$ and $\hat{I}_y B_{\mathrm{e},y}$ contains off-diagonal elements. Terms proportional to $\hat{I}_z$ represent so-called *secular* part of the Hamiltonian, which does not change the $|\alpha\rangle$ and $|\beta\rangle$ states (because they are eigenfunctions of $\hat{I}_z$). Terms proportional to $\hat{I}_x$ and $\hat{I}_y$ are *non-secular* because they change the $|\alpha\rangle$ and $|\beta\rangle$ states ($|\alpha\rangle$ and $|\beta\rangle$ are not eigenfunctions of $\hat{I}_x$ or $\hat{I}_y$). However, eigenvalues of $\hat{I}_x B_{\mathrm{e},x}$ and $\hat{I}_y B_{\mathrm{e},y}$, defining the off-diagonal elements, are much smaller than the eigenvalues of $\hat{H}_{0,\mathrm{lab}}$. *Secular approximation* represents neglecting such small off-diagonal elements in the matrix representation of the total Hamiltonian and keeping only the diagonal secular terms.

$$\hat{H} = -\gamma B_0(1+\delta_\mathrm{i})\hat{I}_z = -\gamma B_0(1+\delta_\mathrm{i})\frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \begin{pmatrix}-\gamma B_0(1+\delta_\mathrm{i})\frac{\hbar}{2} & 0\\ 0 & +\gamma B_0(1+\delta_\mathrm{i})\frac{\hbar}{2}\end{pmatrix} \tag{3.56}$$

The thermal energy at 0 °C is more than 12 000 times higher than $\gamma B_0\hbar/2$ for the most sensitive nuclei (protons) at spectrometers with the highest magnetic fields (1 GHz). The effect of chemical shift is four orders of magnitude lower. Therefore, we can approximate

$$\mathrm{e}^{\pm\frac{\gamma B_0(1+\delta_\mathrm{i})\hbar}{k_\mathrm{B}T}} \approx 1 \pm \frac{\gamma B_0\hbar}{2k_\mathrm{B}T} \tag{3.57}$$

and calculate the populations as

$$P_\alpha^\mathrm{eq} = \frac{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T}}{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T}+\mathrm{e}^{-E_\beta/k_\mathrm{B}T}} = \frac{1+\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}}{1+\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}+1-\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}} = \frac{1+\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}}{2} \tag{3.58}$$

$$P_\beta^\mathrm{eq} = \frac{\mathrm{e}^{-E_\beta/k_\mathrm{B}T}}{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T}+\mathrm{e}^{-E_\beta/k_\mathrm{B}T}} = \frac{1-\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}}{1+\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}+1-\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}} = \frac{1-\frac{\gamma B_0\hbar}{2k_\mathrm{B}T}}{2}. \tag{3.59}$$

Writing the populations as the diagonal elements, the equilibrium density matrix is

$$\hat{\rho}^\mathrm{eq} = \begin{pmatrix}\frac{1}{2}+\frac{\gamma B_0\hbar}{4k_\mathrm{B}T} & 0\\ 0 & \frac{1}{2}-\frac{\gamma B_0\hbar}{4k_\mathrm{B}T}\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \frac{\gamma B_0\hbar}{4k_\mathrm{B}T}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \mathcal{I}_t + \kappa\mathcal{I}_z, \tag{3.60}$$

where

$$\kappa = \frac{\gamma B_0\hbar}{2k_\mathrm{B}T}. \tag{3.61}$$

Note that we derived the quantum description of a *mixed state*. Two populations of the density matrix provide correct results but do not tell us anything about microscopic states of individual magnetic moments. Two-dimensional density matrix does not imply that all magnetic moments are in one of two eigenstates.

3.14 Relaxation due to chemical shift anisotropy

The averaged Hamiltonian allowed us to describe the state of the system in thermal equilibrium, but it does not tell us *how is the equilibrium reached*. The processes leading to the equilibrium states are known as *relaxation*. Description of relaxation represents an example of analysis when the complete Hamiltonian must be used and when Liouville-von Neumann equation cannot be solved simply as rotation in an operator space.

Relaxation is return of a system to thermodynamic equilibrium. It takes places e.g. when the sample is placed into a magnetic field inside the spectrometer or after excitation of the sample by radio wave pulses.

Spontaneous emission is completely inefficient (due to low energy differences of spin states).

Relaxation in NMR is due to interactions with local fluctuating magnetic fields in the molecule. One source of fluctuating fields is the *anisotropy of chemical shift*, described by the axial and rhombic components of the chemical shift tensor. As the molecule moves, the isotropic component of the chemical shift tensor does not change because it is spherically symmetric. However, contributions to the local

fields described by the axial and rhombic components fluctuate even if the constants δ_a do not change because the axial part of the chemical shift depends on the orientation of the molecule.

Theoretical description of relaxation is relatively complicated because we cannot neglect the fluctuating components of the Hamiltonian. Therefore, we first introduce the basic idea by analyzing only one relaxation effect in a classical manner.

3.14.1 Classical analysis: fluctuations $\parallel \vec{B}_0$ and loss of coherence

Motion of a magnetic moment in a magnetic filed is described classically as

$$\frac{\mathrm{d}\vec{\mu}}{\mathrm{d}t} = \vec{\omega} \times \vec{\mu} = -\gamma \vec{B} \times \vec{\mu}, \tag{3.62}$$

or for individual components:

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = \omega_y \mu_z - \omega_z \mu_y \tag{3.63}$$

$$\frac{\mathrm{d}\mu_y}{\mathrm{d}t} = \omega_z \mu_x - \omega_x \mu_z \tag{3.64}$$

$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = \omega_x \mu_y - \omega_y \mu_x \tag{3.65}$$

In this section, we look how fluctuations of B_z affect an ensemble of magnetic moments rotating coherently about B_0 (for the sake of simplicity, let's assume that we observe only one nucleus in each molecule). As the precession frequency of magnetic moments is given by the z-component of the magnetic field (equal to B_0 in the absence of radio waves and microscopic fields of the molecule), we can expect that fluctuations of this component (due to the presence of the microscopic fields of the molecule) result in fluctuations of the precession frequency. As a consequence, the ensemble of magnetic moments that originally precessed coherently (with the same frequency) will loose the coherence. This loss of coherence is manifested as a loss of the macroscopic magnetization in the plane perpendicular to B_0.

Let's now complement the qualitative description with a quantitative analysis. Evolution of each individual magnetic moment of the ensemble can be described as

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = -\omega_z \mu_y = \gamma B_z \mu_y \tag{3.66}$$

$$\frac{\mathrm{d}\mu_y}{\mathrm{d}t} = \omega_z \mu_x = -\gamma B_z \mu_x \tag{3.67}$$

$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = 0 \tag{3.68}$$

Eqs. 3.66–3.68 are very similar to Eqs. 1.63–1.65, so we try the same approach and calculate

$$\frac{\mathrm{d}\mu^+}{\mathrm{d}t} \equiv \frac{\mathrm{d}(\mu_x + \mathrm{i}\mu_y)}{\mathrm{d}t} = \mathrm{i}\omega_z(\mu_x + \mathrm{i}\mu_y) = -\mathrm{i}\gamma B_z(\mu_x + \mathrm{i}\mu_y) \tag{3.69}$$

According to Eq. 3.43,

$$B_z = B_0 + B_{\mathrm{e},z} = B_0(1 + \delta_\mathrm{i} + \delta_\mathrm{a}(3\cos^2\vartheta - 1) + \delta_\mathrm{r}(2\cos^2\psi - 1)\sin^2\vartheta). \tag{3.70}$$

For the sake of simplicity, we assume that the chemical shift tensor is axially symmetric ($\delta_\mathrm{r} = 0$). Then, ω_z can be written as

$$\omega_z = B_0 + B_{\mathrm{e},z} = -\gamma B_0(1+\delta_\mathrm{i}) - \gamma B_0 \delta_\mathrm{a}(3\cos^2\vartheta - 1) = -(a+bc), \tag{3.71}$$

where

$$a = -\gamma B_0(1+\delta_\mathrm{i}) \tag{3.72}$$

$$b = -2\gamma B_0 \delta_\mathrm{a} \tag{3.73}$$

$$c = \frac{3\cos^2\vartheta - 1}{2}. \tag{3.74}$$

Note that Eq. 3.69 cannot be solved as easily as we solved 1.63–1.65 because ω_z is not constant but fluctuates in time. But we can assume, that for a very short time Δt, shorter than the time scale of molecular motions, the orientation of the molecule does not change and c remains constant. We try describe evolution of μ^+ in such small time steps, when

$$\frac{\Delta\mu^+}{\Delta t} \approx \frac{\mathrm{d}\mu^+}{\mathrm{d}t} \approx -\mathrm{i}(a+bc)\Delta\mu^+ \tag{3.75}$$

If the initial value of μ^+ is μ_0^+ and if the values of a, b, c during the first time step are a_1, b_1, c_1, respectively, μ^+ after the first time step is

$$\mu_1^+ = \mu_0^+ + \Delta\mu_1^+ = \mu_0^+ - \mathrm{i}(a_1 + b_1c_1)\Delta t\mu_0^+ = [1 - \mathrm{i}(a_1 + b_1c_1)\Delta t]\mu_0^+. \tag{3.76}$$

After the second step,

$$\mu_2^+ = \mu_1^+ + \Delta\mu_2^+ = \mu_1^+ - \mathrm{i}(a_2 + b_2c_2)\Delta t\mu_1^+ = [1 - \mathrm{i}(a_2 + b_2c_2)\Delta t][1 - \mathrm{i}(a_1 + b_1c_1)\Delta t]\mu_0^+. \tag{3.77}$$

After k steps,

$$\mu_k^+ = [1-\mathrm{i}(a_k+b_kc_k)\Delta t][1-\mathrm{i}(a_{k-1}+b_{k-1}c_{k-1})\Delta t]\cdots[1-\mathrm{i}(a_2)+b_2)c_2)\Delta t][1-\mathrm{i}(a_1+b_1c_1)\Delta t]\mu_0^+. \tag{3.78}$$

3.14.2 Rigid molecules

If the structure of the molecule does not change, the electron distribution is constant and the size and shape of the chemical shift tensor described by δ_i and δ_a does not change in time. Then, a and b are constant and the only time-dependent parameter is c, fluctuating as the orientation of the molecule (described by ϑ) changes.[5] The parameter $a = -\gamma B_0(1+\delta_\mathrm{i})$ represents a constant frequency of coherent rotation under such circumstances. If we describe the evolution of μ^+ in a coordinate frame rotating with the frequency a, the equation simplifies to

$$(\mu_k^+)_\mathrm{rot} = [1 - \mathrm{i}bc_k\Delta t][1 - \mathrm{i}bc_{k-1}\Delta t]\cdots[1 - \mathrm{i} + bc_2\Delta t][1 - \mathrm{i}bc_1\Delta t]\mu_0^+. \tag{3.79}$$

After multiplying the brackets and sorting the resulting terms according to the power of Δt,

$$(\mu_k^+)_\mathrm{rot} = [1-\mathrm{i}b\Delta t(c_k+c_{k-1}+\cdots+c_1)-b^2\Delta t^2(c_k(c_{k-1}+\cdots c_2+c_1)+\ldots+c_2c_1)+\mathrm{i}b^3\Delta t^3(\ldots)+\cdots](\mu_0^+)_\mathrm{rot}. \tag{3.80}$$

[5] Obviously, it is not possible to change z-components of the induced field by rotating the molecule and leave the x and y-components intact. However, we limit our analysis to the z components in order to make the procedure as simple as possible. Later we will see that the effects of fluctuations can be separated also in a more rigorous treatment.

We can now return to the question how random fluctuations change μ^+. Let's express the difference between μ^+ after k and $k-1$ steps:

$$\Delta(\mu_k^+)_{\mathrm{rot}} = (\mu_k^+)_{\mathrm{rot}} - (\mu_{k-1}^+)_{\mathrm{rot}} = -[\mathrm{i}b\Delta t c_k - b^2\Delta t^2 c_k(c_{k-1} + \cdots + c_1) - \mathrm{i}b^3\Delta t^3(\ldots) + \cdots](\mu_0^+)_{\mathrm{rot}}. \quad (3.81)$$

Dividing both sides by Δt

$$\frac{\Delta(\mu_k^+)_{\mathrm{rot}}}{\Delta t} = -[\mathrm{i}bc_k + b^2\Delta t c_k(c_{k-1} + \cdots + c_1) - \mathrm{i}b^3\Delta t^2(\ldots) + \cdots](\mu_0^+)_{\mathrm{rot}} \quad (3.82)$$

and going back from Δt to $\mathrm{d}t$ (neglecting terms with $\mathrm{d}t^2, \mathrm{d}t^3, \ldots$, much smaller than $\mathrm{d}t$),

$$\frac{\mathrm{d}(\mu^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = -\left[\mathrm{i}b\overline{c(t_k)} + b^2\int_0^{t_k}\overline{c(t_k)c(t_k - t_j)}\mathrm{d}t_j\right](\mu_0^+)_{\mathrm{rot}}. \quad (3.83)$$

We see that calculating how fluctuations of B_z affect an individual magnetic moment in time t_k requires knowledge of the orientations of the molecule during the whole evolution ($c(t_k - t_j)$). However, we are not interested in the evolution of a single magnetic moment, but in the evolution of the total magnetization M_+. Total magnetization is given by the sum of all magnetic moments (magnetic moments in all molecules). Therefore, we must average orientations of all molecules in the sample. In the case of the axially symmetric chemical shift tensor, the orientations of molecules are given by orientations of the symmetry axes $\vec{a}$ of the chemical shift tensors of the observed nuclei in the molecules, described by the angles φ and ϑ. As the angle $\vartheta(t)$ is hidden in the function $c(t) = (3\cos\vartheta^2 - 1)/2$ in our equation, the ensemble averaging cen be written as

$$\frac{\mathrm{d}(M^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = -\left[\mathrm{i}b\overline{c(t_k)} + b^2\int_0^{t_k}\overline{c(t_k)c(t_k - t_j)}\mathrm{d}t_j\right](M_0^+)_{\mathrm{rot}}. \quad (3.84)$$

We have already shown that $\overline{c(t_k)} = \overline{(3\cos\vartheta^2 - 1)/2} = 0$ (Eq. 3.52). It explains why we did not neglect already the $b^2\mathrm{d}t$ term – we would obtain zero on the right-hand side in the rotating coordinate frame (this level of simplification would neglect the effects of fluctuations and describe just the coherent motions).

Therefore, the equation describing the loss of coherence (resulting in a loss of transverse magnetization) is

$$\frac{\mathrm{d}(M^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = -\left[b^2\int_0^{t_k}\overline{c(t_k)c(t_k - t_j)}\mathrm{d}t_j\right](M_0^+)_{\mathrm{rot}}, \quad (3.85)$$

where the *time correlation function* $\overline{c(t_k)c(t_k - t_j)}$ plays the key role. Values of $\overline{c(t_k)c(t_k - t_j)}$ can be determined easily for two limit cases:

- $t_j = 0$: If $t_j = 0$, $\overline{c(t_k)c(t_k - t_j)} = \overline{c(t_k)^2}$, i.e., $c(t_k)$ and $c(t_k - t_j)$ are *completely correlated.* In spherical coordinates, averaging of any function $g(\vartheta, \varphi)$ over all directions (over all values of angles φ and ϑ can be written as

$$\overline{g(\vartheta, \varphi)} = \frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\mathrm{d}\vartheta(\sin\vartheta)g(\vartheta, \varphi) \quad (3.86)$$

Therefore,

$$\overline{c(t_k)^2} = \overline{(3\cos^2\vartheta - 1)^2} = \frac{1}{4\pi}\int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\vartheta (\sin\vartheta)(3\cos^2\vartheta - 1)^2 = \frac{1}{5} \tag{3.87}$$

- $t_j \to \infty$: If the changes of orientation (molecular motions) are random, the correlation between $c(t_k)$ and $c(t_k - t_j)$ is lost for very long t_j and they be averaged separately: $\overline{c(t_k)c(t_k - t_j)} = \overline{c(t_k)} \cdot \overline{c(t_k - t_j)}$. But we know that average $c(t) = \overline{3\cos^2\vartheta - 1} = 0$. Therefore, $\overline{c(t_k)c(t_k - t_j)} = 0$ for $t \to 0$.

If the structure of the molecule does not change (*rigid body rotational diffusion*), which is the case we analyze, the analytical form of $\overline{c(t_k)c(t_k - t_j)}$ can be derived. It is equal to a sum of five exponential functions for asymmetric rigid body rotational diffusion, to a sum of three exponential functions for axially symmetric rotational diffusion, or to a single exponential function for spherically symmetric rotational diffusion.

If the motions are really stochastic, it does not matter when we start to measure time. Therefore, we can describe the loss of coherence for any t_k as

$$\frac{\mathrm{d}(M^+)_{\mathrm{rot}}}{\mathrm{d}t} = -\left[b^2 \int_0^{\infty} \overline{c(0)c(t)}\mathrm{d}t\right] (M_0^+)_{\mathrm{rot}}, \tag{3.88}$$

which resembles a first-order chemical kinetics with the rate constant

$$R_0 = b^2 \int_0^{\infty} \overline{c(0)c(t)}\mathrm{d}t. \tag{3.89}$$

For spherically symmetric rotational diffusion, described by a mono-exponential function characterized by the *rotational correlation time* τ_{c},

$$R_0 = b^2 \int_0^{\infty} \frac{1}{5}\mathrm{e}^{t/\tau_{\mathrm{c}}}\mathrm{d}t = \frac{b^2}{5}\tau_{\mathrm{c}}. \tag{3.90}$$

3.14.3 Internal motions changing orientation of chemical shift tensor

What happens if the structure of the molecule changes? Let's first assume that the structural changes are random internal motions which change orientation of the chemical shift tensor relative to the orientation of the whole molecule, but do not affect its size or shape. Then, Eq. 3.79 can be still used and R_0 is still given by Eq. 3.89, but the correlation function is *not* mono-exponential even if the rotational diffusion of the molecule is spherically symmetric. The internal motions contribute to the dynamics together with the rotational diffusion, and in a way that is very difficult to describe exactly. Yet, useful qualitative conclusions can be made.

- If the internal motions are *much faster* than rotational diffusion, correlation between $c(t_k)$ and $c(t_j)$ is lost much faster. The faster the correlation decays, the lower is the result of integration. The internal motions faster than rotational diffusion always *decrease* the value of R_0 (make relaxation slower). Amplitude and rate of the fast internal motions can be estimated using approximative approaches.

- If the internal motions are *much slower* than rotational diffusion, the rate of decay of the correlation function is given by the faster contribution, i.e., by the rotational diffusion. The internal motions slower than rotational diffusion *do not change* the value of R_0. Amplitude and rate of the fast internal motions cannot be measured if the motions do not change size or shape of the diffusion tensor.

3.14.4 Chemical/conformational exchange

If the structural changes alter size and/or shape of the chemical shift tensor,[6] parameters a_j and b_j in Eq. 3.78 vary and cannot be treated as constants. E.g., the parameter a_j is not absorbed into the frequency of the rotating coordinate frame and terms $\overline{a(t_k)a(t_k - t_j)}$ contribute to R_0 even if $\overline{a(t_k)a(t_k - t_j)}$ decays much slower than $\overline{c(t_k)c(t_k - t_j)}$.

- Internal motions or chemical processes changing size and/or shape of the chemical shift tensor may have a dramatic effect on relaxation even if their frequency is much slower than the rotational diffusion of the molecule. If the molecule is present in two inter-converting states (e.g. in two conformations or in a protonated and deprotonated state), the strongest effect is observed if the differences between the chemical shift tensors of the states are large and if the frequency of switching between the states is similar to the difference in $\gamma B_0 \delta_\mathrm{a}$ of the states. Such processes are known as *chemical* or *conformational exchange* and increase the value of R_0.

3.14.5 Quantum description

The Liouville-von Neumann equation describing the relaxing system of magnetic moments interacting with moving electrons in a so-called *interaction frame* (corresponding to the rotating coordinate frame in the classical description) has the form

$$\frac{\mathrm{d}\Delta\hat{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}_{\delta,\mathrm{a}} + \hat{H}_{\delta,\mathrm{r}}, \Delta\hat{\rho}], \tag{3.91}$$

where $\hat{H}_{\delta,\mathrm{a}}$ and $\hat{H}_{\delta,\mathrm{r}}$ are defined by Eqs. 3.47 and 3.48, respectively, and $\Delta\hat{\rho}$ is a difference (expressed in the interaction frame) between density matrix at the given time and density matrix in the thermodynamic equilibrium. Writing $\Delta\hat{\rho}$ in the same bases as used for the Hamiltoninan,

$$\Delta\hat{\rho} = d_t\hat{I}_t + d_z\hat{I}_z + d_+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + d_-\hat{I}_. \tag{3.92}$$

If the chemical shift is axially symmetric and its size or shape do not change,

$$\frac{\mathrm{d}(d_z\hat{I}_z + d_+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + d_-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t})}{\mathrm{d}t} = -\frac{\mathrm{i}b}{\hbar}\left[c^z\hat{I}_z + \sqrt{\frac{3}{8}}c^+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + \sqrt{\frac{3}{8}}c^-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t}, d_z\hat{I}_z + d_+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + d_-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t}\right], \tag{3.93}$$

where $\hat{I}_\pm\mathrm{e}^{\pm\mathrm{i}\omega_0 t}$ are operators $\hat{I}_\pm = \hat{I}_x \pm \hat{I}_y$ in the interaction frame, $\omega_0 = -\gamma B_0(1 + \delta_\mathrm{a})$, and

$$c^z = \frac{1}{2}(3\cos^2\vartheta - 1) \tag{3.94}$$

$$c^+ = \sqrt{\frac{3}{2}}\sin\vartheta\cos\vartheta\mathrm{e}^{-\mathrm{i}\varphi} \tag{3.95}$$

$$c^- = \sqrt{\frac{3}{2}}\sin\vartheta\cos\vartheta\mathrm{e}^{+\mathrm{i}\varphi} \tag{3.96}$$

[6] Examples of such changes are internal motions changing torsion angles and therefore distribution of electrons, or chemical changes (e.g. dissociation of protons) with similar effects.

Analogically to the classical analysis, the evolution can be written as

$$\frac{\mathrm{d}\Delta\hat{\rho}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^\infty \overline{[\hat{H}_{\delta,\mathrm{a}}(0),[\hat{H}_{\delta,\mathrm{a}}(t),\Delta\hat{\rho}]]}\mathrm{d}t. \tag{3.97}$$

The right-hand side can be simplified dramatically by the *secular approximation*: all terms with $\mathrm{e}^{\pm\mathrm{i}\omega_0 t}$ are averaged to zero. Only terms with $\overline{(c^z)^2}$ and $\overline{c^+c^-}$ are non zero (both equal to 1/5 at $t_j = 0$).[7] These are the terms with $[\hat{I}_z,[\hat{I}_z,\Delta\hat{\rho}]]$, $[\hat{I}_+,[\hat{I}_-,\Delta\hat{\rho}]]$, and $[\hat{I}_-,[\hat{I}_+,\Delta\hat{\rho}]]$. Moreover, averaging over all molecules makes all three correlation functions identical in isotropic liquids: $\overline{c^z(0)c^z(t)} = \overline{c^+(0)c^-(t)} = \overline{c^-(0)c^+(t)} = \overline{c(0)c(t)}$.

In order to proceed, the double commutators must be expressed. We start with

$$[\hat{I}_z,\hat{I}_\pm] = [\hat{I}_z,\hat{I}_x] \pm \mathrm{i}[\hat{I}_z,\hat{I}_y] = \pm\hbar(\hat{I}_x \pm \mathrm{i}\hat{I}_y) = \pm\hbar\hat{I}_\pm \tag{3.98}$$

and

$$[\hat{I}_+,\hat{I}_-] = [\hat{I}_x,\hat{I}_x] - \mathrm{i}[\hat{I}_x,\hat{I}_y] + \mathrm{i}[\hat{I}_y,\hat{I}_x] + [\hat{I}_y,\hat{I}_y] = 2\hbar\hat{I}_z. \tag{3.99}$$

Our goal is to calculate relaxation rates for the expectation values of components parallel (M_z) and perpendicular (M_+ or M_-) to $\vec{B}_0$.

3.14.6 Relaxation of M_z

Let's start with M_z. According to Eq. 1.17,

$$\langle M_+\rangle = \mathrm{Tr}\{\hat{M}_+\Delta\hat{\rho}\} \tag{3.100}$$

where $\Delta\langle M_z\rangle$ is the difference from the expectation value of M_z in equilibrium. The operator of M_z for one magnetic moment observed is (Eq. 3.28)

$$\hat{M}_z = \mathcal{N}\gamma\hat{I}_z, \tag{3.101}$$

where $\mathcal{N}$ is the number of molecules detected by the spectrometer. Since the basis matrices are orthogonal, products of $\hat{I}_z$ with the components of the density matrix different from $\hat{I}_z$ are equal to zero and the left-hand side of Eq. 3.97 reduces to

$$\frac{\mathrm{d}d_z}{\mathrm{d}t}\hat{I}_z \tag{3.102}$$

when calculating relaxation rate of $\langle M_z\rangle$. In the right-hand side, we need to calculate three double commutators:

$$[\hat{I}_z,[\hat{I}_z,\hat{I}_z]] = 0 \qquad [\hat{I}_+,[\hat{I}_-,\hat{I}_z]] = 2\hbar^2\hat{I}_z \qquad [\hat{I}_-,[\hat{I}_+,\hat{I}_z]] = 2\hbar^2\hat{I}_z \tag{3.103}$$

After substituting into Eq. 3.97,

$$\frac{\mathrm{d}d_z}{\mathrm{d}t}\mathrm{Tr}\{\hat{I}_z\hat{I}_z\} = -\left(\frac{3}{4}b^2\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \frac{3}{4}b^2\int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right) d_z\mathrm{Tr}\{\hat{I}_z\hat{I}_z\} \tag{3.104}$$

$$\frac{\mathrm{d}\Delta\langle M_z\rangle}{\mathrm{d}t} = -\left(\frac{3}{4}b^2\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \frac{3}{4}b^2\int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right)\Delta\langle M_z\rangle \tag{3.105}$$

[7] We have factored out $\sqrt{3/8}$ in order to make $\overline{c^+c^-} = \overline{(c^z)^2}$.

The relaxation rate R_1 for M_z, known as *longitudinal relaxation rate* in the literature, is the real part of the expression in the parentheses

$$R_1 = \frac{3}{4}b^2\Re\left\{\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right\} \tag{3.106}$$

For stochastic motions,

$$\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \int_{-\infty}^0 \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right) = \frac{1}{2}\int_{-\infty}^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t. \tag{3.107}$$

$$\int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t + \int_{-\infty}^0 \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right) = \frac{1}{2}\int_{-\infty}^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t, \tag{3.108}$$

if the fluctuations are random, they are also stationary: the current orientation of the molecule is correlated with the orientation in the past in the same manner as it is correlated with the orientation in the future.

The right-hand side integrals are identical with the mathematical definition of the Fourier transform of the correlation functions. Real parts of such Fourier transforms are known as *spectral density functions* $J(\omega)$.

The relaxation rate R_1 can be therefore written as

$$R_1 = \frac{3}{4}b^2\left(\frac{1}{2}J(\omega_0) + \frac{1}{2}J(-\omega_0)\right) \approx \frac{3}{4}b^2 J(\omega_0) \tag{3.109}$$

What is the physical interpretation of the obtained equation? Relaxation of M_z is given by the correlation functions $\overline{c^+(0)c^-(t)}$ and $\overline{c^-(0)c^+(t)}$, describing fluctuations of the components of the chemical shift tensor perpendicular to $\vec{B}_0$ (a_x and a_y). Such fluctuating fields resemble the radio waves with $\vec{B}_1 \perp \vec{B}_0$. If the frequency of such fluctuations matches the precession frequency ω_0, the resonance condition is fulfilled and (random) transitions between the $|\alpha\rangle$ and $|\beta\rangle$ states can take place. If the magnetic moments are described by the quantum theory but their surroundings are treated classically, $J(\omega_0) = J(-\omega_0)$ which corresponds to equal probability of transitions $|\alpha\rangle \to |\beta\rangle$ and $|\beta\rangle \to |\alpha\rangle$. If the surroundings are described by quantum theory, $J(\omega_0) = \mathrm{e}^{-\hbar\omega_0/k_\mathrm{B}T}J(-\omega_0)$, and the transition $|\beta\rangle \to |\alpha\rangle$ is slightly more probable. This drives the system back to the equilibrium distribution of magnetic moments.

3.14.7 Relaxation of M_+

Let's continue with M_+. According to Eq. 1.17,

$$\Delta\langle M_+\rangle \equiv \langle M_+\rangle = \mathrm{Tr}\{\hat{M}_+\Delta\hat{\rho}\} \tag{3.110}$$

The expectation value of M_+ in equilibrium is zero, this is why we do not need to calculate the difference for $\langle M_+\rangle$ and why we did not calculate the difference in the classical analysis.

The operator of M_+ for one magnetic moment observed is

$$\hat{M}_+ = \mathcal{N}\gamma\hat{I}_+ = \mathcal{N}\gamma(\hat{I}_x + \mathrm{i}\hat{I}_y). \tag{3.111}$$

Due to the orthogonality of basis matrices, the left-hand side of Eq. 3.97 reduces to

$$\frac{\mathrm{d}d_+}{\mathrm{d}t}\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} \tag{3.112}$$

when calculating relaxation rate of $\Delta\langle M_+\rangle \equiv \langle M_+\rangle$. In the right-hand side, we need to calculate three double commutators:

$$[\hat{I}_z,[\hat{I}_z,\hat{I}_+]] = \hbar^2\hat{I}_+ \qquad [\hat{I}_+,[\hat{I}_-,\hat{I}_+]] = 2\hbar^2\hat{I}_+ \qquad [\hat{I}_-,[\hat{I}_+,\hat{I}_+]] = 0. \tag{3.113}$$

After substituting into Eq. 3.97,

$$\frac{\mathrm{d}d_+}{\mathrm{d}t}\mathrm{Tr}\{\hat{I}_+\hat{I}_+\} = -\left(b^2\int_0^\infty \overline{c^z(0)c^z(t)}\mathrm{d}t + \frac{3}{4}b^2\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right) d_+\mathrm{Tr}\{\hat{I}_+\hat{I}_+\} \tag{3.114}$$

$$\frac{\mathrm{d}\langle M_+\rangle}{\mathrm{d}t} = -\left(b^2\int_0^\infty \overline{c^z(0)c^z(t)}\mathrm{d}t + \frac{3}{4}b^2\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right)\langle M_+\rangle \tag{3.115}$$

The relaxation rate R_2 for M_+, known as *transverse relaxation rate* in the literature, is the real part of the expression in the parentheses.

$$R_1 = b^2\int_0^\infty \overline{c^z(0)c^z(t)}\mathrm{d}t + \Re\left\{\frac{3}{4}b^2\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right\}. \tag{3.116}$$

Note that the first integral in 3.116 is a real number, equal to R_0 derived by the classical analysis. Using the same arguments as for M_z,

$$R_2 = b^2\left(\frac{1}{2}J(0) + \frac{3}{4}\frac{1}{2}J(\omega_0)\right) \approx R_0 + \frac{1}{2}R_1. \tag{3.117}$$

What is the physical interpretation of the obtained equation? Two terms in Eq. 3.117 describe two processes contributing to the relaxation of M_+. The first one is the *loss of coherence* with the rate R_0, given by the correlation function $\overline{c^z(0)c^z(t)}$ and describing fluctuations of the components of the chemical shift tensor parallel with $\vec{B}_0$ (a_z). This contribution was analyzed above using the classical approach. The second contribution is *transitions between the* $|\alpha\rangle$ *and* $|\beta\rangle$ *states* due to fluctuations of the components of the chemical shift tensor perpendicular to $\vec{B}_0$ (a_x and a_y), returning the magnetization vector $\vec{M}$ to its direction in the thermodynamic equilibrium. As $\vec{M}$ is oriented along the z axis in the equilibrium, the transitions renew the equilibrium value of M_z, as described above, but also make the M_x and M_y components to disappear. Note however, that only one correlation function ($\overline{c^+(0)c^-(t)}$) contributes to the relaxation of M_+, while both $\overline{c^+(0)c^-(t)}$ and $\overline{c^-(0)c^+(t)}$ contributes to the relaxation of M_z and only $R_1/2$ contributes to R_2. If we defined R_2 as a relaxation rate of M_-, $\overline{c^-(0)c^+(t)}$ would contribute[8]:

$$R_2 = b^2\left(\frac{1}{2}J(0) + \frac{3}{4}\frac{1}{2}J(-\omega_0)\right) \approx R_0 + \frac{1}{2}R_1. \tag{3.118}$$

[8]Fluctuations with frequency $+\omega_0$ affect M_+ and fluctuations with frequency $-\omega_0$ affect M_-, but both affect M_z. Alternatively, we could define R_2 as a relaxation rate of M_x or M_y. Fluctuations of the $B_{\mathrm{e},y}$ component affect M_x but not M_y, while fluctuations of the $B_{\mathrm{e},x}$ component affect M_y but not M_x. On the other hand, both fluctuations of $B_{\mathrm{e},x}$ and $B_{\mathrm{e},y}$ affect M_z. Working with M_+, M_- or M_x, M_y, the relaxation of M_z due to $B_{\mathrm{e},x}$ and $B_{\mathrm{e},y}$ is always twice faster.

3.15 The one-pulse experiment

At this moment, we have all we need to describe a real NMR experiment for sample consisting of isolated magnetic moments (not interacting with each other). The basic NMR experiment consists of two parts. In the first part, the radio-wave transmitter is switched on for a short time, needed to rotate the magnetization to the plane perpendicular to the magnetic filed $\vec{B}_0$ (a radio-wave *pulse*). In the second time, the radio-wave transmitter is switched off but the receiver is switched on in order to detect rotation of the magnetization vector about the direction of $\vec{B}_0$. We will analyze evolution of the density matrix during these two periods and calculate the magnetization contributing to the detected signal.

3.15.1 Excitation by radio wave pulses

At the beginning of the experiment, the density matrix describes thermal equilibrium (Eq. 3.60):

$$\hat{\rho}(0) = \mathcal{I}_t + \kappa \mathcal{I}_z. \tag{3.119}$$

The Hamiltonian governing evolution of the system during the first part of the experiments consists of coherent and fluctuating terms. The fluctuating contributions result in *relaxation*, described by relaxation rates R_1 and R_2. The coherent contributions include

$$\mathcal{H} = \varepsilon_t \cdot 2\mathcal{I}_t - \gamma B_0(1+\delta_\mathrm{i})\mathcal{I}_z - \gamma B_1(1+\delta_\mathrm{i})\cos(\omega_\mathrm{radio}t)\mathcal{I}_x - \gamma B_1(1+\delta_\mathrm{i})\sin(\omega_\mathrm{radio}t)\mathcal{I}_y, \tag{3.120}$$

where $\hbar\varepsilon_t$ is the total energy of the system outside the magnetic field, and the choice of the directions x and y is given by the $\cos(\omega_\mathrm{radio}t)$ and $\sin(\omega_\mathrm{radio}t)$ terms

The Hamiltonian simplifies in a coordinate system rotating with $\omega_\mathrm{rot} = \omega_\mathrm{radio}$

$$\mathcal{H} = \varepsilon_t \cdot 2\mathcal{I}_t \underbrace{-\gamma B_0(1+\delta_\mathrm{i})}_{\Omega}\mathcal{I}_z \underbrace{-\gamma B_1(1+\delta_\mathrm{i})}_{\omega_1}\mathcal{I}_x, \tag{3.121}$$

but it still contains non-commuting terms ($\mathcal{I}_x$ *vs.* $\mathcal{I}_z$). Let's check what can be neglected to keep only commuting terms, which allows us to solve the Liouville-von Neumann equation using the simple geometric approach.

- The value of ε_t is unknown and huge, but $\mathcal{I}_t$ commutes with all matrices (it is proportional to the unit matrix). As a consequence, this term can be ignored because it does not have any effect on evolution of $\hat{\rho}$.
- The value of ω_1 defines how much magnetization is rotated to the x, y plane. The maximum effect is obtained for $\omega_1\tau_\mathrm{p} = \pi/2$, where τ_p is the length of the radio-wave pulse. Typical values of τ_p for proton are approximately $10\,\mu$s, corresponding to frequency of rotation of 25 kHz (90° rotation in $10\,\mu$s corresponds to $40\,\mu$s corresponds for a full circle, $1/40\,\mu\mathrm{s} = 25\,\mathrm{kHz}$).
- Typical values of R_1 are $10^{-1}\,\mathrm{s}^{-1}$ to $10^{0}\,\mathrm{s}^{-1}$ and typical values of R_2 are $10^{-1}\,\mathrm{s}^{-1}$ to $10^{2}\,\mathrm{s}^{-1}$ for protons in organic molecules and biomacromolecules. Therefore, effects of relaxations can be safely neglected during τ_p.
- When observing a single type of proton (or other nucleus), Ω can be set to zero by the choice of ω_radio. However, variation of Ω is what we observe in real samples, containing protons (or other nuclei) with various δ_i. The typical range of proton δ_i is 10 ppm, corresponding to 5 kHz at a 500 MHz spectrometer.[9] The carrier frequency ω_radio is often set to the precession frequency of

[9] Chosen as a compromise here: spectra of small molecules are usually recored at 300 MHz–500 MHz, while spectra of biomacromolecules are recorded at 500 MHz–1 GHz.

the solvent. In the case of water, it is roughly in the middle of the spectrum (4.7 ppm at pH 7). So, we need to cover ±2.5 kHz. We see that $|\Omega| < |\omega_1|$, but the ratio is only 10 % at the edge of the spectrum.

In summary, we see that we can safely ignore $\mathcal{I}_t$ and fluctuating contributions, but we must be careful when neglecting $\Omega\mathcal{I}_z$. The latter approximation allows us to use the geometric solution of the Liouville-von Neumann equation, but is definitely not perfect for larger Ω resulting in *offset effects*.

Using the simplified Hamiltonian $\mathcal{H} = \omega_1\mathcal{I}_x$, evolution of $\hat{\rho}$ during τ_p can be described as a rotation about the "$\mathcal{I}_x$ axis":

$$\hat{\rho}(0) = \mathcal{I}_t + \kappa\mathcal{I}_z \longrightarrow \hat{\rho}(\tau_\mathrm{p}) = \mathcal{I}_t + \kappa(\mathcal{I}_z\cos(\omega_1\tau_\mathrm{p}) - \mathcal{I}_y\sin(\omega_1\tau_\mathrm{p})). \tag{3.122}$$

For a 90° pulse,

$$\hat{\rho}(\tau_\mathrm{p}) = \mathcal{I}_t - \kappa\mathcal{I}_y. \tag{3.123}$$

3.15.2 Evolution of chemical shift after excitation

After switching off the transmitter, $\omega_1\mathcal{I}_x$ disappears from the Hamiltonian, which now contains only commuting terms. On the other hand, signal is typically acquired for a relatively long time (0.1 s to 10 s) to achieve a good frequency resolution. Therefore, the relaxation effects cannot be neglected.

The coherent evolution can be described as a rotation about the "$\mathcal{I}_z$ axis" with the angular frequency Ω

$$\hat{\rho}(t) = \mathcal{I}_t + \kappa(-\mathcal{I}_y\cos(\Omega t) + \mathcal{I}_x\sin(\Omega t)) = \mathcal{I}_t + \kappa\left(\mathcal{I}_x\cos\left(\Omega t + \frac{\pi}{2}\right) + \mathcal{I}_y\sin\left(\Omega t + \frac{\pi}{2}\right)\right). \tag{3.124}$$

We see that the system rotates in the operator spacewith angular frequency Ω and the original phase of $\pi/2$. However, this is true only if we the evolution starts *exactly* at $t = 0$. In practice, this is impossible to achieve for various technical reasons (instrumental delays and phase shifts, evolution starts already during τ_p, etc.). Therefore, the rotation has an unknown phase shift ϕ (including the $\pi/2$ shift among other contributions), which is removed by an empirical correction during signal processing. We will ignore the phase shift and write the phase-corrected spectral density

$$\hat{\rho}(t) = \mathcal{I}_t + \kappa(\mathcal{I}_x\cos(\Omega t) + \mathcal{I}_y\sin(\Omega t)) \tag{3.125}$$

The measured quantity M_+ can be expressed as (Eq. 1.17)

$$\langle M_+\rangle = \mathrm{Tr}\{\hat{M}_+\hat{\rho}(t)\} = \mathcal{N}\gamma B_0\frac{\hbar}{2}\mathrm{Tr}\{\mathcal{I}_+(\mathcal{I}_t + \kappa(\mathcal{I}_x\cos(\Omega t) + \mathcal{I}_y\sin(\Omega t))\}. \tag{3.126}$$

The relevant traces are

$$\mathrm{Tr}\{\mathcal{I}_+\mathcal{I}_t\} = \mathrm{Tr}\left\{\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}\frac{1}{2}&0\\0&\frac{1}{2}\end{pmatrix}\right\} = \mathrm{Tr}\left\{\begin{pmatrix}0&\frac{1}{2}\\0&0\end{pmatrix}\right\} = 0 \tag{3.127}$$

$$\mathrm{Tr}\{\mathcal{I}_+\mathcal{I}_x\} = \mathrm{Tr}\left\{\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}0&-\frac{\mathrm{i}}{2}\\\frac{\mathrm{i}}{2}&0\end{pmatrix}\right\} = \mathrm{Tr}\left\{\begin{pmatrix}\frac{\mathrm{i}}{2}&0\\0&0\end{pmatrix}\right\} = \frac{\mathrm{i}}{2} \tag{3.128}$$

$$\mathrm{Tr}\{\mathcal{I}_+\mathcal{I}_y\} = \mathrm{Tr}\left\{\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}0&\frac{1}{2}\\\frac{1}{2}&0\end{pmatrix}\right\} = \mathrm{Tr}\left\{\begin{pmatrix}\frac{1}{2}&0\\0&0\end{pmatrix}\right\} = \frac{1}{2} \tag{3.129}$$

Including relaxation and expressing κ

$$\langle M_+ \rangle = \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2 t}(\cos(\Omega t) + \mathrm{i}\sin(\Omega t)) = \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2 t}\mathrm{i}\mathrm{e}^{\mathrm{i}\Omega t}. \tag{3.130}$$

In general, the analysis of an ideal one-pulse experiment leads to the following conclusions:

- if the analysis of an NMR experiment shows that the density matrix evolves during analysis as

$$\hat{\rho}(t) \propto (\mathcal{I}_x \cos(\Omega t + \phi) + \mathcal{I}_x \sin(\Omega t) + \phi) + \text{terms orthogonal to } \mathcal{I}_+, \tag{3.131}$$

  the magnetization rotates during signal acquisition as

$$\langle M_+ \rangle = |M_+|\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega t} \tag{3.132}$$

  (with some unimportant phase shift which is empirically corrected),

- Fourier transform of the signal gives the complex signal

$$\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\left(\frac{R_2}{R_2^2 + (\omega - \Omega)^2} - \mathrm{i}\frac{\omega - \Omega}{R_2^2 + (\omega - \Omega)^2}\right), \tag{3.133}$$

- the cosine modulation of $\mathcal{I}_x$ can be taken as the real component of the signal and the sine modulation of $\mathcal{I}_y$ can be taken as the imaginary component of the signal.

Chapter 4

Ensembles of spins interacting through space

4.1 Product operators

Mutual interactions – interactions with fields generated by other nuclei. Description of such fields involves spin eigenfunctions.

If two spin magnetic moments interact *mutually*, they cannot be described using the same basis. Eigenfunctions are influenced by the interactions. State of the first spin depends on the state of the second spin. For two spin-1/2 nuclei, $2 \times 2 = 4$ states.

Density matrix for four states – a 4×4 matrix. Basis used for such density matrices must consist of $4^2 = 16$ matrices.

Density matrix for N states – a $N \times N$ matrix. Basis used for such density matrices must consist of 4^N matrices.

The basis can be derived by the *direct product* of basis matrices of spins without mutual interactions. For two spins,

$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_t(12) \tag{4.1}$$
$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_x(2) = \mathcal{I}_{1x}(12) \tag{4.2}$$
$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_y(2) = \mathcal{I}_{1y}(12) \tag{4.3}$$
$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_z(2) = \mathcal{I}_{1z}(12) \tag{4.4}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_{2x}(12) \tag{4.5}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_{2y}(12) \tag{4.6}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_{2z}(12) \tag{4.7}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_x(2) = 2\mathcal{I}_{1x}\mathcal{I}_{2x}(12) \tag{4.8}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_y(2) = 2\mathcal{I}_{1x}\mathcal{I}_{2y}(12) \tag{4.9}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_z(2) = 2\mathcal{I}_{1x}\mathcal{I}_{2z}(12) \tag{4.10}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_x(2) = 2\mathcal{I}_{1y}\mathcal{I}_{2x}(12) \tag{4.11}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_y(2) = 2\mathcal{I}_{1y}\mathcal{I}_{2y}(12) \tag{4.12}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_z(2) = 2\mathcal{I}_{1y}\mathcal{I}_{2z}(12) \tag{4.13}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_x(2) = 2\mathcal{I}_{1z}\mathcal{I}_{2x}(12) \tag{4.14}$$

$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_y(2) = 2\mathcal{I}_{1z}\mathcal{I}_{2y}(12) \tag{4.15}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_z(2) = 2\mathcal{I}_{1z}\mathcal{I}_{2z}(12), \tag{4.16}$$

where the numbers in parentheses specify which nuclei constitute the spin system described by the given matrix (these numbers are not written in practice). The matrices on the right-hand side are known as *product operators*. Note that $\mathcal{I}_t$, equal to[1] $\frac{1}{2}\hat{1}$, is not written in the product operators for the sake of simplicity. Note also that e.g. $\mathcal{I}_x(1)$ and $\mathcal{I}_x(2)$ are the same 2 matrices, but $\mathcal{I}_{1x}(12)$ and $\mathcal{I}_{2x}(12)$ are different 4 matrices. Basis matrices for more nuclei are derived in the same manner, e.g. $2\mathcal{I}_{1z}\mathcal{I}_{2x}(12) \otimes \mathcal{I}_y(3) = 4\mathcal{I}_{1z}\mathcal{I}_{2x}\mathcal{I}_{3y}(123)$.

4.2 Liouville-von Neumann equation

The Liouville - von Neumann equation can be written in the same form as for spins without mutual interactions (Eq. 3.19):

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = \mathrm{i}(\hat{\rho}\mathcal{H} - \mathcal{H}\hat{\rho}) = \mathrm{i}[\hat{\rho}, \mathcal{H}] = -\mathrm{i}[\mathcal{H}, \hat{\rho}], \tag{4.17}$$

but the density matrix and Hamiltonian are now $N \times N$ matrices described in the appropriate basis. The same simple geometric solution as for spins without mutual interactions is possible if the Hamiltonian does not vary in time and consists of commuting matrices only. However, the operator space is now N^2 dimensional (16-dimensional for two spin-1/2 nuclei). Therefore, the appropriate three-dimensional subspace must be selected for each rotation. The subspaces are defined by the commutator relations, which can be defined for spin systems consisting of any number of spin-1/2 nuclei using the following equations.

$$[\mathcal{I}_{n,x}, \mathcal{I}_{n,y}] = \mathrm{i}\mathcal{I}_{n,z} \qquad [\mathcal{I}_{n,y}, \mathcal{I}_{n,z}] = \mathrm{i}\mathcal{I}_{n,x} \qquad [\mathcal{I}_{n,z}, \mathcal{I}_{n,x}] = \mathrm{i}\mathcal{I}_{n,y} \tag{4.18}$$

$$[\mathcal{I}_{n,j}, 2\mathcal{I}_{n,k}\mathcal{I}_{n',l}] = 2[\mathcal{I}_{n,j}, \mathcal{I}_{n,k}]\mathcal{I}_{n',l} \tag{4.19}$$

$$[2\mathcal{I}_{n,j}\mathcal{I}_{n',l}, 2\mathcal{I}_{n,k}\mathcal{I}_{n',m}] = 2[\mathcal{I}_{n,j}, \mathcal{I}_{n,k}]\delta_{lm}, \tag{4.20}$$

where n and n' specify the nucleus, $j, k, l \in \{x, y, z\}$, and $\delta_{lm} = 1$ for $l = m$ and $\delta_{lm} = 0$ for $l \neq m$.

4.3 Through-space dipole-dipole interaction (dipolar coupling)

If spin magnetic moments of two spin-1/2 nuclei interact with each other, the magnetic moment of nucleus 1 is influenced by the magnetic field $\vec{B}_2$ of the magnetic moment of nucleus 2. $\vec{B}_2$ is given by the classical electrodynamics as

$$\vec{B}_2 = \vec{\nabla} \times \vec{A}_2, \tag{4.21}$$

where

$$\vec{\nabla} \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \tag{4.22}$$

and the *vector potential* of the magnetic moment 2 is

[1] $\hat{1}$ is the unit matrix.

$$\vec{A}_2 = \frac{\mu_0}{4\pi}\frac{\vec{\mu}_2 \times r}{r^3}, \tag{4.23}$$

where $\vec{r}$ is a vector defining the mutual position of nuclei 1 and 2 (inter-nuclear vector). Calculation of $\vec{B}_2$ thus includes two vector products

$$\vec{B}_2 = \frac{\mu_0}{4\pi}\frac{\vec{\nabla} \times (\vec{\mu}_2 \times \vec{r})}{r^3}. \tag{4.24}$$

As a consequence, each component of $\vec{B}_2$ depends on all components of $\vec{\mu}_2$:

$$B_{2,x} = \frac{\mu_0}{4\pi r^5}((3r_x^2 - r^2)\mu_{2,x} + 3r_x r_y \mu_{2,y} + 3r_x r_z \mu_{2,z}) \tag{4.25}$$

$$B_{2,y} = \frac{\mu_0}{4\pi r^5}(3r_x r_y \mu_{2,x} + (3r_y^2 - r^2)\mu_{2,y} + 3r_y r_z \mu_{2,z}) \tag{4.26}$$

$$B_{2,z} = \frac{\mu_0}{4\pi r^5}(3r_x r_z \mu_{2,x} + 3r_y r_z \mu_{2,y} + (3r_z^2 - r^2)\mu_{2,z}), \tag{4.27}$$

which can by described by a matrix equation

$$\begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} = \frac{\mu_0}{4\pi r^5}\begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}. \tag{4.28}$$

The matrix in Eq. 4.28 represents a tensor describing the geometric relations of the dipolar coupling and has the same form as the matrix in Eq. 3.44, describing the anisotropic contribution to the chemical shift tensor: the vector defining the symmetry axis of the chemical shift tensor $\vec{a}$ is just replaced with the inter-nuclear vector $\vec{r}$ in Eq. 4.28. Like the anisotropic part of the chemical shift tensor, the matrix in Eq. 4.28 simplifies to

$$\frac{\mu_0}{4\pi r^3}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{4.29}$$

in a coordinate system with axis $z \parallel \vec{r}$. Rotation to the laboratory frame is described by angles φ and ϑ defining orientation of $\vec{r}$ in the laboratory frame

$$\delta_{\mathrm{a}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \longrightarrow \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix}, \tag{4.30}$$

where $r_x = r\sin\vartheta\cos\varphi$, $r_y = r\sin\vartheta\sin\varphi$, and $r_z = r\cos\vartheta$.

4.4 Hamiltonian of dipolar coupling

Describing the magnetic moments by the operators $\hat{\mu}_{1,j}\gamma_1\hat{I}_{1,j}$ and $\hat{\mu}_{2,j}\gamma_1\hat{I}_{2,j}$, where j is x, y, and z, the Hamiltonian of dipolar coupling $\hat{H}_D$ can be written as

$$\hat{H}_D = -\gamma_1(\hat{I}_{1,x}B_{2,x} + \hat{I}_{1,y}B_{2,y} + \hat{I}_{1,z}B_{2,z}) = -\gamma_1(\,\hat{I}_{1,x}\ \hat{I}_{1,y}\ \hat{I}_{1,z}\,)\begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} =$$

$$= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^5}(\,\hat{I}_{1,x}\ \hat{I}_{1,y}\ \hat{I}_{1,z}\,)\begin{pmatrix} 3r_x^2 - r^2 & 3r_xr_y & 3r_xr_z \\ 3r_xr_y & 3r_y^2 - r^2 & 3r_yr_z \\ 3r_xr_z & 3r_yr_z & 3r_z^2 - r^2 \end{pmatrix}\begin{pmatrix} \hat{I}_{2,x} \\ \hat{I}_{2,y} \\ \hat{I}_{2,z} \end{pmatrix} = \hat{\vec{I}}_1 \cdot \underline{D} \cdot \hat{\vec{I}}_2, \tag{4.31}$$

where $\underline{D}$ is the tensor of direct dipole-dipole interactions (dipolar coupling).
The Hamiltonian can be written in spherical coordinates as

$$\begin{aligned}\hat{H}_D = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3} + \Big(& (3\sin^2\vartheta\cos^2\varphi - 1)\hat{I}_{1x}\hat{I}_{2x} + (3\sin^2\vartheta\sin^2\varphi - 1)\hat{I}_{1y}\hat{I}_{2y} + (3\cos^2\vartheta - 1)\hat{I}_{1z}\hat{I}_{2z} + \\ & + 3\sin^2\vartheta\sin\varphi\cos\varphi\hat{I}_{1x}\hat{I}_{2y} + 3\sin\vartheta\cos\vartheta\cos\varphi\hat{I}_{1x}\hat{I}_{2z} + 3\sin\vartheta\cos\vartheta\sin\varphi\hat{I}_{1y}\hat{I}_{2z} \\ & + 3\sin^2\vartheta\sin\varphi\cos\varphi\hat{I}_{1y}\hat{I}_{2x} + 3\sin\vartheta\cos\vartheta\cos\varphi\hat{I}_{1z}\hat{I}_{2x} + 3\sin\vartheta\cos\vartheta\sin\varphi\hat{I}_{1z}\hat{I}_{2y}\Big)\end{aligned} \tag{4.32}$$

4.5 Secular approximation and averaging

The Hamiltonian of dipolar coupling can be simplified in many cases.

- Magnetic moments with the same γ *and* chemical shift precess about the z axis with *the same precession frequency*. In addition to the precession, the magnetic moments moves with random molecular motions, described by re-orientation of $\vec{r}$. In a coordinate system rotating with the common precession frequency, $\vec{r}$ quickly rotates about the z axis in addition to the random molecular motions. On a time scale slower than nanoseconds, the rapid oscillations of r_x, r_y, and r_z are neglected (secular approximation). The values of r_x^2 and r_y^2 do not oscillate about zero, but about a value $\langle r_x^2\rangle = \langle r_y^2\rangle$, which is equal to[2] $(r^2 - \langle r_z^2\rangle)/2$ because $\langle r_x^2 + r_y^2 + r_z^2\rangle = \langle r^2\rangle = r^2$. Therefore, the secular approximations (i.e., neglecting the oscillations and keeping the average values) simplifies the Hamiltonian to

$$\hat{H}_D = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^5}\left(3\langle r_z^2\rangle - r^2\right)\left(\hat{I}_{1,z}\hat{I}_{2,z} - \frac{1}{2}\hat{I}_{1,x}\hat{I}_{2,x} - \frac{1}{2}\hat{I}_{1,y}\hat{I}_{2,y}\right) \tag{4.33}$$

$$= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\frac{3\langle\cos^2\vartheta\rangle - 1}{2}\left(2\hat{I}_{1,z}\hat{I}_{2,z} - \hat{I}_{1,x}\hat{I}_{2,x} - \hat{I}_{1,y}\hat{I}_{2,y}\right). \tag{4.34}$$

- Magnetic moments with different γ and/or chemical shift precess with *different precession frequencies*. Therefore, the x and y components of $\vec{\mu}_2$ rapidly oscillate in a frame rotating with the precession frequency of $\vec{\mu}_1$ and vice versa. When neglecting the oscillating terms (secular approximation), the Hamiltonian reduces to

$$\hat{H}_D = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^5}\left(3\langle r_z^2\rangle - r^2\right)\hat{I}_{1,z}\hat{I}_{2,z} = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\frac{3\langle\cos^2\vartheta\rangle - 1}{2}2\hat{I}_{1,z}\hat{I}_{2,z}. \tag{4.35}$$

- Averaging over all molecules in isotropic liquids has the same effect as described for the anisotropic part of the chemical shielding tensor because both tensors have the same form:

$$\overline{r_x^2} = \overline{r_y^2} = \overline{r_z^2}. \tag{4.36}$$

Finally,

$$r_x^2 + r_y^2 + r_z^2 = r^2 \Rightarrow \overline{r_x^2 + r_y^2 + r_z^2} = \overline{3r_z^2} = r^2 \Rightarrow \overline{3r_z^2 - r^2} = r\overline{(3\cos^2\vartheta - 1)} = 0. \tag{4.37}$$

[2] Note that $\langle r_x^2\rangle = \langle r_y^2\rangle \neq \langle r_z^2\rangle$ in general.

Unlike the chemical shift Hamiltonian, the Hamiltonian of the dipolar coupling does not have any isotropic part. As a consequence, the dipole-dipole interactions are not observable in isotropic liquids. On the other hand, their effect is huge in solid state NMR and they can be also be measured e.g. in liquid crystals or mechanically stretched gels.

4.6 Relaxation due to the dipole-dipole interactions

Rotation of the molecule (and internal motions) change the orientation of the inter-nuclear vector and cause fluctuations of the field of magnetic moment $\vec{\mu}_2$ sensed by the magnetic moment $\vec{\mu}_1$. It leads to the loss of coherence in the same manner as described for the anisotropic part of the chemical shift (cf. Eqs 3.44 and 4.28. However, the relaxation effects of the dipole-dipole interactions are more complex, reflecting the higher complexity of the Hamiltonian of the dipolar coupling.

In order to describe the dipole-dipole relaxation on the quantum level, it is useful to work in spherical coordinates and to convert the product operators to a different basis. Single quantum operators are transformed using the relation $\hat{I}_\pm = \hat{I}^x \pm \mathrm{i}\hat{I}_y$):

$$\hat{I}_{1x}\hat{I}_{2z} = \frac{1}{2}(+\hat{I}_{1+}\hat{I}_{2z} + \hat{I}_{1-}\hat{I}_{2z}) \tag{4.38}$$

$$\hat{I}_{1y}\hat{I}_{2z} = \frac{\mathrm{i}}{2}(-\hat{I}_{1+}\hat{I}_{2z} + \hat{I}_{1-}\hat{I}_{2z}) \tag{4.39}$$

$$\hat{I}_{1z}\hat{I}_{2x} = \frac{1}{2}(+\hat{I}_{1z}\hat{I}_{2+} + \hat{I}_{1z}\hat{I}_{2-}) \tag{4.40}$$

$$\hat{I}_{1z}\hat{I}_{2y} = \frac{\mathrm{i}}{2}(-\hat{I}_{1z}\hat{I}_{2+} + \hat{I}_{1z}\hat{I}_{2-}). \tag{4.41}$$

Since

$$\cos\varphi + \mathrm{i}\sin\varphi = \mathrm{e}^{\mathrm{i}\varphi} \tag{4.42}$$

$$\cos\varphi - \mathrm{i}\sin\varphi = \mathrm{e}^{-\mathrm{i}\varphi}, \tag{4.43}$$

$$\begin{aligned} &3\sin\vartheta\cos\vartheta(\hat{I}_{1x}\hat{I}_{2z}\cos\varphi + \hat{I}_{1y}\hat{I}_{2z}\sin\varphi + \hat{I}_{1z}\hat{I}_{2x}\cos\varphi + \hat{I}_{1z}\hat{I}_{2y}\sin\varphi) \\ &= \frac{3}{2}\sin\vartheta\cos\vartheta(\hat{I}_{1+}\hat{I}_{2z}\mathrm{e}^{-\mathrm{i}\varphi} + \hat{I}_{1-}\hat{I}_{2z}\mathrm{e}^{\mathrm{i}\varphi} + \hat{I}_{1z}\hat{I}_{2+}\mathrm{e}^{-\mathrm{i}\varphi} + \hat{I}_{1z}\hat{I}_{2-}\mathrm{e}^{\mathrm{i}\varphi}) \end{aligned} \tag{4.44}$$

The double-quantum/zero-quantum operators are transformed in a similar fashion

$$\begin{aligned} \hat{I}_{1x}\hat{I}_{2y} &= \frac{\mathrm{i}}{4}(+\hat{I}_{1+}\hat{I}_{2-} - \hat{I}_{1-}\hat{I}_{2+} - \hat{I}_{1+}\hat{I}_{2+} + \hat{I}_{1-}\hat{I}_{2-}) \\ \hat{I}_{1y}\hat{I}_{2x} &= \frac{\mathrm{i}}{4}(-\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+} - \hat{I}_{1+}\hat{I}_{2+} + \hat{I}_{1-}\hat{I}_{2-}) \\ \hat{I}_{1x}\hat{I}_{2x} &= \frac{1}{4}(+\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+} + \hat{I}_{1+}\hat{I}_{2+} + \hat{I}_{1-}\hat{I}_{2-}) \\ \hat{I}_{1y}\hat{I}_{2y} &= \frac{1}{4}(+\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+} - \hat{I}_{1+}\hat{I}_{2+} - \hat{I}_{1-}\hat{I}_{2-}) \end{aligned}$$

and

$$3\sin^2\vartheta(\hat{I}_{1x}\hat{I}_{2x}\cos^2\varphi + \hat{I}_{1y}\hat{I}_{2y}\sin^2\varphi + \hat{I}_{1x}\hat{I}_{2y}\sin\varphi\cos\varphi + \hat{I}_{1y}\hat{I}_{2x}\sin\varphi\cos\varphi) - (\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y})$$

$$
\begin{aligned}
&= \frac{3}{4}\sin^2\vartheta\,(\ \hat{I}_{1+}\hat{I}_{2-}(\cos^2\varphi+\sin^2\varphi+\mathrm{i}\sin\varphi\cos\varphi-\mathrm{i}\sin\varphi\cos\varphi)\\
&\qquad +\hat{I}_{1-}\hat{I}_{2+}(\cos^2\varphi+\sin^2\varphi-\mathrm{i}\sin\varphi\cos\varphi+\mathrm{i}\sin\varphi\cos\varphi)\\
&\qquad +\hat{I}_{1+}\hat{I}_{2+}(\cos^2\varphi-\sin^2\varphi-\mathrm{i}\sin\varphi\cos\varphi-\mathrm{i}\sin\varphi\cos\varphi)\\
&\qquad +\hat{I}_{1-}\hat{I}_{2-}(\cos^2\varphi-\sin^2\varphi+\mathrm{i}\sin\varphi\cos\varphi+\mathrm{i}\sin\varphi\cos\varphi)\ )\\
&\qquad -\frac{1}{4}(2\hat{I}_{1+}\hat{I}_{2-}+2\hat{I}_{1-}\hat{I}_{2+})\\
&\qquad = \frac{1}{4}\hat{I}_{1+}\hat{I}_{2-}(3\sin^2\vartheta-2)+\frac{1}{4}\hat{I}_{1-}\hat{I}_{2+}(3\sin^2\vartheta-2)\\
&\qquad\quad +\frac{1}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\vartheta\mathrm{e}^{-\mathrm{i}2\varphi}+\frac{1}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\vartheta\mathrm{e}^{\mathrm{i}2\varphi}\\
&\qquad = -\frac{1}{4}\hat{I}_{1+}\hat{I}_{2-}(3\cos^2\vartheta-1)-\frac{1}{4}\hat{I}_{1-}\hat{I}_{2+}(3\cos^2\vartheta-1)\\
&\qquad\quad +\frac{1}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\vartheta\mathrm{e}^{-\mathrm{i}2\varphi}+\frac{1}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\vartheta\mathrm{e}^{\mathrm{i}2\varphi}.
\end{aligned}
\tag{4.45}
$$

Using Eqs. 4.44 and 4.45 and moving to the interaction frame ($\hat{I}_{n\pm}\rightarrow\hat{I}_{n\pm}\mathrm{e}^{\pm\mathrm{i}\omega_n t}$), Eq. 4.32 is converted to

$$
\begin{aligned}
\hat{H}_D^I &= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\Big(\hat{I}_{1z}\hat{I}_{2z}(3\cos^2\vartheta-1)\\
&\quad -\frac{1}{4}\hat{I}_{1+}\hat{I}_{2-}(3\cos^2\vartheta-1)\mathrm{e}^{\mathrm{i}(\omega_1-\omega_2)t}-\frac{1}{4}\hat{I}_{1-}\hat{I}_{2+}(3\cos^2\vartheta-1)\mathrm{e}^{-\mathrm{i}(\omega_1-\omega_2)t}\\
&\quad +\frac{3}{2}\hat{I}_{1+}\hat{I}_{2z}\sin\vartheta\cos\vartheta\mathrm{e}^{-\mathrm{i}\varphi}\mathrm{e}^{\mathrm{i}(\omega_1)t}+\frac{3}{2}\hat{I}_{1-}\hat{I}_{2z}\sin\vartheta\cos\vartheta\mathrm{e}^{\mathrm{i}\varphi}\mathrm{e}^{-\mathrm{i}(\omega_1)t}\\
&\quad +\frac{3}{2}\hat{I}_{1z}\hat{I}_{2+}\sin\vartheta\cos\vartheta\mathrm{e}^{-\mathrm{i}\varphi}\mathrm{e}^{\mathrm{i}(\omega_2)t}+\frac{3}{2}\hat{I}_{1z}\hat{I}_{2-}\sin\vartheta\cos\vartheta\mathrm{e}^{\mathrm{i}\varphi}\mathrm{e}^{-\mathrm{i}(\omega_2)t}\\
&\quad +\frac{3}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\vartheta\mathrm{e}^{-\mathrm{i}2\varphi}\mathrm{e}^{\mathrm{i}(\omega_1+\omega_2)t}+\frac{3}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\vartheta\mathrm{e}^{\mathrm{i}2\varphi}\mathrm{e}^{-\mathrm{i}(\omega_1+\omega_2)t}\ \Big)\\
&= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\Bigg(2\hat{I}_{1z}\hat{I}_{2z}c^{zz}-\frac{1}{2}c^{+-}\hat{I}_{1+}\hat{I}_{2-}-\frac{1}{2}c^{-+}\hat{I}_{1-}\hat{I}_{2+}\\
&\quad +\sqrt{\frac{3}{2}}\Big(c^{+z}\hat{I}_{1+}\hat{I}_{2z}+c^{-z}\hat{I}_{1-}\hat{I}_{2z}+c^{z+}\hat{I}_{1z}\hat{I}_{2+}+c^{z-}\hat{I}_{1z}\hat{I}_{2-}+c^{++}\hat{I}_{1+}\hat{I}_{2+}+c^{--}\hat{I}_{1-}\hat{I}_{2-}\Big)\ \Bigg)
\end{aligned}
\tag{4.46}
$$

Similarly to Eq. 3.97, the dipole-dipole relaxation is described by

$$
\frac{\mathrm{d}\Delta\hat{\rho}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^\infty \overline{[\hat{H}_D(0),[\hat{H}_D(t),\Delta\hat{\rho}]]}\mathrm{d}t. \tag{4.47}
$$

The right-hand side can be simplified dramatically by the *secular approximation* as in Eq. 3.97: all terms with $\mathrm{e}^{\pm\mathrm{i}\omega_n t}$ are averaged to zero. Only terms with $\overline{(c^{zz})^2}$, $\overline{c^{z+}c^{z-}}$, $\overline{c^{+z}c^{-z}}$, $\overline{c^{+-}c^{-+}}$, and $\overline{c^{++}c^{--}}$ are non zero (all equal to 1/5 at $t_j=0$).[3] This reduces the number of double commutators to be expressed from 81 to 9 for each density matrix component. The double commutators needed to describe relaxation rates of the contributions of the first nucleus to the magnetization $\langle M_{1z}\rangle$ and $\langle M_{1+}\rangle$ are, respectively,

$$
\Big[\hat{I}_{1z}\hat{I}_{2z},[\hat{I}_{1z}\hat{I}_{2z},\hat{I}_{1z}]\Big]=0 \tag{4.48}
$$

[3] Averaging over all molecules makes all correlation functions identical in isotropic liquids.

$$\left[\hat{I}_{1-}\hat{I}_{2+},[\hat{I}_{1+}\hat{I}_{2-},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}-\hat{I}_{2z}) \tag{4.49}$$

$$\left[\hat{I}_{1+}\hat{I}_{2-},[\hat{I}_{1-}\hat{I}_{2+},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}-\hat{I}_{2z}) \tag{4.50}$$

$$\left[\hat{I}_{1+}\hat{I}_{2z},[\hat{I}_{1-}\hat{I}_{2z},\hat{I}_{1z}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1z} \tag{4.51}$$

$$\left[\hat{I}_{1-}\hat{I}_{2z},[\hat{I}_{1+}\hat{I}_{2z},\hat{I}_{1z}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1z} \tag{4.52}$$

$$\left[\hat{I}_{1z}\hat{I}_{2+},[\hat{I}_{1z}\hat{I}_{2-},\hat{I}_{1z}]\right] = 0 \tag{4.53}$$

$$\left[\hat{I}_{1z}\hat{I}_{2-},[\hat{I}_{1z}\hat{I}_{2+},\hat{I}_{1z}]\right] = 0 \tag{4.54}$$

$$\left[\hat{I}_{1+}\hat{I}_{2+},[\hat{I}_{1-}\hat{I}_{2-},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}+\hat{I}_{2z}) \tag{4.55}$$

$$\left[\hat{I}_{1-}\hat{I}_{2-},[\hat{I}_{1+}\hat{I}_{2+},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}+\hat{I}_{2z}) \tag{4.56}$$

$$\left[\hat{I}_{1z}\hat{I}_{2z},[\hat{I}_{1z}\hat{I}_{2z},\hat{I}_{1+}]\right] = \frac{1}{4}\hbar^2\hat{I}_{1+} \tag{4.57}$$

$$\left[\hat{I}_{1+}\hat{I}_{2-},[\hat{I}_{1-}\hat{I}_{2+},\hat{I}_{1+}]\right] = \hbar^2\hat{I}_{1+} \tag{4.58}$$

$$\left[\hat{I}_{1-}\hat{I}_{2+},[\hat{I}_{1+}\hat{I}_{2-},\hat{I}_{1+}]\right] = 0 \tag{4.59}$$

$$\left[\hat{I}_{1+}\hat{I}_{2z},[\hat{I}_{1-}\hat{I}_{2z},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+} \tag{4.60}$$

$$\left[\hat{I}_{1-}\hat{I}_{2z},[\hat{I}_{1+}\hat{I}_{2z},\hat{I}_{1+}]\right] = 0 \tag{4.61}$$

$$\left[\hat{I}_{1z}\hat{I}_{2+},[\hat{I}_{1z}\hat{I}_{2-},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+} \tag{4.62}$$

$$\left[\hat{I}_{1z}\hat{I}_{2-},[\hat{I}_{1z}\hat{I}_{2+},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+} \tag{4.63}$$

$$\left[\hat{I}_{1+}\hat{I}_{2+},[\hat{I}_{1-}\hat{I}_{2-},\hat{I}_{1+}]\right] = 0 \tag{4.64}$$

$$\left[\hat{I}_{1-}\hat{I}_{2-},[\hat{I}_{1+}\hat{I}_{2+},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+}. \tag{4.65}$$

The relaxation rates can be then derived as described for the relaxation due to the chemical shift. The following equations are obtained:

$$\begin{aligned}
\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} &= -\frac{1}{8}b^2(2J(\omega_1-\omega_2)+6J(\omega_1)+12J(\omega_1+\omega_2))\Delta\langle M_{1z}\rangle \\
&+ \frac{1}{8}b^2(2J(\omega_1-\omega_2)-12J(\omega_1+\omega_2))\Delta\langle M_{2z}\rangle \\
&= -R_{\mathrm{a1}}\Delta\langle M_{1z}\rangle + R_{\mathrm{x}}\Delta\langle M_{2z}\rangle
\end{aligned} \tag{4.66}$$

$$\begin{aligned}
\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} &= -\frac{1}{8}b^2(2J(\omega_1-\omega_2)+6J(\omega_2)+12J(\omega_1+\omega_2))\Delta\langle M_{2z}\rangle \\
&+ \frac{1}{8}b^2(2J(\omega_1-\omega_2)-12J(\omega_1+\omega_2))\Delta\langle M_{1z}\rangle \\
&= -R_{\mathrm{a2}}\Delta\langle M_{2z}\rangle + R_{\mathrm{x}}\Delta\langle M_{1z}\rangle
\end{aligned} \tag{4.67}$$

$$\frac{\mathrm{d}\langle M_{1+}\rangle}{\mathrm{d}t} = -\frac{1}{8}b^2(4J(0)+6J(\omega_2)+J(\omega_1-\omega_2)+3J(\omega_1)+6J(\omega_1+\omega_2))\langle M_{1+}\rangle \tag{4.68}$$

$$= -R_2\langle M_{1+}\rangle = -\left(R_0 + \frac{1}{2}R_1\right)\langle M_{1+}\rangle \tag{4.69}$$

where

$$b = -\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r^3}. \tag{4.70}$$

The relaxation rate $R1$ of the dipole-dipole relaxation is the rate of relaxation of the z-component of the total magnetization $\langle M_z\rangle = \langle M_{1z}\rangle + \langle M_{2z}\rangle$. R_1 is derived by solving the set of Eqs. 4.66 and 4.67. The solution is simple if $J(\omega_1) = J(\omega_2) = J(\omega) \Rightarrow R_{\mathrm{a}1} = R_{\mathrm{a}2} = R_{\mathrm{a}}$ (this is correct e.g. if both nuclei have the same γ, if the molecule rotates as a sphere, and if internal motions are negligible or identical for both nuclei).[4]

$$\frac{\mathrm{d}\Delta\langle M_z\rangle}{\mathrm{d}t} = -\frac{1}{8}b^2(6J(\omega) + 24J(2\omega_1))\Delta\langle M_z\rangle = -(R_{\mathrm{a}} - R_{\mathrm{x}})\Delta\langle M_z\rangle \tag{4.71}$$

There are several remarkable differences between relaxation due to the chemical shift anisotropy and dipole-dipole interactions:

- The rate constants describing the return to the equilibrium polarization is more complex than for the chemical shift anisotropy relaxation. In addition to the $3b^2J(\omega_1)/4$ term, describing the $|\alpha\rangle \leftrightarrow |\beta\rangle$ transition[5] of nucleus 1, the *auto-relaxation rate* $R_{\mathrm{a}1}$ contains terms depending on the sum and difference of the precession frequency of $\vec{\mu}_1$ and $\vec{\mu}_2$. These terms correspond to the *zero-quantum* ($|\alpha\beta\rangle \leftrightarrow |\beta\alpha\rangle$) and *double-quantum* ($|\alpha\alpha\rangle \leftrightarrow |\beta\beta\rangle$) transitions, respectively.

- Return to the equilibrium polarization of nucleus 1 depends also on the actual polarization *of nucleus 2*. This effect, resembling chemical kinetics of a reversible reaction, is known as *cross-relaxation*, or *nuclear Overhauser effect* (NOE), and described by the *cross-relaxation constant* R_{x}. The value of R_{x} is proportional to r^{-6} and thus provides information about inter-atomic distances. NOE is a useful tool in analysis of small molecules and the most important source of structural information for large biological molecules.

- The relaxation constant R_0, describing the loss of coherence, contains an additional term, depending on the frequency of *the other nucleus*, $3b^2J(\omega_2)/4$. This term has the following physical significance. The field generated by the second magnetic moment depends on its state. The state is changing due to $|\alpha\rangle \leftrightarrow |\beta\rangle$ transitions the with the rate given by $3b^2J(\omega_2)/4$. Such changes have the similar effect as the *chemical or conformational exchange*, modifying the size of the chemical shift tensor. Therefore, $3b^2J(\omega_2)/4$ adds to R_0 like the exchange contribution.

4.7 2D spectroscopy based on dipole-dipole interactions

Three 90° pulses and two delays before data acquisition:

$$_{\mathrm{a}}(\pi/2)_{x\mathrm{b}} - t_1 -_{\mathrm{c}} (\pi/2)_{x\mathrm{d}} - \tau_{\mathrm{m}} -_{\mathrm{e}} (\pi/2)_{x\mathrm{f}} - t_2(\mathrm{acquire})$$

Homonuclear experiments - all nuclei the same γ.

[4]The general solution gives $R_1 = \frac{1}{2}\left(R_{\mathrm{a}1} + R_{\mathrm{a}2} - \sqrt{(R_{\mathrm{a}1} - R_{\mathrm{a}2})^2 + 4R_{\mathrm{x}}^2}\right)$.

[5]The $|\alpha\alpha\rangle \leftrightarrow |\beta\alpha\rangle$ and $|\alpha\beta\rangle \leftrightarrow |\beta\beta\rangle$ transitions in a two-spin system

4.7.1 Two-dimensional spectroscopy

In order to describe principles of 2D spectroscopy, we first analyze the experiment for two non-interacting magnetic moments, e.g. of two protons with different chemical shift δ_{i} too far from each other.

We describe the density matrix just before and after pulses, as labeled by letters "a" to "f".

- $\hat{\rho}(\mathrm{a}) = \mathcal{I}_t + \kappa(\mathcal{I}_{1z} + \mathcal{I}_{2z})$
  thermal equilibrium, the matrices are different than for the noninteracting spin, but the constant is the same.

- $\hat{\rho}(\mathrm{b}) = \mathcal{I}_t + \kappa(-\mathcal{I}_{1y} - \mathcal{I}_{2y})$
  90° pulse, see the one-pulse experiment

- $\hat{\rho}(\mathrm{c}) = \mathcal{I}_t + \kappa\left(-\mathrm{e}^{-R_2 t_1}\cos(\Omega_1 t_1)\mathcal{I}_{1y} + e^{-R_2 t_1}\sin(\Omega_1 t_1)\mathcal{I}_{1x} - \mathrm{e}^{-R_2 t_1}\cos(\Omega_2 t_1)\mathcal{I}_{2x} + e^{-R_2 t_1}\sin(\Omega_2 t_1)\mathcal{I}_{2y}\right)$
  $\hat{\rho}(\mathrm{c}) = \mathcal{I}_t + \kappa\left(-c_{11}\mathcal{I}_{1y} + s_{11}\mathcal{I}_{1x} - c_{21}\mathcal{I}_{2y} + s_{21}\mathcal{I}_{2x}\right)$
  evolution after excitation, the same as in the one-pulse experiment. No effect of the dipolar coupling (averaged to zero in isotropic liquids). Relaxation included as the exponential factors with the same R_2 (differ in general).

- $\hat{\rho}(\mathrm{d}) = \mathcal{I}_t + \kappa\left(-c_{11}\mathcal{I}_{1z} + s_{11}\mathcal{I}_{1x} - c_{21}\mathcal{I}_{2z} + s_{21}\mathcal{I}_{2x}\right)$
  90° x-pulse does not affect x magnetization, rotates $-y$ magnetization further to $-z$ - $\parallel \vec{B}_0$ but inverted polarization, similar to a $\rightarrow$ b.

- $\hat{\rho}(\mathrm{e}) =$? Delay τ_{m} is usually longer than 0.1 s. New, should be analyzed (here for a large molecule such as a small protein): In proteins, M_x, M_y relax with $R_2 > 10\,\mathrm{s}^{-1}$ and M_z with $R_1 \approx 1\,\mathrm{s}^{-1}$. Let's assume $\tau_{\mathrm{m}} = 0.2\,\mathrm{s}$ and $R_2 = 20\,\mathrm{s}^{-1}$. After 0.2 s, $\mathrm{e}^{-R_2\tau_{\mathrm{m}}} = \mathrm{e}^{-20\times 0.2} = \mathrm{e}^{-4} \approx 0.02$. We see that M_x, M_y relaxes almost completely $\Rightarrow \mathcal{I}_{1x}, \mathcal{I}_{1y}, \mathcal{I}_{2x}, \mathcal{I}_{2y}$ can be neglected. On the other hand, $\mathrm{e}^{-R_1\tau_{\mathrm{m}}} = \mathrm{e}^{-1\times 0.2} = \mathrm{e}^{-0.2} \approx 0.82$. We see that M_z does not relax too much $\Rightarrow$ we continue analysis with $\mathcal{I}_{1z}, \mathcal{I}_{2z}$. The $\mathcal{I}_{1z}, \mathcal{I}_{2z}$ terms do not evolve because they commute with $\mathcal{H} = \Omega_1\mathcal{I}_{1z} + \Omega_2\mathcal{I}_{2z}$. Therefore,
  $\hat{\rho}(\mathrm{e}) = \mathcal{I}_t + \kappa\left(-\mathrm{e}^{-R_1\tau_{\mathrm{m}}}c_{11}\mathcal{I}_{1z} - \mathrm{e}^{-R_1\tau_{\mathrm{m}}}c_{21}\mathcal{I}_{2z}\right) = \mathcal{I}_t - \mathcal{A}_1\mathcal{I}_{1z} - \mathcal{A}_2\mathcal{I}_{2z}$

- $\hat{\rho}(\mathrm{e}) = \mathcal{I}_t + \mathcal{A}_1\mathcal{I}_{1y} + \mathcal{A}_2\mathcal{I}_{2y}$
  see the first pulse

- $\hat{\rho}(t_2) =$
  $\mathcal{I}_t + \mathcal{A}_1(\mathrm{e}^{-R_2 t_2}\cos(\Omega_1 t_2)\mathcal{I}_{1y} - \mathrm{e}^{-R_2 t_2}\sin(\Omega_1 t_2)\mathcal{I}_{1x}) + \mathcal{A}_2(\mathrm{e}^{-R_2 t_2}\cos(\Omega_2 t_2)\mathcal{I}_{2y} - \mathrm{e}^{-R_2 t_2}\sin(\Omega_2 t_2)\mathcal{I}_{2x})$
  evolution during data acquisition, correction of the phase gives $\hat{\rho}$ in the same form as in Eq. 3.131:
  $\hat{\rho}(t_2) =$
  $\mathcal{I}_t + \mathcal{A}_1(\mathrm{e}^{-R_2 t_2}\cos(\Omega_1 t_2)\mathcal{I}_{1x} + \mathrm{e}^{-R_2 t_2}\sin(\Omega_1 t_2)\mathcal{I}_{1y}) + \mathcal{A}_2(\mathrm{e}^{-R_2 t_2}\cos(\Omega_2 t_2)\mathcal{I}_{2x} + \mathrm{e}^{-R_2 t_2}\sin(\Omega_2 t_2)\mathcal{I}_{2y})$
  Therefore, Fourier transform of the signal provides spectrum in the form (see Eq. 3.133)

$$\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_{\mathrm{B}}T}\left(\frac{\mathcal{A}_1 R_2}{R_2^2 + (\omega - \Omega_1)^2} + \frac{\mathcal{A}_2 R_2}{R_2^2 + (\omega - \Omega_2)^2} - \mathrm{i}\left(\frac{\mathcal{A}_1(\omega - \Omega_1)}{R_2^2 + (\omega - \Omega_1)^2} + \frac{\mathcal{A}_2(\omega - \Omega_2)}{R_2^2 + (\omega - \Omega_2)^2}\right)\right). \tag{4.72}$$

In the one-dimensional experiment, $\mathcal{A}_1$ and $\mathcal{A}_2$ just scale the peak height. However, they depend on the length of the delay t_1. If the measurement is repeated many times and t_1 is increased by an increment Δt each time, the obtained series of 1D spectra is *amplitude modulated* by $c_{11} = \mathrm{e}^{-R_2 t_2}\cos(\Omega_1 t_1)$ and $c_{21} = \mathrm{e}^{-R_2 t_2}\cos(\Omega_2 t_1)$. Since the data are stored in a computer in a digital form, they can be treated as a two-dimensional array (table), depending on the real time t_2 in one direction and on the length of the incremented delay t_1 in the other directions. These directions are referred to as *direct dimension* and *indirect dimension*. Fourier transform can be performed in each dimension.

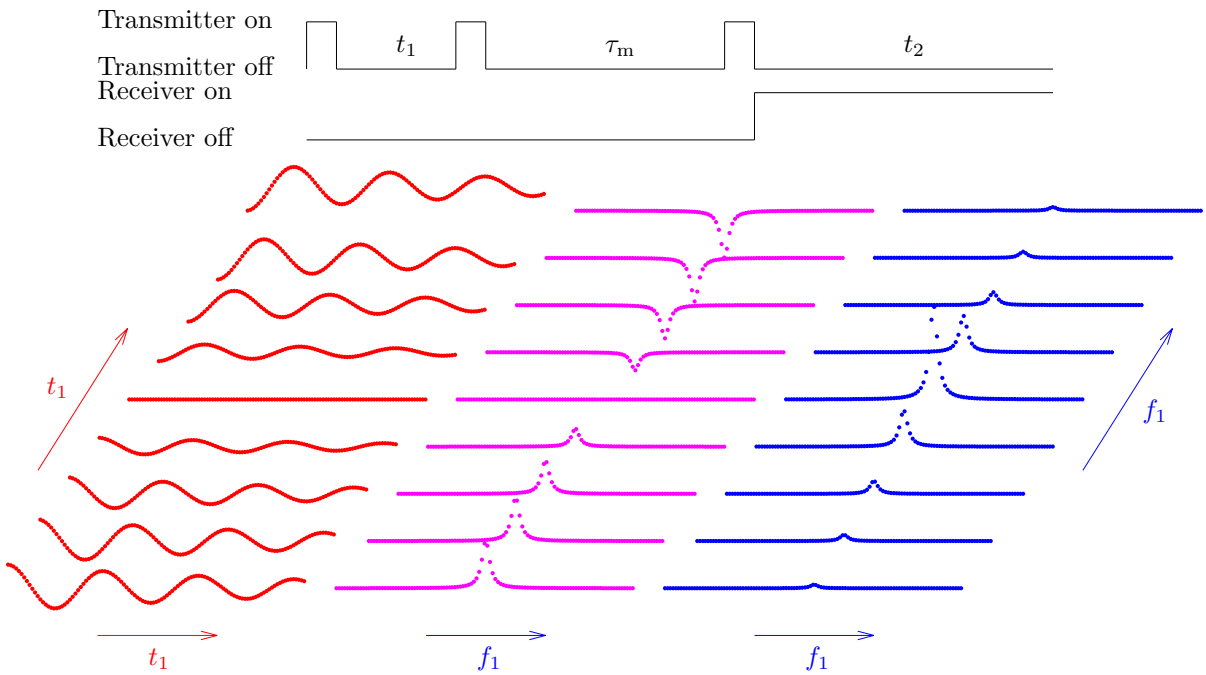

Figure 4.1: Principle of two-dimensional spectroscopy (experiment NOESY). The acquired signal is shown in red, the signal after Fourier transform in the direct dimension is shown in magenta, and the signal after Fourier transform in both dimensions is shown in blue.

Since we acquire signal as a series of complex numbers, it is useful to introduce the complex numbers in the indirect dimension as well. It is possible e.g. by repeating the measurement twice for each value of t_1, once with the x-phase (the same phase as the first pulse) of the second pulse, as described above, and then with the y-phase (phase-shifted from the first pulse by 90°). In the latter case, the $\mathcal{I}_{1y}$ and $\mathcal{I}_{2y}$ components are not affected and relax during τ_m, while the $\mathcal{I}_{1x}$ and $\mathcal{I}_{2x}$ are rotated to $-\mathcal{I}_{1z}$ and $-\mathcal{I}_{2z}$, respectively, and converted to the measurable signal by the third pulse. Because the $\mathcal{I}_{1x}$ and $\mathcal{I}_{2x}$ coherences are modulated by s_{11} and s_{21}, $\mathcal{A}_1$ and $\mathcal{A}_2$ oscillate as a sine function, not cosine function, in the even spectra. So, we obtain cosine modulation in odd spectra and sine modulation in even spectra. The cosine- and sine- signals are then treated as the real and imaginary component of the complex signal in the indirect dimension. Complex Fourier transform in both dimensions provides a two-dimensional spectrum.

4.7.2 Nuclear Overhauser efect spectroscopy (NOESY)

The two-dimensional spectra described in the preceding section are not very useful because they do not bring any new information. The same frequencies are measured in the direct and indirect dimension and all peaks are found along the diagonal of the spectrum. What makes the experiment really useful is the interaction between magnetic moments during τ_m.

As described by Eq. 4.66, relaxation of nucleus 1 is influenced by the state of nucleus 2 (and vice versa):

$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}1}\Delta\langle M_{1z}\rangle + R_{\mathrm{x}}\Delta\langle M_{2z}\rangle \tag{4.73}$$

$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}2}\Delta\langle M_{2z}\rangle + R_{\mathrm{x}}\Delta\langle M_{1z}\rangle. \tag{4.74}$$

The analysis greatly simplifies if the auto-relaxation rates are identical for both magnetic moments. Then,

$$\Delta\langle M_{1z}\rangle = ((1-\zeta)\Delta\langle M_{1z}\rangle(0) + \zeta\Delta\langle M_{2z}\rangle(0))\,\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})t}, \tag{4.75}$$

where $\zeta = (\mathrm{e}^{2R_{\mathrm{x}}t} - 1)/2$. Therefore,
$\hat{\rho}(\mathrm{e}) = \mathcal{I}_t - \mathcal{A}_1\mathcal{I}_{1z} - \mathcal{A}_2\mathcal{I}_{2z} = \mathcal{I}_t - \kappa\,((1-\zeta)c_{11} + \zeta c_{21})\,\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})\tau_{\mathrm{m}}}\mathcal{I}_{1z} - \kappa\,((1-\zeta)c_{21} + \zeta c_{11})\,\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})\tau_{\mathrm{m}}}\mathcal{I}_{2z}$
Now, the amplitudes $\mathcal{A}_1$ and $\mathcal{A}_2$ depend on *both frequencies* Ω_1 and Ω_2 (contain both c_{11} and c_{21}. Therefore, the spectrum contains both diagonal peaks (with the frequencies of the given magnetic moment in both dimensions) and off-diagonal *cross-peaks* (with the frequencies of the given magnetic moment in the direct dimension and the frequency of its interaction partner in the indirect dimension). The overall loss of signal ("leakage") due to the R_1 relaxation is given by $\mathrm{e}^{-(R_{\mathrm{a}}-R_{\mathrm{x}})\tau_{\mathrm{m}}}$ and intensities of the cross-peaks are given by the factor

$$\zeta\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})\tau_{\mathrm{m}}} = \frac{1}{2}\left(\mathrm{e}^{R_{\mathrm{x}}\tau_{\mathrm{m}}} - \mathrm{e}^{-R_{\mathrm{x}}\tau_{\mathrm{m}}}\right) \approx R_{\mathrm{x}}\tau_{\mathrm{m}} = \frac{\mu_0}{8\pi}\frac{\gamma^4\hbar^2}{r^6}(J(0) - 6J(2\omega))\tau_{\mathrm{m}}, \tag{4.76}$$

where the difference of the precession frequencies due to different chemical shifts was neglected ($\omega_1 = \omega_2$ because $\gamma_1 = \gamma_2$). Hence, the cross-peak intensity is proportional to r^{-6} in the linear approximation.

Chapter 5

Ensembles of spins interacting through bonds

Magnetic moments of nuclei connected by covalent bonds interact also indirectly, via interactions with magnetic moments of the electrons of the bonds. The simplest example is a pair of nuclei (e.g., ^{1}H and ^{13}C) connected by a σ bond. In such system, the states $|\alpha\beta\rangle$ and $|\alpha\beta\rangle$ allow all interacting particles to be in the opposite state (H$^\uparrow$-e$^\downarrow$-e$^\uparrow$-C$^\downarrow$ and H$^\downarrow$-e$^\uparrow$-e$^\downarrow$-C$^\uparrow$, respectively) and are energetically more favorable than the $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$ states, which require too interacting particles to be in the same state (H$^\uparrow$-e$^\downarrow$-e$^\uparrow$-C$^\uparrow$ or H$^\uparrow$-e$^\uparrow$-e$^\downarrow$-C$^\uparrow$ and H$^\downarrow$-e$^\downarrow$-e$^\uparrow$-C$^\downarrow$ or H$^\downarrow$-e$^\uparrow$-e$^\downarrow$-C$^\downarrow$, respectively). The relations are more complex in the case of interactions through multiple bonds.

Again, each component of the field felt by magnetic moment 1 (e.g. of ^{1}H) depends on all components of the magnetic moment 2 (e.g. of ^{13}C). Therefore, the interaction is described by tensors (like chemical shift or dipolar coupling):

$$\hat{H}_J = -\gamma(\hat{I}_{x1}B_{2,x} + \hat{I}_{y1}B_{2,y} + \hat{I}_z B_{2,z1}) = -\gamma(\,\hat{I}_{x1}\;\hat{I}_{y1}\;\hat{I}_{z1}\,)\begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} =$$

$$= 2\pi(\,\hat{I}_x\;\hat{I}_y\;\hat{I}_z\,)\begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix}\begin{pmatrix} \hat{I}_{x1} \\ \hat{I}_{y1} \\ \hat{I}_{z1} \end{pmatrix} = 2\pi\hat{\vec{I}}_1 \cdot \underline{J} \cdot \hat{\vec{I}}_2 \tag{5.1}$$

Anisotropic part of the J-tensor is usually small (and difficult to distinguish from the dipolar coupling) and is neglected in practice. Therefore, only the isotropic (scalar) part of the tensor is considered and the interaction is called *scalar coupling*:

$$2\pi\begin{pmatrix} J_{xx} & 0 & 0 \\ 0 & J_{yy} & 0 \\ 0 & 0 & J_{zz} \end{pmatrix} = 2\pi\frac{J_{xx}+J_{yy}+J_{zz}}{3}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 2\pi J\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{5.2}$$

The scalar coupling is observed as splitting of peaks by $2\pi J$ in NMR spectra. Proton-proton coupling is significant (exceeding 10 Hz) up to three bonds and observable for 4 or 5 bonds in special cases (planar geometry like in aromatic systems). Interactions of other nuclei are weaker, but the one-bond couplings are always significant (as strong as 700 Hz for ^{31}P-^{1}H, 140 Hz to 200 Hz for ^{13}C-^{1}H, 90 Hz for ^{15}N-^{1}H in amides, 30 Hz to 60 Hz for ^{13}C-^{13}C, 10 Hz to 15 Hz for ^{13}C-^{15}N). The value of J is given by the distribution of electrons in bonds and thus reflect the local geometry of the molecule. Three-bond scalar couplings can be used to measure torsion angles in molecules.

5.1 Secular approximation and averaging

If the anisotropic part of the J-tensor is neglected, the J-coupling does not depend on orientation (*scalar* coupling) and no ensemble averaging is needed. The secular approximation is applied like in the case of the dipolar coupling.

- In the case of magnetic moments with the same γ *and* chemical shift, precessing about the z axis with *the same precession frequency*,

$$\hat{H}_J = \pi J \left(2\hat{I}_{1,z}\hat{I}_{2,z} + 2\hat{I}_{1,x}\hat{I}_{2,x} + 2\hat{I}_{1,y}\hat{I}_{2,y} \right). \tag{5.3}$$

- In the case of magnetic moments with different γ and/or chemical shift, precessing about the z axis with *different precession frequencies*,

$$\hat{H}_J = 2\pi J \hat{I}_{1,z}\hat{I}_{2,z} = \pi J \left(2\hat{I}_{1,z}\hat{I}_{2,z} \right). \tag{5.4}$$

5.2 Relaxation due to the J-coupling

In principle, the anisotropic part of the J-tensor would contribute to relaxation like the anisotropic part of the chemical shift tensor, but it is small and usually neglected. Scalar coupling (isotropic part of the J-tensor) does not depend on the orientation. Therefore, it can contribute to the relaxation only through a conformational or chemical exchange. Conformational effects are usually small: one-bond and two-bond couplings do not depend on torsion angles and three-bond coupling constants are small. In summary, relaxation due to the J-coupling is rarely observed.

5.3 2D spectroscopy based on scalar coupling

5.3.1 Evolution in the presence of the scalar coupling

In the presence of the scalar coupling, the Hamiltonian describing evolution after a 90° pulse is complicated even in a coordinate system rotating with $\omega_{\mathrm{rot}} = \omega_{\mathrm{radio}}$

$$\mathcal{H} = \varepsilon_t \cdot 2\mathcal{I}_t \underbrace{-\gamma_1 B_0 (1+\delta_{\mathrm{i}1})}_{\Omega_1} \mathcal{I}_{1z} \underbrace{-\gamma_1 B_0 (1+\delta_{\mathrm{i}2})}_{\Omega_2} \mathcal{I}_{2z} + \pi J \left(2\mathcal{I}_{1z}\mathcal{I}_{2z} + 2\mathcal{I}_{1x}\mathcal{I}_{2x} + 2\mathcal{I}_{1y}\mathcal{I}_{2y} \right). \tag{5.5}$$

However, if the precession frequencies differ, the Hamiltonian simplifies to a form where all components commute. Therefore, the Liouville - von Neumann equation can be used geometrically as rotations in three-dimensional subspaces of the 16-dimensional operator space. Rotations described by different components of the Hamiltonian are independent and can be performed consecutively, in any order.

For a density matrix $\hat{\rho}(\mathrm{b}) = \mathcal{I}_t + \kappa(-\mathcal{I}_{1y} - \mathcal{I}_{2y})$ after a 90° pulse, the evolution due to the chemical shift (described by Ω_1 and Ω_2 and scalar coupling (described by πJ) can be analyzed as follows

$$\mathcal{I}_{1t} \longrightarrow \mathcal{I}_{1t} \longrightarrow \mathcal{I}_{1t} \tag{5.6}$$

$$-\mathcal{I}_{1y} \longrightarrow \begin{cases} -c_1\mathcal{I}_{1y} \longrightarrow \begin{cases} -c_1 c_J \ \mathcal{I}_{1y} \\ +c_1 s_J \ 2\mathcal{I}_{1x}\mathcal{I}_{2z} \end{cases} \\ +s_1\mathcal{I}_{1x} \longrightarrow \begin{cases} +s_1 c_J \ \mathcal{I}_{1x} \\ +s_1 s_J \ 2\mathcal{I}_{1y}\mathcal{I}_{2z} \end{cases} \end{cases} \tag{5.7}$$

$$-\mathcal{I}_{2y} \longrightarrow \begin{cases} -c_2\mathcal{I}_{2y} \longrightarrow \begin{cases} -c_2c_J\ \mathcal{I}_{2y} \\ +c_2s_J\ 2\mathcal{I}_{2x}\mathcal{I}_{1z} \end{cases} \\ +s_2\mathcal{I}_{2x} \longrightarrow \begin{cases} +s_2c_J\ \mathcal{I}_{2x} \\ +s_2s_J\ 2\mathcal{I}_{2y}\mathcal{I}_{1z} \end{cases} \end{cases} \tag{5.8}$$

where the first arrows represent rotation "about" $\mathcal{I}_{1z}$ or $\mathcal{I}_{2z}$ by the angle $\Omega_1 t$ or $\Omega_2 t$, the second arrows represent rotation "about" $2\mathcal{I}_{1z}\mathcal{I}_{2z}$ by the angle $\pi J t$, and

$$c_1 = \cos(\Omega_1 t) \qquad s_1 = \sin(\Omega_1 t) \tag{5.9}$$
$$c_2 = \cos(\Omega_2 t) \qquad s_2 = \sin(\Omega_2 t) \tag{5.10}$$
$$c_J = \cos(\pi J t) \qquad s_J = \sin(\pi J t) \tag{5.11}$$

Only $\mathcal{I}_{1x}, \mathcal{I}_{1y}, \mathcal{I}_{2x}, \mathcal{I}_{2y}$ contribute to the expected value of M_+, giving non-zero trace when multiplied by $\hat{I}_+$ (orthogonality).

Including relaxation and applying a phase shift by 90 °, the expected value of M_+ evolves as

$$\frac{1}{4}\mathrm{e}^{-R_2 t}\left(\mathrm{e}^{-\mathrm{i}(\Omega_1-\pi J)t} + \mathrm{e}^{-\mathrm{i}(\Omega_1+\pi J)t} + \mathrm{e}^{-\mathrm{i}(\Omega_2-\pi J)t} + \mathrm{e}^{-\mathrm{i}(\Omega_2+\pi J)t}\right) \tag{5.12}$$

which gives two doublets in the spectrum after Fourier transform:

$$\begin{aligned} &\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\left(\frac{R_2}{R_2^2+(\omega-\Omega_1+\pi J)^2} + \frac{R_2}{R_2^2+(\omega-\Omega_2-\pi J)^2} + \frac{R_2}{R_2^2+(\omega-\Omega_1+\pi J)^2} + \frac{R_2}{R_2^2+(\omega-\Omega_2-\pi J)^2}\right) \\ &-\mathrm{i}\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\left(\frac{(\omega-\Omega_1+\pi J)}{R_2^2+(\omega-\Omega_1+\pi J)^2} + \frac{(\omega-\Omega_2-\pi J)}{R_2^2+(\omega-\Omega_2-\pi J)^2} + \frac{(\omega-\Omega_1+\pi J)}{R_2^2+(\omega-\Omega_1+\pi J)^2} + \frac{(\omega-\Omega_2-\pi J)}{R_2^2+(\omega-\Omega_2-\pi J)^2}\right). \end{aligned} \tag{5.13}$$

5.4 Spin echoes

Experiments utilizing scalar coupling are based on "spin alchemy" - artificial manipulations of quantum states of the studied system.

Spin echoes are basic tools of spin alchemy, providing the possibility to control evolution of the chemical shift and scalar coupling separately.

Here we analyze three types of spin echoes for a heteronucler system (two nuclei with different γ, ^{1}H and ^{13}C in our example). In order to distinguish the heteronuclear systems from homonuclear ones, we will use symbols $\mathcal{I}_j$ and $\mathcal{S}_j$ for operators of nucleus 1 and 2, repsectively, if $\gamma_1 \neq \gamma_2$. For the sake of simplicity, relaxation is not included.

Vector analysis: Solid arrow - component of $\mu_1 \perp \vec{B}_0$ for spin 2 in $|\alpha\rangle$, dashed arrow - component of $\mu_1 \perp \vec{B}_0$ for spin 2 in $|\beta\rangle$, colors - different δ_i

5.4.1 Free evolution (Figure 5.1A)

Evolution of the system of two nuclei in the presence of scalar coupling was already described in Section 5.3.1.

- $\hat{\rho}(\mathrm{a}) = \mathcal{I}_t + \kappa_1\mathcal{I}_z + \kappa_2\mathcal{S}_z$
  thermal equilibrium, the constants κ_1 and κ_2 are different because the nuclei have different γ.

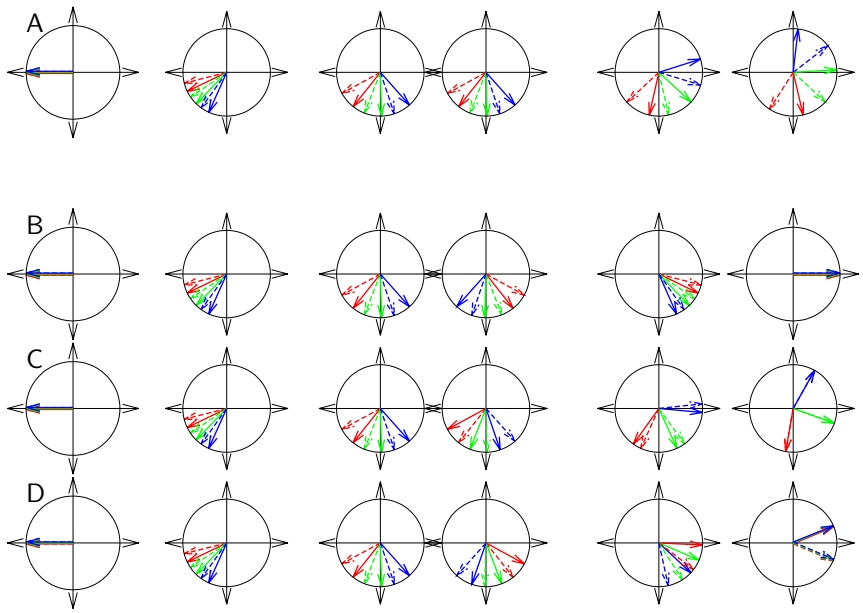

Figure 5.1: Vector analysis of spin echoes for ^{1}H (nucleus 1) and ^{13}C (nucleus 2) in an isolated –CH– group. In individual rows, evolution of magnetization vectors in the plane $\perp \vec{B}_0$ is shown for three protons (distinguished by colors) with slightly different precession frequency due to the different chemical shifts δ_i. The protons are bonded to ^{13}C. Solid arrows are components of proton magnetization for ^{13}C in $|\beta\rangle$, dashed arrow are components of proton magnetization for ^{13}C in $|\alpha\rangle$. The first column shows magnetization vectors at the beginning of the echo (after the initial 90° pulse at the proton frequency), the second column shows magnetization vectors in the middle of the first delay τ, the third and fourth columns show magnetization immediately before and after the 180° pulse(s) in the middle of the echo, respectively, the fifths column shows magnetization vectors in the middle of the second delay τ, the sixth column shows magnetization vectors at the end of the echo. Row A corresponds to an experiment when no 180° pulse is applied, row B corresponds to the echo with the 180° pulse applied at the proton frequency, row C corresponds to the echo with the 180° pulse applied at the ^{13}C frequency, and row D corresponds to the echo with the 180° pulses applied at both frequencies. The x-axis points down, the y-axis points to the right.

- $\hat{\rho}(\mathrm{b}) = \mathcal{I}_t - \kappa_1 \mathcal{I}_y + \kappa_2 \mathcal{S}_z$
  90° pulse applied to nucleus 1 only

- $\hat{\rho}(\mathrm{e}) = \mathcal{I}_t + \kappa_1 \left(-c_1 c_J \mathcal{I}_y + s_1 c_J \mathcal{I}_x + c_1 s_J 2\mathcal{I}_x \mathcal{S}_z + s_1 s_J 2\mathcal{I}_y \mathcal{S}_z\right) + \kappa_2 \mathcal{S}_z$
  free evolution during 2τ ($t \to 2\tau$ in c_1 etc.)

For nuclei with $\gamma > 0$, magnetizations of nucleus 1 (proton) evolve faster if nucleus 2 (^{13}C) is in $|\beta\rangle$ (the energy difference between $|\alpha\beta\rangle$ and $|\beta\beta\rangle$ is larger than the energy difference between $|\alpha\alpha\rangle$ and $|\beta\alpha\rangle$) - solid arrows rotated by a large angle than dashed arrows in Fig. 5.1A.

The $2\mathcal{I}_x\mathcal{S}_z$, $2\mathcal{I}_y\mathcal{S}_z$ coherences do not give non-zero trace when multiplied by $\mathcal{I}_+$ (they are not measurable per se), but *cannot be ignored* if the pulse sequence continues because they can *evolve* into measurable coherences later (note that the scalar coupling Hamiltonian $2\pi J \mathcal{I}_z \mathcal{S}_z$ converts them to $\mathcal{I}_y$, $\mathcal{I}_x$, respectively).

5.4.2 Refocusing echo (Figure 5.1B)

90° pulse exciting magnetic moment 1 and 180° pulse on the excited nucleus in the middle of the echo

$$_{\mathrm{a}}(\pi/2)_{1x_{\mathrm{b}}} - \tau -_{\mathrm{c}} (\pi)_{1x_{\mathrm{d}}} - \tau -_{\mathrm{e}}$$

The middle 180° pulse flips all vectors from left to right (rotation about the vertical axis x by 180°). The faster vectors start to evolve with a handicap at the beginning of the second delay τ and they reach the slower vectors at the end of the echo regardless of the actual speed of rotation.

Even without a detailed analysis of product operators, we see that the final state of the system does not depend on chemical shift or scalar coupling: the evolution of both chemical shift and scalar coupling is *refocused* during this echo.

The initial state of protons was described (after the 90° pulse) by $-\mathcal{I}_y$ in terms of product operators and by an arrow with the $-y$ orientation. As the vector only changed its sign at the end of the experiment (arrow with the $+y$ orientation), we can deduce that the final state of protons is $+\mathcal{I}_y$:
$\hat{\rho}(\mathrm{e}) = \mathcal{I}_t + \kappa_1 \mathcal{I}_y + \kappa_2 \mathcal{S}_z$

5.4.3 Decoupling echo (Figure 5.1C)

90° pulse exciting magnetic moment 1 and 180° pulse on the other nucleus in the middle of the echo

$$_{\mathrm{a}}(\pi/2)_{1x_{\mathrm{b}}} - \tau -_{\mathrm{c}} (\pi)_{2x_{\mathrm{d}}} - \tau -_{\mathrm{e}}$$

The middle 180° is applied at the ^{13}C frequency. It does not affect vectors of proton magnetization but *inverts* polarization (populations) of ^{13}C (solid arrows change to dashed ones and vice versa). The faster vectors become slower, the slower vectors become faster, and they meet at the end of the echo.

Without a detailed analysis of product operators, we see that the final state of the system does not depend on scalar coupling (the difference between solid and dashed arrows disappeared) but the evolution due to the chemical shift took place (arrows of different colors rotated by different angles $2\Omega_1\tau$). As the effects of scalar coupling are masked, this echo is known as the *decoupling* echo.

As the vectors at the end of the echo have the same orientations as if the nuclei were not coupled at all, we can deduce that the final state of protons is identical to the density matrix evolving due to the chemical shift only:
$\hat{\rho}(\mathrm{e}) = \mathcal{I}_t + \kappa_1 \left(c_1 \mathcal{I}_y - s_1 \mathcal{I}_x\right) - \kappa_2 \mathcal{S}_z$

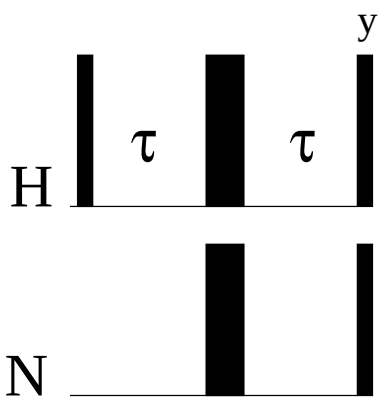

Figure 5.2: INEPT pulse sequence applied to ^{1}H and ^{15}N.

5.4.4 Recoupling echo (Figure 5.1D)

90° pulse exciting magnetic moment 1 and 180° pulses on both nuclei in the middle of the echo

$$_{\mathrm{a}}(\pi/2)_{1x_{\mathrm{b}}} - \tau -_{\mathrm{c}} (\pi)_{1x}(\pi)_{2x_{\mathrm{d}}} - \tau -_{\mathrm{e}}$$

180° pulses are applied at ^{1}H and ^{13}C frequencies in the middle of the echo, resulting in combination of both effects described in Figs. 5.1B and C. The proton pulse flips vectors of proton magnetization and the ^{13}C flips polarization (populations) of ^{13}C (solid arrows change to dashed ones and vice versa). As a result, the average direction of dashed and solid arrows is refocused at the end of the echo but the difference due to the coupling is preserved (the handicapped vectors were made slower by the inversion of polarization of ^{13}C).

Without a detailed analysis of product operators, we see that the effect of the chemical shift is removed (the hypothetical arrows showing average direction of vectors of the same color just change the sign), but the final state of the system depends on scalar coupling (the solid and dashed arrows disappeared) but the evolution due to the chemical shift took place (arrows of different colores rotated by different angles $2\Omega_1\tau$). As the effects of scalar coupling are masked, this echo is known as the *decoupling* echo.

We can deduce that the final state of the system is obtained by rotation "about" $2\mathcal{I}_z\mathcal{S}_z$, but not "about" $\mathcal{I}_z$ in the product operator space, and by changing the sign of the resulting coherences as indicated by the vector analysis:

$\hat{\rho}(\mathrm{e}) = \mathcal{I}_t + \kappa_1 \left(c_J\mathcal{I}_y - s_J 2\mathcal{I}_y\mathcal{S}_z\right) - \kappa_2\mathcal{S}_z$

5.5 INEPT

INEPT is an NMR experiment based on the recoupling echo. It differs from the simple echo in two issues:

- The length of the delay τ is set to $1/4J$
- The echo is followed by two 90° pulses, one at the frequency of the excited nucleus – this one must be phase-shifted by 90 ° from the excitation pulse, and one at the frequency of the other nucleus (^{15}N in Fig. 5.2).

With $\tau = 1/4J$, $2\pi\tau = \pi/2$, $c_J = 0$, and $s_J = 0$. Therefore, the density matrix at the end of the echo is
$\hat{\rho}(\mathrm{e}) = \mathcal{I}_t - \kappa_1 (2\mathcal{I}_y\mathcal{S}_z) - \kappa_2\mathcal{S}_z$
$\longrightarrow \mathcal{I}_t + \kappa_1 (2\mathcal{I}_z\mathcal{S}_z) - \kappa_2\mathcal{S}_z$ after the first pulse and
$\longrightarrow \mathcal{I}_t - \kappa_1 (2\mathcal{I}_z\mathcal{S}_y) + \kappa_2\mathcal{S}_y$ after the second pulse.

If the experiment continues by acquisition, the density matrix evolves as

$$\mathcal{I}_t \longrightarrow \mathcal{I}_t \longrightarrow \mathcal{I}_t \tag{5.14}$$

$$-2\mathcal{I}_z\mathcal{S}_y \longrightarrow \begin{cases} -c_1\ 2\mathcal{I}_z\mathcal{S}_y \longrightarrow \begin{cases} -c_1c_J\ 2\mathcal{I}_z\mathcal{S}_y \\ +c_1s_J\ \mathcal{S}_x \end{cases} \\ +s_1\ 2\mathcal{I}_x\mathcal{S}_z \longrightarrow \begin{cases} +s_1c_J\ 2\mathcal{I}_z\mathcal{S}_x \\ +s_1s_J\ \mathcal{S}_y \end{cases} \end{cases} \tag{5.15}$$

$$-\mathcal{S}_y \longrightarrow \begin{cases} -c_2\mathcal{S}_y \longrightarrow \begin{cases} -c_2c_J\ \mathcal{S}_y \\ +c_2s_J\ 2\mathcal{S}_x\mathcal{I}_z \end{cases} \\ +s_2\mathcal{S}_x \longrightarrow \begin{cases} +s_2c_J\ \mathcal{S}_x \\ +s_2s_J\ 2\mathcal{S}_y\mathcal{I}_z \end{cases} \end{cases} \tag{5.16}$$

Both the "blue" coherence $2\mathcal{I}_z\mathcal{S}_y$ and the "green" coherence $\mathcal{S}_y$ evolve into measurable product operators, giving non-zero trace when multiplied by $\mathcal{S}_+$.

After calculating the traces, including relaxation, and applying a phase shift by 90 °, the expected value of M_{2+} evolves as

$$\frac{\kappa_2}{4}\mathrm{e}^{-R_2t}\left(-\mathrm{e}^{-\mathrm{i}(\Omega_2-\pi J)t} + \mathrm{e}^{-\mathrm{i}(\Omega_2+\pi J)t}\right) + \frac{\kappa_1}{4}\mathrm{e}^{-R_2t}\left(\mathrm{e}^{-\mathrm{i}(\Omega_2-\pi J)t} + \mathrm{e}^{-\mathrm{i}(\Omega_2+\pi J)t}\right) \tag{5.17}$$

The real part of the spectrum obtained by Fourier transform is

$$\begin{aligned} &\frac{\mathcal{N}{\gamma_2}^2\hbar^2B_0}{4k_\mathrm{B}T}\left(-\frac{R_2}{R_2^2+(\omega-\Omega_2+\pi J)^2} + \frac{R_2}{R_2^2+(\omega-\Omega_2-\pi J)^2}\right) + \\ &\frac{\mathcal{N}{\gamma_1}^2\hbar^2B_0}{4k_\mathrm{B}T}\left(+\frac{R_2}{R_2^2+(\omega-\Omega_2+\pi J)^2} + \frac{R_2}{R_2^2+(\omega-\Omega_2-\pi J)^2}\right) \end{aligned} \tag{5.18}$$

- The "blue" coherence $2\mathcal{I}_z\mathcal{S}_y$ gives a signal with *opposite phase* of the peaks at $\Omega_2 - \pi J$ and $\Omega_2 + \pi J$. Accordingly, it is called the *anti-phase* coherence.
- The "green" coherence $\mathcal{S}_y$ gives a signal with the *same phase* of the peaks at $\Omega_2 - \pi J$ and $\Omega_2 + \pi J$. Accordingly, it is called the *in-phase* coherence.
- More importantly, the "blue" coherence $2\mathcal{I}_z\mathcal{S}_y$ gives a signal proportional to γ_1^2 while the "green" coherence $\mathcal{S}_y$ gives a signal proportional to γ_2^2. The amplitude of the "green" signal corresponds to the amplitude of a regular 1D ^{15}N spectrum. The "blue" signal "inherited" the amplitude with γ_1^2 from the excited nucleus, proton. In case of ^{1}H and ^{15}N, γ_1 is approximately ten times higher than γ_2. Therefore, the blue signal is two orders of magnitude stronger. This is why this experiment is called *Insensitive Nuclei Enhanced by Polarization Transfer*.
- As described, the "blue" and "green" signals are combined, which results in different heights of the $\Omega_2 - \pi J$ and $\Omega_2 + \pi J$ peaks. The "blue" and "green" signals can be separated if we repeat the measurement twice with the phase of the proton y pulse shifted by 180 °(i.e., with $-y$). It does not affect the "green" signal, but changes the sign of the "blue" signal. If we subtract the spectra, we obtained a pure "blue" signal. This trick - repeating acquisition with different phases - is known as *phase cycling* and is used routinely in NMR spectroscopy to remove unwanted signals.

5.6 Heteronuclear Single-Quantum Correlation (HSQC)

HSQC is a 2D pulse sequence using scalar coupling to correlate frequencies of two magnetic moments with different γ (Fig. 5.3).

- After a 90° pulse at the proton frequency, polarization is transfered to the other nucleus (usually ^{15}N or ^{13}C). The density matrix at the end of the INEPT is $\hat{\rho}(\mathrm{e}) = \mathcal{I}_t - \kappa_1 (2\mathcal{I}_z\mathcal{S}_y) + \kappa_2\mathcal{S}_y$
- During an echo with a decoupling 180° pulse at the proton frequency (red pulse in Fig. 5.3), anti-phase single quantum coherences evolve according to the chemical shift
  $\hat{\rho}(\mathrm{e}) \longrightarrow \mathcal{I}_t + \kappa_1 (\cos(\Omega_2 t_1)2\mathcal{I}_z\mathcal{S}_y - \sin(\Omega_2 t_1)2\mathcal{I}_z\mathcal{S}_x) + \kappa_2 (c_{11}\mathcal{S}_y + s_{11}\mathcal{S}_y)$.
  We assume that the green coherences are discarded by phase cycling, as describe above, and ignore them. Also, we ignore the red term which never evolves to a measurable coherence because it commutes with all Hamiltonians.
- Two 90° pulses convert $2\mathcal{I}_z\mathcal{S}_y$ to $2\mathcal{I}_y\mathcal{S}_z$ and $2\mathcal{I}_z\mathcal{S}_x$ to $2\mathcal{I}_y\mathcal{S}_x$. The magenta operator is a *multiple quantum coherence* (a combination of zero-quantum and double-quantum coherence), which can be converted to a single quantum coherence only by a 90° pulse. Since the pulse sequence does not contain any more 90° pulses and since no multiple-quantum coherence is measurable, we ignore $2\mathcal{I}_y\mathcal{S}_x$.
- The last echo allows the scalar coupling to evolve but refocuses evolution of the scalar coupling. If the delays $\tau = 1/4J$, the measurable components of the density matrix evolve to $-\kappa_1 \cos(\Omega_2 t_1)\mathcal{I}_y$ (rotation "about" $2\mathcal{I}_z\mathcal{S}_z$ by 90° and change of the sign by the last 180° pulse at the proton frequency).
- During acquisition, both chemical shift and scalar coupling evolve in the experiment described in Fig. 5.3. Therefore, we obtain a doublet in the proton dimension of the spectrum. The second dimension is introduced by repeating the measurement with t_1 being incremented. Each increment is measured twice with a different phase of one of the 90° pulses applied to nucleus 2, which provides real (modulated by $\cos(\Omega_2 t_1)$) and imaginary (modulated by $\sin(\Omega_2 t_1)$) component of a complex signal, like in the NOESY experiment. After calculating the trace, including relaxation (with different rates R_2 in the direct and indirect dimensions), phase shift by 90° and Fourier transforms in both t_1 and t_2 dimensions, we obtain a 1D spectrum with peaks at Ω_2 chemical shift in the indirect dimension and a doublet at $\Omega_1 \pm \pi J$ in the direct (proton) dimension. Note that the spitting by $\pm\pi J$ was removed by the red decoupling pulse in the indirect dimension.

5.6.1 Decoupling trains

Splitting of peaks in the direct dimension in spectra recorded by the pulse sequence in Fig. 5.3 is undesirable. On the other hand, we acquire signal in real time and cannot remove the splitting by a decoupling echo. In principle, we can divide the acquisition time into short fragments and apply a 180° pulse at the frequency of nucleus 2 (^{13}C or ^{15}N) in the middle of each such echo. In practice, imperfections of such a long series of echoes, affecting especially magnetic moments with large Ω_2, are significant. However, more sophisticated series of pulses have much better performance. Typical examples of decoupling pulse sequences are

- WALTZ - a series of 90°, 180°, and 270° pulses with phase of 0° (x), or 180° ($-x$), repeating in complex patterns
- DIPSI - a similar series of pulses with non-integer rotation angles
- GARP - computer-optimized sequence of pulses with non-integer rotation angles and phases.

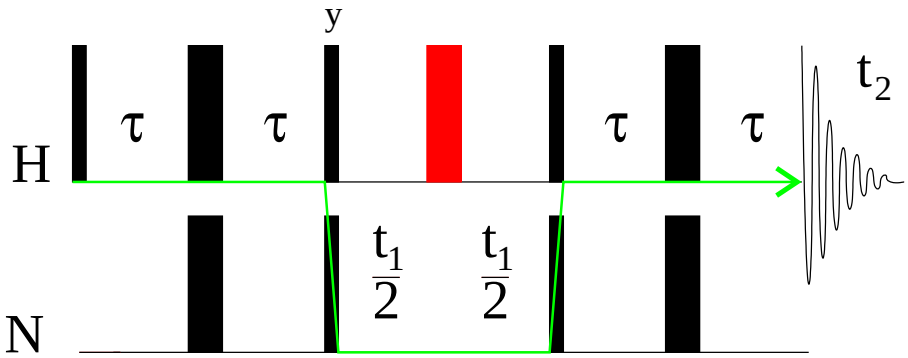

Figure 5.3: ^{1}H,^{15}N HSQC pulse sequence.

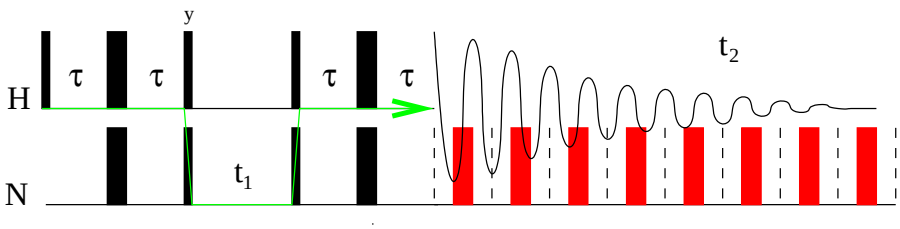

Figure 5.4: Idea of the decoupling in the direct dimension.

5.6.2 Benefits of HSQC

- ^{13}C or ^{15}N frequency measured with *high sensitivity* (higher by $(\gamma_1/\gamma_2)^{5/2}$ than provided by the direct detection)
- expansion to the second dimension and reducing the number of peaks in spectrum (only ^{13}C or ^{15}N-bonded protons and only protonated ^{13}C or ^{15}N nuclei are visible) provides *high resolution*
- ^{1}H-^{13}C and ^{1}H-^{15}N correlation is *important structural information* (which proton is attached to which ^{13}C or ^{15}N)

5.7 Systems with multiple protons - attached proton test (APT

Systems CH_n (C, CH, CH_2, CH_3).

Refocusing echo, but with excitation of ^{13}C (nucleus 2), followed by ^{13}C acquisition with proton decoupling. The ^{13}C operators are labeled $\mathcal{S}_x$, $\mathcal{S}_y$, $\mathcal{S}_z$, relaxation is ignored for the sake of simplicity.

- $\hat{\rho}(\mathrm{a}) = \mathcal{I}_t + \kappa_1 \sum_{j=1}^{n} (\mathcal{I}_{jz}) + \kappa_2 \mathcal{S}_z$
- $\hat{\rho}(\mathrm{b}) = \mathcal{I}_t + \kappa_1 \sum_{j=1}^{n} (\mathcal{I}_{jz}) - \kappa_2 \mathcal{S}_y$
- refocusing echo: evolution of Ω_2 is refocused, scalar coupling evolves for 2τ as $\cos(2\pi j\tau)$ and $\sin(2\pi j\tau)$, nucleus 1 (proton) is never excited (no proton 90° pulse) $\Rightarrow$ only $\mathcal{I}_{jz}$ contributions

- $\hat{\rho}(\mathrm{a}) = \mathcal{I}_t + \kappa_1 \sum_{j=1}^{n} (\mathcal{I}_{jz}) + \kappa_2 \begin{cases} n=0: & \mathcal{S}_y \\ n=1: & c\mathcal{S}_y - s2\mathcal{I}_{1z}\mathcal{S}_x \\ n=2: & c^2\mathcal{S}_y - sc(2\mathcal{I}_{1z}\mathcal{S}_x + 2\mathcal{I}_{2z}\mathcal{S}_x) - s^2 4\mathcal{I}_{1z}\mathcal{I}_{2z}\mathcal{S}_y \\ n=3: & c^3\mathcal{S}_y - sc^2(\mathcal{I}_{1z}\mathcal{S}_x + \mathcal{I}_{2z}\mathcal{S}_x + \mathcal{I}_{3z}\mathcal{S}_x) \\ & -s^2c(4\mathcal{I}_{1z}\mathcal{I}_{2z}\mathcal{S}_y + 4\mathcal{I}_{1z}\mathcal{I}_{3z}\mathcal{S}_y + 4\mathcal{I}_{2z}\mathcal{I}_{3z}\mathcal{S}_y) + s^3 8\mathcal{I}_{1z}\mathcal{I}_{2z}\mathcal{I}_{3z}\mathcal{S}_x \end{cases}$
  where $s = \sin(2\pi J\tau)$ and $c = \cos(2\pi J\tau)$.

- Since decoupling is applied during acquisition, only the $\mathcal{S}_y$ coherences give a measurable signal. They evolve under the influence of chemical shift, exactly like in a one-pulse experiment. If τ is set to $\tau = 2J$, then $c = \cos\pi = -1$. Therefore, signals of C and CH_2 are positive and signals of CH and CH_3 are negative $\Rightarrow$ useful chemical information.

5.8 Homonucler correlation based on scalar coupling (COSY)

We started the discussion of experiments based on scalar couplings with heteronuclear correlations because they are easier to analyze. The basic (and very popular) *homonuclear* experiment is COSY (COrrelated SpectroscopY). Its pulse sequence is very simple, consisting of only two 90° pulses separated by an incremented delay t_1 (which provides the second dimension), but the evolution of the density matrix is relatively complex. Here, we analyze evolution for a pair of interacting nuclei (protons).

- $\hat{\rho}(\mathrm{a}) = \mathcal{I}_t + \kappa(\mathcal{I}_{1z} + \mathcal{I}_{2z})$
  thermal equilibrium, the matrices are different than for the noninteracting spin, but the constant is the same.

- $\hat{\rho}(\mathrm{b}) = \mathcal{I}_t + \kappa(-\mathcal{I}_{1y} - \mathcal{I}_{2y})$
  90° pulse, see the one-pulse experiment

- $\hat{\rho}(\mathrm{c}) = \mathcal{I}_t$
  $+\kappa(-c_{11}c_{J1}\mathcal{I}_{1y} + s_{11}c_{J1}\mathcal{I}_{1x} + c_{11}s_{J1}2\mathcal{I}_{1x}I_{2z} + s_{11}s_{J1}2\mathcal{I}_{1y}I_{2z})$
  $+\kappa(-c_{21}c_{J1}\mathcal{I}_{2y} + s_{21}c_{J1}\mathcal{I}_{2x} + c_{21}s_{J1}2\mathcal{I}_{1z}I_{2x} + s_{21}s_{J1}2\mathcal{I}_{1z}I_{2y})$,
  where $c_{i1} = \cos(\Omega_i t_1)$, $s_{i1} = \sin(\Omega_i t_1)$, $c_{J1} = \cos(\pi J t_1)$, and $s_{J1} = \sin(\pi J t_1)$ – evolution of the chemical shift and coupling.

- The second 90° pulse creates the following coherences $\hat{\rho}(\mathrm{d}) = \mathcal{I}_t$
  $+\kappa(-c_{11}c_{J1}\mathcal{I}_{1z} + \boxed{s_{11}c_{J1}\mathcal{I}_{1x}} - c_{11}s_{J1}2\mathcal{I}_{1x}I_{2y} - \boxed{s_{11}s_{J1}2\mathcal{I}_{1z}I_{2y}})$
  $+\kappa(-c_{21}c_{J1}\mathcal{I}_{2z} + \boxed{s_{21}c_{J1}\mathcal{I}_{2x}} - c_{21}s_{J1}2\mathcal{I}_{1y}I_{2x} - \boxed{s_{21}s_{J1}2\mathcal{I}_{1y}I_{2z}})$.
  The red terms contain polarization operators, not coherences, they do not contribute to the signal. The green terms contain in-phase single-quantum coherences, only they give non-zero trace when multiplied with $\hat{M}_+ \propto (\mathcal{I}_{1x} + \mathrm{i}\mathcal{I}_{1y} + \mathcal{I}_{2x} + \mathrm{i}\mathcal{I}_{2y})$. The blue terms contain anti-phase single-quantum coherences, they do not contribute to the signal directly, but they evolve into in-phase coherences during acquisition due to the scalar coupling. The magenta terms contain multiple-quantum coherences. They do not contribute to the signal, but can be converted to single-quantum coherences by 90° pulses. Such pulses are not applied in the discussed pulse sequence, but are used in some versions of the experiment.

- The terms in black frames evolve with the chemical shift of the first nucleus during acquisition:
  $\boxed{s_{11}c_{J1}\mathcal{I}_{1x} \rightarrow s_{11}c_{J1}c_{12}c_{J2}\mathcal{I}_{1x} + s_{11}c_{J1}s_{12}c_{J2}\mathcal{I}_{1y} + \text{unmeasurable anti-phase coherences}}$
  $\boxed{-s_{21}s_{J1}2\mathcal{I}_{1y}\mathcal{I}_{2z} \rightarrow s_{21}s_{J1}c_{12}s_{J2}\mathcal{I}_{1x}s_{21}s_{J1}s_{12}s_{J2}\mathcal{I}_{1y} + \text{unmeasurable anti-phase coherences}}$,

where $c_{i2} = \cos(\Omega_i t_2)$, $s_{i2} = \sin(\Omega_i t_2)$, $c_{J2} = \cos(\pi J t_2)$, and $s_{J2} = \sin(\pi J t_2)$. Using the following trigonometric relations

$$c_{ik}c_{iJ} = \frac{c_{ik}^- + c_{ik}^+}{2} \quad s_{ik}s_{iJ} = \frac{c_{ik}^- - c_{ik}^+}{2} \quad c_{ik}s_{iJ} = \frac{-s_{ik}^- + s_{ik}^+}{2} \quad s_{ik}c_{iJ} = \frac{s_{ik}^- + s_{ik}^+}{2}, \tag{5.19}$$

where $c_{ik}^\pm = \cos((\Omega_i \pm \pi J)t_k)$ and $s_{ik}^\pm = \sin((\Omega_i \pm \pi J)t_k)$, the terms contributing to the signal can be written as

$$\left(\underbrace{(s_{11}^- + s_{11}^+)(c_{12}^- + c_{12}^+)}_{[\Omega_1,\Omega_1]} + \underbrace{(s_{21}^- + s_{21}^+)(c_{12}^- + c_{12}^+)}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1x}$$
$$+\left(\underbrace{(s_{11}^- + s_{11}^+)(c_{12}^- + c_{12}^+)}_{[\Omega_1,\Omega_1]} + \underbrace{(s_{21}^- + s_{21}^+)(c_{12}^- + c_{12}^+)}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1y}$$

The first and second line show coherences providing the real and imaginary component of the complex signal acquired in the direct dimension (t_2). The imaginary signal in the indirect dimension is obtained by repeating acquisition for each increment of t_1 with a different phase (shifted by 90 °).

- The green component of the signal evolves with the same chemical shift in both dimensions, providing *diagonal* signal (at frequencies $[\Omega_1, \Omega_1]$ in the 2D spectrum). The blue (originally anti-phase) component of the signal also evolves with Ω_1 in the direct dimension, but with Ω_2. It provides *off-diagonal* signal, a *cross-peak* at frequencies $[\Omega_1, \Omega_1]$ in the 2D spectrum. Note that the blue and green components have the phase different by 90 °. Therefore, either diagonal peaks or cross-peaks have the undesirable dispersion shape (it is not possible to phase both diagonal peaks or cross-peaks, they always have phases differing by 90 °). Typically, the spectrum is phased so that the cross-peaks have a nice absorptive shape because they carry a useful chemical information - they show which protons are connected by 2 or 3 covalent bonds.

- The diagonal peaks are not interesting, but their dispersive shape may obscure cross-peaks close to the diagonal. The problem with the phase can be solved if one more 90 ° pulse is introduced. Such a pulse converts the magenta multi-quantum coherences to anti-phase single-quantum coherences, which evolve into the measurable signal. The point is that other coherences can be removed by phase cycling, which results in a spectrum with a pure phase.[1] This version of the experiment is known as *double-quantum filetered* COSY (DQF-COSY). Its disadvantage is a lower sensitivity – we lose a half of the signal.

- Also, note that each peak is split into doublets in both dimensions. More complex multiplets are obtained if more than two nuclei are coupled. The distance of peaks in the multiplets is given by the interaction constant J. In the case of nuclei connected by three bonds, J depends on the torsion angle defined by these three bonds. So, COSY spectra can be used to determine torsion angles in the molecule.

- The terms in gray frames evolve with the chemical shift of the second nucleus during acquisition as $\boxed{s_{21}c_{J1}\mathcal{I}_{1x} \rightarrow s_{21}c_{J1}c_{12}c_{J2}\mathcal{I}_{1x} + s_{21}c_{J1}s_{12}c_{J2}\mathcal{I}_{1y} + \text{ unmeasurable anti-phase coherences}}$ $\boxed{-s_{11}s_{J1}2\mathcal{I}_{1y}\mathcal{I}_{2z} \rightarrow s_{11}s_{J1}c_{12}s_{J2}\mathcal{I}_{1x}s_{11}s_{J1}s_{12}s_{J2}\mathcal{I}_{1y} + \text{ unmeasurable anti-phase coherences}}$ and give a similar type of signal for the other nucleus:

[1] Phase cycling can distinguish multi-quantum coherences from single-quantum ones, it cannot distinguish anti-phase single quantum coherences from in-phase single quantum coherences.

$$\left(\underbrace{(s_{21}^{-}+s_{21}^{+})(c_{22}^{-}+c_{22}^{+})}_{[\Omega_1,\Omega_1]}+\underbrace{(s_{11}^{-}+s_{11}^{+})(c_{22}^{-}+c_{22}^{+})}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1x}$$
$$+\left(\underbrace{(s_{21}^{-}+s_{21}^{+})(c_{22}^{-}+c_{22}^{+})}_{[\Omega_1,\Omega_1]}+\underbrace{(s_{11}^{-}+s_{11}^{+})(c_{22}^{-}+c_{22}^{+})}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1y}$$