C5320 Theoretical Concepts of NMR

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Part I

Classical Introduction

Chapter 1

Classical electromagnetism

Literature: Discussed in[1] L2 and B11, with mathematical background in B4.

1.1 Electric field, electric charge, electric dipole

Objects having a property known as the *electric charge* (Q) experience forces ($\vec{F}$) described as the *electric field*. Since the force depends on both charge and field, a quantity $\vec{E} = \vec{F}/Q$ known as *electric intensity* has been introduced:

$$\vec{F} = Q\vec{E}. \tag{1.1}$$

Field lines are often used to visualize the fields: direction of the line shows the direction of $\vec{E}$, density of the lines describes the size of $\vec{E}$ ($|E|$). A homogeneous static electric field is described by straight parallel field lines.

Two point electric charges of the same size and opposite sign ($+Q$ and $-Q$) separated by a distance r constitute an *electric dipole*. Electric dipoles in a homogeneous static electric field experience a *moment of force*, or *torque* $\vec{\tau}$:

$$\vec{\tau} = \vec{r} \times \vec{F} = \vec{r} \times Q\vec{E} = Q\vec{r} \times \vec{E} = \vec{\mu}_{\mathrm{e}} \times \vec{E}, \tag{1.2}$$

where $\vec{\mu}_{\mathrm{e}}$ is the *electric dipole moment*.

$$\vec{\tau} = \vec{\mu}_{\mathrm{e}} \times \vec{E}, \tag{1.3}$$

is another possible definition of $\vec{E}$.

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[1] The references consist of a letter specifying the textbook and a number specifying the section. The letters refer to the following books: **B**, Brown: Essential mathematics for NMR and MRI spectroscopists, Royal Society of Chemistry 2017; **C**, Cavanagh et al., Protein NMR spectroscopy, 2nd. ed., Academic Press 2006; **K**, Keeler, Understanding NMR spectroscopy, 2nd. ed., Wiley 2010; **L** Levitt: Spin dynamics, 2nd. ed., Wiley 2008.

Potential energy[2] of the electric dipole can be calculated easily as a sum of potential energies of the individual charges. Potential energy is defined as the work done by moving the charge from a position (1) to a reference position (0). If we choose a coordinate system so that the z-axis is parallel with $\vec{E}$, the dipole is in the yz-plane, and the origin is in the middle of the distance r between the charges, then the force acts only in the z-direction ($F_z = |\vec{F}| = Q|\vec{E}|$ for the positive charge and $F_z = -|\vec{F}| = -Q|\vec{E}|$ for the negative charge). Therefore, it is sufficient to follow only how the z-coordinates of the charges change because changes of other coordinates do not change the energy. In the chosen coordinate system, z-coordinates of the charges are always opposite, e.g., the reference value $z_{-,0}$ of the negative charge is equal to minus the reference z coordinate of the positive charge ($z_{+,0}$). The natural choice of the reference position is that the z coordinates are the same for both charges, which requires $z_{+,0} = z_{-,0} = 0$. Changing the z coordinate of the positive charge from $z_{+,0} = 0$ to $z_{+,1} \equiv z$ results in a work

$$Q|\vec{E}|(z_{+,0} - z_{+,1}) = -Q|\vec{E}|z. \tag{1.4}$$

Changing the z coordinate of the positive charge from $z_{-,0} = 0$ to $z_{-,1} = -z_{+,1}$ results in a work

$$-Q|\vec{E}|z_{-,0} - (z_{-,1}) = -Q|\vec{E}|z. \tag{1.5}$$

Adding the works

$$E = -2Q|\vec{E}|z = -2Q|\vec{E}|\frac{r}{2}\cos\theta = -\vec{\mu}_{\mathrm{e}} \cdot \vec{E}, \tag{1.6}$$

where θ is the angle between $\vec{E}$ and $\vec{\mu}_{\mathrm{e}}$.

Equivalently, the potential energy can be defined as the work done by the torque $\vec{\tau}$ on $\vec{\mu}_{\mathrm{e}}$ when rotating it from the reference orientation to the orientation described by the angle θ (between $\vec{E}$ and $\vec{\mu}_{\mathrm{e}}$). The reference angle for $z_{+,0} = z_{-,0} = 0$ is $\pi/2$, therefore,

$$E = \int\limits_{\frac{\pi}{2}}^{\theta} |\vec{\tau}|\mathrm{d}\theta' = \int\limits_{\frac{\pi}{2}}^{\theta} |\vec{\mu}_{\mathrm{e}}||\vec{E}|\sin\theta'\mathrm{d}\theta' = -|\vec{\mu}_{\mathrm{e}}||\vec{E}|\cos\theta = -\vec{\mu}_{\mathrm{e}} \cdot \vec{E}. \tag{1.7}$$

Potential energy of an electric dipole is

$$E = -\vec{\mu}_{\mathrm{e}} \cdot \vec{E}. \tag{1.8}$$

1.2 Magnetic field and magnetic dipole

There is no "magnetic charge", but magnetic moments exist:

$$\vec{\tau} = \vec{\mu}_{\mathrm{m}} \times \vec{B}, \tag{1.9}$$

where $\vec{\mu}_{\mathrm{m}}$ is the *magnetic dipole moment* (because this course is about magnetic resonance, we will write simple $\vec{\mu}$). This is *the definition* of the *magnetic induction* $\vec{B}$ as a quantity describing magnetic field. As a consequence, potential energy of a magnetic dipole can be derived as described by Eq. 1.7 for the electric dipole.

Potential energy of a magnetic moment $\vec{\mu}$ is

$$E = -\vec{\mu} \cdot \vec{B}. \tag{1.10}$$

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[2] Do not get confused: E (scalar) is the energy and $\vec{E}$ (vector) is electric intensity.

1.3 Origin of the electric field

The source of the electric field is the *electric charge.* The charge (i) feels (a surrounding) field and (ii) makes (its own) field. Charge at rest is a source of a static electric field. Parallel plates with homogeneous distribution of charges (a capacitor) are a source of a homogeneous static electric field.

Force between charges is described by the *Coulomb's law.* The force between two charges is given by

$$\vec{F} = \frac{1}{4\pi\epsilon_0}\frac{Q_1Q_2}{r^2}\frac{\vec{r}}{|r|}, \tag{1.11}$$

where $\epsilon_0 = 8.854187817 \times 10^{-12}\,\mathrm{F\,m^{-1}}$ is the vacuum electric permittivity. Consequently, the electric intensity generated by a point charge is

$$\vec{E} = \frac{1}{4\pi\epsilon_0}\frac{Q}{r^2}\frac{\vec{r}}{|r|}. \tag{1.12}$$

The electric intensity generated by a charge density ρ is

$$\vec{E} = \frac{1}{4\pi\epsilon_0}\int\limits_V \mathrm{d}V\frac{\rho}{r^2}\frac{\vec{r}}{|r|} \tag{1.13}$$

Coulomb's law implies that electric fields lines of a resting charge

1. are going out of the charge (diverge), i.e., the static electric field has a source (the charge)

2. are not curved (do not have curl or rotation), i.e., the static electric field does not circulate

This can been written mathematically in the form of *Maxwell equations*[3] :

$$\mathrm{div}\ \vec{E} = \frac{\rho}{\epsilon_0}, \tag{1.14}$$

$$\mathrm{rot}\ \vec{E} = 0. \tag{1.15}$$

where div $\vec{E}$ is a scalar equal to $\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z}$ and rot $\vec{E}$ is a vector with the x, y, z components equal to $\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z}, \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x}, \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y}$, respectively. These expressions can be written in a much more compact form, if we introduce a vector operator $\vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$. Using this formalism, the Maxwell equation have the form

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[3] The first equation is often written using *electric induction* $\vec{D} = \epsilon_0\vec{E}$ as div $\vec{D} = \rho$.

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\epsilon_0}, \tag{1.16}$$

$$\vec{\nabla} \times \vec{E} = 0. \tag{1.17}$$

1.4 Origin of the magnetic field

Electric charge at rest does not generate a magnetic field, but a *moving* charge does. The magnetic force is a *relativistic effect* (consequence of the contraction of distances in the direction of the motion, described by Lorentz transformation).[4] Magnetic field of a moving point charge is moving with the charge. Constant *electric current* generates a stationary magnetic field. Constant electric current in an *ideal solenoid* generates a *homogeneous* stationary magnetic field inside the solenoid.

Magnetic induction generated by a current density $\vec{j}$ (*Biot-Savart law*):

$$\vec{B} = \frac{1}{4\pi\epsilon_0 c^2} \int\limits_V \mathrm{d}V \frac{\vec{j}}{r^2} \times \frac{\vec{r}}{|r|} = \frac{\mu_0}{4\pi} \int\limits_V \mathrm{d}V \frac{\vec{j}}{r^2} \times \frac{\vec{r}}{|r|} \tag{1.18}$$

Biot-Savart law implies that magnetic field lines of a constant current in a straight wire

1. do not diverge, i.e., the static magnetic field does not have a source
2. make closed loops around the wire (have curl or rotation), i.e., the magnetic field circulates around the wire

This can been written mathematically in the form of *Maxwell equations*[5]:

$$\vec{\nabla} \cdot \vec{B} = 0, \tag{1.19}$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{j}. \tag{1.20}$$

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[4] A charge close to a very long straight wire which is uniformly charged experiences an electrical force $F_\perp$ in the direction perpendicular to the wire. If the charges in the wire move with a velocity v_0 and the charge close to the wire moves along the wire with a velocity v_1, the perpendicular force changes to $F_\perp(1 - \frac{v_0 v_1}{c^2})$, were c is the speed of light in vacuum. The modifying factor is clearly relativistic (B11.5).

[5] The second equation is often written using *magnetic intensity* $\vec{H} = \vec{B}/\mu_0$ as $\vec{\nabla} \times \vec{H} = \vec{j}$.

1.5 Current loop as a magnetic dipole

Now we derive what is the magnetic dipole of a circular loop with an electric current.

The magnetic moment is defined by the torque $\vec{\tau}$ it experiences in a magnetic field $\vec{B}$ (Eq. 1.9):

$$\vec{\tau} = \vec{\mu} \times \vec{B}, \tag{1.21}$$

Therefore, we can calculate the magnetic moment of a current loop if we place it in a magnetic field $\vec{B}$. Let us first define the geometry of our setup. Let the axis z is the normal of the loop and let $\vec{B}$ is in the xz plane ($\Rightarrow B_y = 0$). The vector product in Eq. 1.9 then simplifies to

$$\begin{aligned} \tau_x &= \mu_y B_z, & (1.22)\\ \tau_y &= \mu_z B_x - \mu_x B_z, & (1.23)\\ \tau_z &= -\mu_y B_x. & (1.24) \end{aligned}$$

As the second step, we describe the electric current in the loop. The electric current is a motion of the electric charge. We describe the current as a charge Q homogeneously distributed in a ring (loop) of a mass m which rotates with a circumferential speed v. Then, each element of the loop of a infinitesimally small length $\mathrm{d}l = r\mathrm{d}\varphi$ contains the same fraction of the charge $\mathrm{d}Q$, moving with the velocity $\vec{v}$. The direction of the vector $\vec{v}$ is tangent to the loop and the amount of the charge per the length element is $Q/2\pi r$. The motion of the charge element $\mathrm{d}Q$ can be described, as any circular motion, by the *angular momentum*

$$\vec{L} = \vec{r} \times \vec{p} = m(\vec{r} \times \vec{v}), \tag{1.25}$$

where r is the vector defining the position of the charge element $\mathrm{d}Q$. In our geometry, $\vec{r}$ is radial and therefore always perpendicular to $\vec{v}$. Since both $\vec{r}$ and $\vec{v}$ are in the xy plane, $\vec{L}$ must have the same direction as the normal of the plane:

$$\begin{aligned} L_x &= 0, & (1.26)\\ L_y &= 0, & (1.27)\\ L_z &= mrv. & (1.28) \end{aligned}$$

As the third step, we examine forces acting on $\mathrm{d}Q$. The force acting on a moving charge in a magnetic field (the Lorentz force) is equal to

$$\vec{F} = Q(\vec{E} + \vec{v} \times \vec{B}), \tag{1.29}$$

but we are now only interested in the magnetic component $\vec{F} = Q(\vec{v} \times \vec{B})$. The force acting on a single charge element $\mathrm{d}Q$ is

$$\mathrm{d}\vec{F} = \mathrm{d}Q(\vec{v} \times \vec{B}) = \frac{Q}{2\pi r}\mathrm{d}l(\vec{v} \times \vec{B}) = \frac{Q}{2\pi}(\vec{v} \times \vec{B})\mathrm{d}\varphi. \tag{1.30}$$

The key step in our derivation is the definition of the torque

$$\vec{\tau} = \vec{r} \times \vec{F} = Q\vec{r} \times (\vec{v} \times \vec{B}), \tag{1.31}$$

which connects our analysis of the circular motion with the definition of $\vec{\mu}$ (Eq. 1.9). The torque acting on a charge element is

$$\mathrm{d}\vec{\tau} = \vec{r} \times \mathrm{d}\vec{F} = \frac{Q}{2\pi}\vec{r} \times (\vec{v} \times \vec{B})\mathrm{d}\varphi = \frac{Q}{2\pi}\left(\vec{v}(\vec{r} \cdot \vec{B}) - \vec{B}\underbrace{(\vec{r} \cdot \vec{v})}_{=0}\right)\mathrm{d}\varphi = \frac{Q}{2\pi}(\vec{r} \cdot \vec{B})\vec{v}\mathrm{d}\varphi. \tag{1.32}$$

where a useful vector identity $\vec{a} \times (\vec{b} \times \vec{c}) = (\vec{a} \cdot \vec{c})\vec{b} - (\vec{a} \cdot \vec{b})\vec{c}$ helped us to simplify the equation because $\vec{r} \perp \vec{v}$). Eq. 1.32 tells us that the torque has the same direction as the velocity $\vec{v}$ ($\vec{v}$ is the only vector on the right-hand side because $\vec{r} \cdot \vec{B}$ is a scalar). In our coordinate frame, $v_x = -v\sin\varphi$, $v_y = v\cos\varphi$, $v_z = 0$, and $\vec{r} \cdot \vec{B} = B_x r \cos\varphi$. Therefore, we can calculate the components of the overall torque $\vec{\tau}$ as

$$\tau_x = -\frac{Qrv}{2\pi}B_x\int\limits_0^{2\pi}\sin\varphi\cos\varphi\mathrm{d}\varphi = -\frac{Qrv}{4\pi}B_x\int\limits_0^{2\pi}\sin(2\varphi)\mathrm{d}\varphi = 0, \tag{1.33}$$

$$\tau_y = \frac{Qrv}{2\pi}B_x\int\limits_0^{2\pi}\cos^2\varphi\mathrm{d}\varphi = \frac{Qrv}{4\pi}B_x\int\limits_0^{2\pi}(1+\cos(2\varphi))\mathrm{d}\varphi = \frac{Qrv}{2}B_x, \tag{1.34}$$

$$\tau_z = 0. \tag{1.35}$$

Comparison with Eqs. 1.22–1.24 immediately shows that

$$\mu_x = 0, \tag{1.36}$$

$$\mu_y = 0, \tag{1.37}$$

$$\mu_z = \frac{Qrv}{2} \tag{1.38}$$

and comparison with Eqs. 1.26–1.28 reveals that the magnetic dipole moment of the current loop is closely related to the angular momentum $\vec{L} = \vec{r}\times m\vec{v}$:

$$\vec{\mu} = \frac{Q}{2m}\vec{L}. \tag{1.39}$$

We have derived that the magnetic moment of a current loop is proportional the angular momentum of the circulating charge. The classical theory does not explain why particles like electrons or nuclei have their own magnetic moments, even when they do not move in circles (because the classical theory does not explain why such particles have their own angular momenta). However, if we take the nuclear magnetic moment as a fact (or if we obtain it using a better theory), the classical results are useful. It can be shown that the magnetic moment is *always* proportional to the angular momentum[6], but the proportionality constant is not always $Q/2m$; it is difficult to obtain for nuclei.

Magnetic dipolar moment $\vec{\mu}$ is proportional to the angular momentum $\vec{L}$

$$\vec{\mu} = \gamma\vec{L}, \tag{1.40}$$

where γ is known as the *magnetogyric ratio.*

1.6 Precession

Magnetic dipole in a static homogeneous magnetic field does not adopt the energetically most favored orientation (with the same direction of $\vec{\mu}$ as $\vec{B}$), but rotates around $\vec{B}$ without changing the angle between $\vec{\mu}$ and $\vec{B}$. This motion on a cone is known as *precession.*

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[6] A consequence of the rotational symmetry of space described mathematically by the Wigner-Eckart theorem.

This is not a result of quantum mechanics, but a classical effect – riding a bicycle is based on the same effect.[7] We can use another example of an object with an angular momentum in the gravitational field, the spinning top, to derive the frequency of the precession.[8]

The position of the center of the mass is given by vector $\vec{r}$ ($\parallel \vec{L}$), described by constant distance $|r|$ and inclination ϑ and by the changing azimuth φ. The gravitational force $\vec{F}$ points down, the torque is horizontal ($\vec{\tau} = \vec{r} \times \vec{F}$). What is the change of $\vec{L}$?

$$\frac{\mathrm{d}\vec{L}}{\mathrm{d}t} = m\frac{\mathrm{d}(\vec{r}\times\vec{v})}{\mathrm{d}t} = m\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\times\vec{v} + m\vec{r}\times\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = m\underbrace{(\vec{v}\times\vec{v})}_{0} + r\times m\vec{a} = r\times\vec{F} = \vec{\tau}. \tag{1.41}$$

Rotation of $\vec{L}$ can be described using the angular frequency $\vec{\omega}$ (its magnitude is the speed of the rotation in radians per second and its direction is the axis of the rotation):

$$\frac{\mathrm{d}\vec{L}}{\mathrm{d}t} = \vec{\omega}\times\vec{L}. \tag{1.42}$$

In the case of a magnetic field,

$$\vec{\tau} = \vec{\mu}\times\vec{B} = \gamma\vec{L}\times\vec{B} = -\gamma\vec{B}\times\vec{L}. \tag{1.43}$$

Comparison with Eq. 1.42 immediately shows that $\vec{\omega} = -\gamma\vec{B}$.

Angular frequency of the precession of a magnetic dipolar momentum $\vec{\mu}$ in a magnetic field $\vec{B}$ is

$$\vec{\omega} = -\gamma\vec{B}. \tag{1.44}$$

1.7 Electrodynamics and magnetodynamics

Similarly to the electric charge, the magnetic dipole (i) feels the surrounding magnetic field and (ii) generates its own magnetic field. The magnetic field generated by a precessing magnetic dipole is not stationary, it varies. To describe variable fields, the Maxwell equations describing rotation must be modified[9]:

$$\vec{\nabla}\times\vec{E} = -\frac{\mathrm{d}\vec{B}}{\mathrm{d}t}, \tag{1.45}$$

$$\vec{\nabla}\times\vec{B} = \frac{1}{c^2}\frac{\mathrm{d}\vec{E}}{\mathrm{d}t} + \mu_0\vec{j}. \tag{1.46}$$

Note that electric and magnetic fields are coupled in the dynamic equations. Not only electric currents current, but also temporal variation of $\vec{E}$ induces circulation of $\vec{B}$, and circulation of $\vec{E}$ is possible if $\vec{B}$ varies. This has many important consequences: it

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[7] If you sit on a bike which does not move forward, gravity soon pulls you down to the ground. But if the bike has a certain speed and you lean to one side, you do not fall down, you just turn a corner.

[8] A qualitative discussion of precession using the spinning top and riding a bicycle is presented in L2.4–L2.5.

[9] The second equation can be written as $\vec{\nabla}\times\vec{H} = \frac{\mathrm{d}\vec{D}}{\mathrm{d}t} + \vec{j}$.

explains electromagnetic waves in vacuum and has numerous fundamental applications in electrical engineering, including those used in NMR spectroscopy.

Eq. 1.45 shows us how the frequency of the precession motion can be measured. A magnetic dipole in a magnetic field $\vec{B}_0$ generates a magnetic field $\vec{B}'$ with the component $\parallel \vec{B}_0$ constant and the component $\perp \vec{B}_0$ rotating around $\vec{B}_0$. If we place a loop of wire next to the precessing dipole, with the axis of the loop perpendicular to the axis of precession, the rotating component of $\vec{B}'$ induces circulation of $\vec{E}$ which creates a measurable oscillating electromotoric force (voltage) in the loop. As a consequence, an oscillating electric current flows in the loop (L2.8).

We can use a simple example to analyze the induced voltage quantitatively. This voltage (the electromotoric force) is an integral of the electric intensity along the detector loop. Stokes' theorem (see B9) allows us to calculate such integral from Eq. 1.45.

$$\oint_L \vec{E}\mathrm{d}\vec{l} = -\int_S \frac{\partial \vec{B}}{\partial t}\mathrm{d}\vec{S} = \frac{\partial \vec{B}}{\partial t}S, \tag{1.47}$$

where S is the area of the loop. If the distance r of the magnetic moment from the detector is much larger than the size of the loop, the magnetic induction of a field which is generated by a magnetic moment $\vec{\mu}$ rotating in a plane perpendicular to the detector loop and which crosses the loop (let us call it B_x) is[10]

$$B_x = \frac{\mu_0}{4\pi}\frac{2\mu_x}{r^3}. \tag{1.48}$$

As $\vec{\mu}$ rotates with the angular frequency ω, $\mu_x = |\mu|\cos(\omega t)$, and

$$\frac{\partial B_x}{\partial t} = -\frac{\mu_0}{4\pi}\frac{2}{r^3}|\mu|\omega\sin(\omega t). \tag{1.49}$$

Therefore, the oscillating induced voltage is

$$\oint_L \vec{E}\mathrm{d}\vec{l} = \frac{\mu_0}{4\pi}\frac{2|\mu|S}{r^3}\omega\sin(\omega t). \tag{1.50}$$

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[10] We describe the field generated by a magnetic moment in more detail later in Section 9.1 when we analyze mutual interactions of magnetic moments of nuclei.

Chapter 2

Diffusion

2.1 Translational diffusion

Diffusion can be viewed as a result of collisions of the observed molecule with other molecules. Collisions change position of the molecule is space (cause *translation*) and orientation of the molecule (cause *rotation*). *Rotational diffusion* is important for NMR relaxation. *Translational diffusion* influences NMR experiments only if the magnetic filed is inhomogeneous. Translational diffusion can be described as a random walk in a three-dimensional space, rotational diffusion can be described as a random walk on a surface of a sphere. Although we are primarily interested in relaxation and we do not discuss magnetic field inhomogeneity at this moment, we start our discussion with the random walk in a three-dimensional space because the random walk on a surface of a sphere is just a special case of the general walk in three directions.

We start with several definitions. Let us assume that the position of our molecule is described by coordinates x, y, z and its orientation is described by angles φ, ϑ, χ.

- Probability that the molecule is inside a cubic box of a volume $\Delta V = \Delta x \Delta y \Delta z$ centered around x, y, z is

  $$P(x,y,z,t,\Delta x,\Delta y,\Delta z) = \int\limits_{x-\frac{\Delta x}{2}}^{x+\frac{\Delta x}{2}} \int\limits_{y-\frac{\Delta y}{2}}^{y+\frac{\Delta y}{2}} \int\limits_{z-\frac{\Delta z}{2}}^{z+\frac{\Delta z}{2}} \rho(x,y,z,t)\mathrm{d}x\mathrm{d}y\mathrm{d}z,$$

  where $\rho(x,y,z,t)$ is *probability density* at x, y, z, corresponding to local concentration in a macroscopic picture. If the box is small enough so that $\rho(x,y,z,t)$ does not change significantly inside the box, the equation with the triple integral can be simplified to

  $$P(x,y,z,t,\Delta x,\Delta y,\Delta z) = \rho(x,y,z,t)\Delta V.$$

- Probability that the molecule crosses one side of the box centered around x, y, z and jumps into the box centered around $x + \Delta x, y, z$ during a time interval δt is proportional to the area of the side between boxes centered around x, y, z and around $x + \Delta x, y, z$. This area is equal to $\Delta y \Delta z = \Delta V/\Delta x$ and the probability of jumping from the box centered around x, y, z to the box centered around $x + \Delta x, y, z$ can be written as

  $$P(x \to x+\Delta x; x,y,z,t,\Delta x,\Delta y,\Delta z,\Delta t) = \Phi_{x\to x+\Delta x}\Delta y \Delta z = \Phi_{x\to x+\Delta x}\Delta V/\Delta x,$$

  where $\Phi_{x\to x+\Delta x}$ is the *flux* from the box centered around x, y, z to the box centered around $x + \Delta x, y, z$ (per unit area). The corresponding *probability density* is

  $$\rho(x \to x+\Delta x; x,y,z,t,\Delta t) = P(x \to x+\Delta x; x,y,z,t,\Delta x,\Delta y,\Delta z,\Delta t)/\Delta V = \Phi_{x\to x+\Delta x}/\Delta x.$$

  The probability of jumping to the box centered around $x + \Delta x, y, z$ is also proportional to the probability that the molecule is inside the box centered around x, y, z (equal to $\rho(x,y,z,t)\Delta V$ if the box is small enough). If the probability of escaping the box is the same in all directions,

  $$\rho(x \to x+\Delta x; x,y,z,t,\Delta t) = \xi\rho(x,y,z,t),$$

$$\rho(y \to y + \Delta y; x, y, z, t, \Delta t) = \xi \rho(x, y, z, t),$$

$$\rho(z \to z + \Delta z; x, y, z, t, \Delta t) = \xi \rho(x, y, z, t),$$

where ξ is a proportionality constant describing frequency of crossing a side of a box (per unit volume and including the physical description of the collisions).

- The *net flux* in the x direction is given by

  $$\Phi_x = \Phi_{x \to x+\Delta x} - \Phi_{x+\Delta x \to x} = \xi \Delta x(\rho(x, y, z, t) - \rho(x + \Delta x, y, z, t)) = -\xi \Delta x \Delta \rho = -\xi (\Delta x)^2 \frac{\partial \rho}{\partial x} = -D^{\mathrm{tr}} \frac{\partial \rho}{\partial x},$$

  where $D^{\mathrm{tr}} = \xi (\Delta x)^2$ is the *translational diffusion coefficient.*

- The net flux in all directions is

  $$\vec{\Phi} = -D^{\mathrm{tr}} \vec{\nabla} \rho,$$

  which is *the first Fick's law.*

- The *continuity equation*

  $$\int_V \frac{\partial \rho}{\partial t} \mathrm{d}V + \oiint_S \vec{\Phi} \mathrm{d}S = 0$$

  states that any time change of probability that the molecule is in a volume V is due to the total flux through a surface S enclosing the volume V (molecules are not created or annihilated). Using the divergence theorem,

  $$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{\Phi} = \frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \left(-D^{\mathrm{tr}} \vec{\nabla} \rho\right) \quad \Rightarrow \quad \frac{\partial \rho}{\partial t} = D^{\mathrm{tr}} \nabla^2 \rho,$$

  which is *the second Fick's law.*

- If the diffusion is not isotropic, the diffusion coefficient is replaced by a diffusion tensor. If we define a coordinate frame so that the diffusion tensor is represented by a diagonal matrix with elements $D^{\mathrm{tr}}_{xx}, D^{\mathrm{tr}}_{yy}, D^{\mathrm{tr}}_{zz}$, the second Fick's law has the following form:

  $$\frac{\partial \rho}{\partial t} = D^{\mathrm{tr}}_{xx} \frac{\partial}{\partial x} \frac{\partial \rho}{\partial x} + D^{\mathrm{tr}}_{yy} \frac{\partial}{\partial y} \frac{\partial \rho}{\partial y} + D^{\mathrm{tr}}_{zz} \frac{\partial}{\partial z} \frac{\partial \rho}{\partial z} = \left(D^{\mathrm{tr}}_{xx} \frac{\partial^2}{\partial x^2} + D^{\mathrm{tr}}_{yy} \frac{\partial^2}{\partial y^2} + D^{\mathrm{tr}}_{zz} \frac{\partial^2}{\partial z^2}\right) \rho.$$

2.2 Isotropic rotational diffusion

Isotropic rotational diffusion can be viewed as random motions of a vector describing orientation of the molecule. Such motions are equivalent to a random wandering of a point particle on a surface of a sphere with a unit diameter. In order to describe such a random walk on a spherical surface, it is convenient to express the second Fick's law in spherical coordinates

$$\frac{\partial \rho}{\partial t} = \frac{D^{\mathrm{rot}}}{r^2 \sin\vartheta} \left(\frac{\partial}{\partial r} \left(r^2 \sin\vartheta \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \vartheta} \left(\sin\vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{\partial}{\partial \varphi} \left(\frac{1}{\sin\vartheta} \frac{\partial}{\partial \varphi} \right) \right) \rho. \tag{2.1}$$

Since r is constant and equal to unity,

$$\frac{\partial \rho}{\partial t} = \frac{D^{\mathrm{rot}}}{\sin\vartheta} \left(\frac{\partial}{\partial \vartheta} \left(\sin\vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{\partial}{\partial \varphi} \left(\frac{1}{\sin\vartheta} \frac{\partial}{\partial \varphi} \right) \right) \rho. \tag{2.2}$$

Using the substitution $u = \cos\vartheta$ (and $\partial u = -\sin\vartheta \partial\vartheta$),

$$\frac{\partial \rho}{\partial t} = D^{\mathrm{rot}} \left((1 - u^2) \frac{\partial^2}{\partial \vartheta^2} - 2u \frac{\partial}{\partial \vartheta} + \frac{1}{1 - u^2} \frac{\partial^2}{\partial \varphi^2} \right) \rho. \tag{2.3}$$

Let us now try if time and space coordinates can be separated, i.e. if ρ can be expressed as a product $\rho(\vartheta, \varphi, t) = f(\vartheta, \varphi) g(t)$.

$$f \frac{\partial g}{\partial t} = g D^{\mathrm{rot}} \left((1 - u^2) \frac{\partial^2}{\partial \vartheta^2} - 2u \frac{\partial}{\partial \vartheta} + \frac{1}{1 - u^2} \frac{\partial^2}{\partial \varphi^2} \right) f. \tag{2.4}$$

Dividing both sides of the equation by $D^{\mathrm{rot}}\rho = D^{\mathrm{rot}} f g$,

$$\frac{1}{D^{\mathrm{rot}}}\frac{1}{g}\frac{\partial g}{\partial t} = \frac{1}{f}\left((1-u^2)\frac{\partial^2}{\partial \vartheta^2} - 2u\frac{\partial}{\partial \vartheta} + \frac{1}{1-u^2}\frac{\partial^2}{\partial \varphi^2}\right) f. \tag{2.5}$$

If the separation of time and space coordinates is possible, i.e., if Eq. 2.5 is true for any t and any ϑ, φ independently, both sides of the equation must be equal to the same constant (called λ bellow).

$$\frac{1}{D^{\mathrm{rot}}}\frac{1}{g}\frac{\partial g}{\partial t} = \lambda \tag{2.6}$$

$$\frac{1}{f}\left((1-u^2)\frac{\partial^2}{\partial u^2} - 2u\frac{\partial}{\partial u} + \frac{1}{1-u^2}\frac{\partial^2}{\partial \varphi^2}\right) = \lambda. \tag{2.7}$$

Solution of the first equation is obviously

$$g(t) = g(0)\mathrm{e}^{\lambda D^{\mathrm{rot}} t}, \tag{2.8}$$

where λ is obtained by solving the second equation.

Chapter 3

Nuclear magnetic resonance

Literature: A general introduction can be found in L2.6 and L2.7. A nice and detailed discussion, emphasizing the importance of relaxation, is in Szántay et al.: Anthropic awareness, Elsevier 2015, Section 2.4. A useful review of relevant statistical concepts is presented in B6. Chemical shift is introduced by Levitt in L3.7 and discussed in detail in L9.1 (using a quantum approach, but the classical treatment can be obtained simply by using energy E_j instead of $\hat{H}_j$ and magnetic moment $\vec{\mu}_{jk}$ instead of $\gamma_j \hat{I}_{jk}$ in Eqs. 9.11–9.14). A nice discussion of the offset effects (and more) can be found in K4.

3.1 Nuclear magnetic moments in chemical substances

The classical theory does not explain the origin of the magnetic moment of some nuclei, but describes macroscopic effects of the nuclear magnetic moments.

3.1.1 Symmetric distribution

Nuclei have permanent microscopic magnetic moments, but the macroscopic magnetic moment is induced only in the magnetic field. This is the effect of symmetry. Outside a magnet, all orientations of the microscopic magnetic moments have the same energy and are equally probable ⇒ the bulk magnetic moment is zero and the bulk magnetization $\vec{M}$ (magnetic moment per unit volume) is zero (Fig. 3.1).

3.1.2 Polarization

In a static homogeneous magnetic field $\vec{B}_0$, the orientations of $\vec{\mu}$ are no longer equally probable: the orientation of $\vec{\mu}$ along $\vec{B}_0$ is energetically most favored and the opposite orientation is least favored. The symmetry is broken in the direction of $\vec{B}_0$, this direction is used to define the z axis of a coordinate system we work in. However, the state with all magnetic moments in the energetically most favorable orientation is not most probable. Orienting all magnetic moments along the magnetic field represents only one *microstate*. In contrast, there exist a large number of microstates with somewhat higher energy. The correct balance between energy and probability is described by the Boltzmann distribution law, which can be derived from purely statistical arguments. Thermodynamics thus helps us to describe the polarization along z quantitatively.[1]

The average value of the z-component of $\vec{\mu}$ is calculated as[2]

---

[1] Thermodynamics also tells us that the energy of the whole (isolated) system must be conserved. Decreased energy of magnetic moments is compensated by increased rotational kinetic energy of molecules of the sample, coupled with the magnetic moments via magnetic fields of the tumbling molecules, as discussed in the next chapter.

[2] The integral represents summation (integration) over all possible orientations with respect to $\vec{B}_0$, described by the inclination angles ϑ.

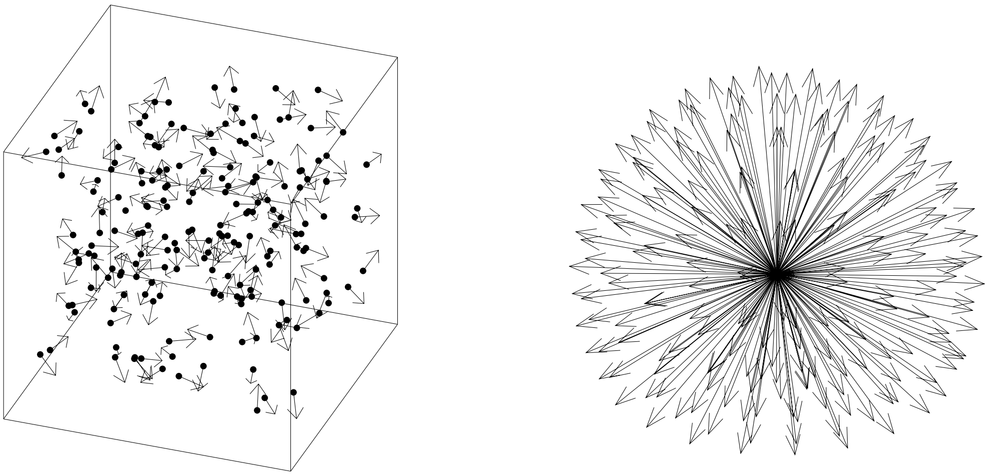

Figure 3.1: Distribution of magnetic moments in the absence of a magnetic field. Left, a schematic representation of an NMR sample. Dots represent molecules, arrows represent magnetic moments (only one magnetic moment per molecule is shown for the sake of simplicity, like e.g. in compressed $^{13}\mathrm{C}^{16}\mathrm{O}_2$). Right, the molecules are superimposed to make the distribution of magnetic moments visible.

$$\overline{\mu}_z^{\mathrm{eq}} = \int\limits_0^\pi P^{\mathrm{eq}}(\vartheta)\mu_z \sin\vartheta\,\mathrm{d}\vartheta = \int\limits_0^\pi P^{\mathrm{eq}}(\vartheta)|\mu|\cos\vartheta\sin\vartheta\,\mathrm{d}\vartheta, \tag{3.1}$$

where ϑ is the inclination (angle between $\vec{\mu}$ and axis z) and $P^{\mathrm{eq}}(\vartheta)$ is the probability of $\vec{\mu}$ to be tilted by the angle ϑ. If the magnetic dipoles are in a thermodynamic equilibrium, the angular distribution of the $\vec{\mu}$ orientation is given by the Boltzmann law[3]

$$P^{\mathrm{eq}}(\vartheta) = \frac{\mathrm{e}^{-\frac{E(\vartheta)}{k_\mathrm{B}T}}}{\int\limits_0^\pi \mathrm{e}^{-\frac{E(\vartheta')}{k_\mathrm{B}T}}\sin\vartheta'\mathrm{d}\vartheta'}, \tag{3.3}$$

where T is the thermodynamic temperature, $k_\mathrm{B} = 1.38064852 \times 10^{-23}\,\mathrm{m}^2\,\mathrm{kg}\,\mathrm{s}^{-2}\,\mathrm{K}^{-1}$ is the Boltzmann constant, and $E = -|\mu||B_0|\cos\vartheta$ is the magnetic potential energy of the dipole. The distribution is axially symmetric, all values of the azimuth φ are equally possible.

Using the substitutions

$$u = \cos\vartheta \Rightarrow \mathrm{d}u = \frac{\mathrm{d}u}{\mathrm{d}\vartheta}\mathrm{d}\vartheta = \frac{\mathrm{d}\cos\vartheta}{\mathrm{d}\vartheta}\mathrm{d}\vartheta = -\sin\vartheta\mathrm{d}\vartheta \tag{3.4}$$

and

$$w = \frac{|\mu||B_0|}{k_\mathrm{B}T}, \tag{3.5}$$

---

[3] Probability of a system to be in the state with the energy E_j at the temperature T is given by

$$P^{\mathrm{eq}}(\vartheta) = \frac{\mathrm{e}^{-\frac{E_j}{k_\mathrm{B}T}}}{Z}, \tag{3.2}$$

where Z is sum of the $\mathrm{e}^{-\frac{E_k}{k_\mathrm{B}T}}$ terms of all possible states.

$$P^{\mathrm{eq}}(\vartheta) = \frac{\mathrm{e}^{-\frac{E(\vartheta)}{k_{\mathrm{B}}T}}}{\int\limits_0^\pi \mathrm{e}^{-\frac{E(\vartheta')}{k_{\mathrm{B}}T}} \sin\vartheta' \mathrm{d}\vartheta'} = \frac{\mathrm{e}^{uw}}{\int\limits_1^{-1} -\mathrm{e}^{u'w}\mathrm{d}u'} = \frac{\mathrm{e}^{uw}}{\int\limits_{-1}^{1} \mathrm{e}^{u'w}\mathrm{d}u'} = \frac{\mathrm{e}^{uw}}{\frac{1}{w}\left[\mathrm{e}^{u'w}\right]_{-1}^{1}} = \frac{w}{\mathrm{e}^{w}-\mathrm{e}^{-w}}\mathrm{e}^{uw} = P^{\mathrm{eq}}(u). \tag{3.6}$$

Knowing the distribution, the average z-component of $\vec{\mu}$ can be calculated

$$\overline{\mu}_z^{\mathrm{eq}} = \int\limits_0^\pi P^{\mathrm{eq}}(\vartheta)|\mu|\cos\vartheta\sin\vartheta\mathrm{d}\vartheta = \int\limits_{-1}^{1} |\mu| u P^{\mathrm{eq}}(u)\mathrm{d}u = \frac{|\mu|w}{\mathrm{e}^{w}-\mathrm{e}^{-w}} \int\limits_{-1}^{1} u\mathrm{e}^{uw}\mathrm{d}u. \tag{3.7}$$

Using the chain rule,

$$\overline{\mu}_z^{\mathrm{eq}} = \frac{|\mu|w}{\mathrm{e}^{w}-\mathrm{e}^{-w}}\left[\frac{1}{w^2}\mathrm{e}^{uw}(uw-1)\right]_{-1}^{1} = |\mu|\left(\frac{\mathrm{e}^{w}+\mathrm{e}^{-w}}{w} - \frac{\mathrm{e}^{w}-\mathrm{e}^{-w}}{w^2}\right) = |\mu|\left(\frac{\mathrm{e}^{w}+\mathrm{e}^{-w}}{\mathrm{e}^{w}-\mathrm{e}^{-w}} - \frac{1}{w}\right) = |\mu|\left(\coth(w) - \frac{1}{w}\right). \tag{3.8}$$

The function $\coth(w)$ can be expanded as a Taylor series

$$\coth(w) \approx \frac{1}{w} + \frac{w}{3} - \frac{w^3}{45} + \frac{2w^5}{945} - \cdots \quad \Rightarrow \quad \overline{\mu}_z \approx |\mu|\left(\frac{w}{3} - \frac{w^3}{45} + \frac{2w^5}{945} - \cdots\right). \tag{3.9}$$

At the room temperature, $|\mu||B_0| \ll k_{\mathrm{B}}T$ even in the strongest NMR magnets. Therefore, w is a very small number and its high powers in the Taylor series can be neglected. In summary, the angular distribution can be approximated by

$$\overline{\mu}_z^{\mathrm{eq}} = \frac{1}{3}\frac{|\mu|^2|B_0|}{k_{\mathrm{B}}T}, \tag{3.10}$$

while

$$\overline{\mu}_x^{\mathrm{eq}} = \overline{\mu}_y^{\mathrm{eq}} = 0. \tag{3.11}$$

The derived average magnetic moments allow us to calculate the bulk magnetization of the NMR sample containing nuclei with $\vec{\mu}$:

$$M_x^{\mathrm{eq}} = 0 \qquad M_y^{\mathrm{eq}} = 0 \qquad M_z^{\mathrm{eq}} = \frac{\mathcal{N}}{3}\frac{|\mu|^2|B_0|}{k_{\mathrm{B}}T}, \tag{3.12}$$

where $\mathcal{N}$ is the number of dipoles per unit volume.

In summary, dipoles are polarized in the static homogeneous magnetic fields. In addition, all dipoles precess with the frequency $\vec{\omega} = -\gamma\vec{B}_0$, but the precession cannot be observed at the macroscopic level because the bulk magnetization is parallel with the axis of precession (Fig. 3.2).

3.1.3 Coherence

In order to observe precession, we need to break the axial symmetry and introduce a *coherent* motion of magnetic moments. This is achieved by applying another magnetic field $\vec{B}_1 \perp \vec{B}_0$ and oscillating with the frequency close to (ideally equal to) $\gamma|B_0|/2\pi$. In NMR, sources of the oscillatory field are radio waves. Mathematically, such a radio field can be decomposed into two components $\vec{B}^{+}_{\mathrm{radio}}$ and $\vec{B}^{-}_{\mathrm{radio}}$ rotating with the same angular frequency but in opposite directions ($\vec{\omega}_{\mathrm{radio}}$ and $-\vec{\omega}_{\mathrm{radio}}$, respectively). The component

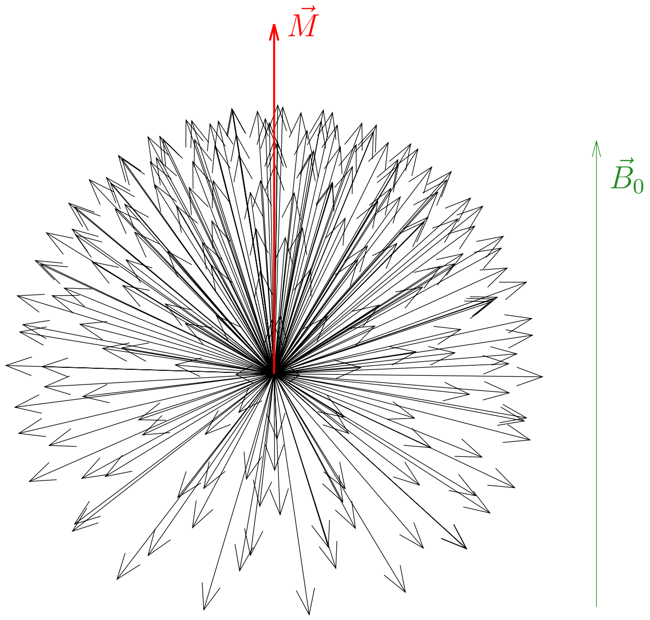

Figure 3.2: Distribution of magnetic moments in a homogeneous magnetic field B_0. The red value represents the bulk magnetization.

rotating in the same direction as the precessing dipoles ($\vec{B}^{-}_{\mathrm{radio}} \equiv \vec{B}_1$ in this text) tilts the magnetization vector $\vec{M}$ from the z direction, the other component can be neglected as long as $|B_1| \ll |B_0|$. This process represents a double rotation, the first rotation is precession around the direction of $\vec{B}_0$, the second rotation around $\vec{B}_1$ is known as *nutation*. The description can be simplified (the effect of the precession removed), if we use $\vec{B}_1$ to define the x axis of our coordinate frame. As $\vec{B}_1$ rotates about $\vec{B}_0$ with an angular frequency $\vec{\omega}_{\mathrm{rot}} = -\vec{\omega}_{\mathrm{radio}}$, we work in a *rotating frame*. In order to define the direction of x in the rotating frame, we must also define the phase ϕ_{rot}.

The components of the field $\vec{B}_1$ rotating with the angular frequency $-\vec{\omega}_{\mathrm{radio}}$ are in the laboratory frame

$$
\begin{aligned}
B_{1,x} &= |B_1|\cos(\omega_{\mathrm{rot}}t + \phi_{\mathrm{rot}}) = |B_1|\cos(-\omega_{\mathrm{radio}}t + \phi_{\mathrm{rot}}), && (3.13)\\
B_{1,y} &= |B_1|\sin(\omega_{\mathrm{rot}}t + \phi_{\mathrm{rot}}) = |B_1|\sin(-\omega_{\mathrm{radio}}t + \phi_{\mathrm{rot}}), && (3.14)\\
B_{1,z} &= 0 && (3.15)
\end{aligned}
$$

and in the rotating frame

$$
\begin{aligned}
B_{1,x} &= |B_1|\cos(\phi_{\mathrm{rot}}), && (3.16)\\
B_{1,y} &= |B_1|\sin(\phi_{\mathrm{rot}}), && (3.17)\\
B_{1,z} &= 0. && (3.18)
\end{aligned}
$$

Consequently, the rotation of magnetization is given by the angular frequency vector

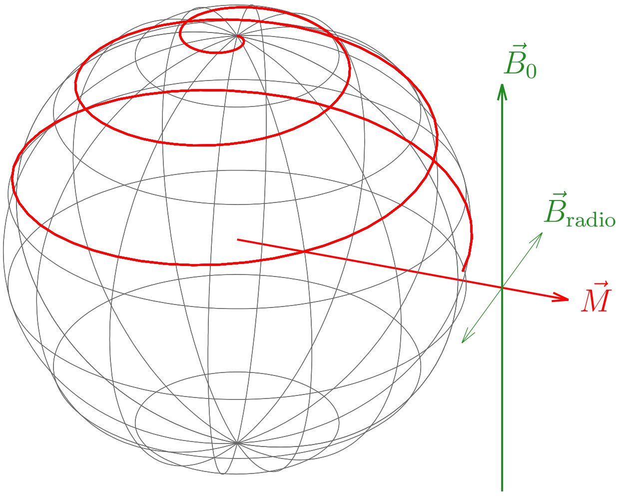

Figure 3.3: Effect of the radio waves on the bulk magnetization. The thin green line shows oscillation of the magnetic induction vector of the radio waves, the red trace shows evolution of the magnetization during irradiation. The length of the irradiation period was chosen so that the magnetization is rotated to the plane perpendicular to $\vec{B}_0$ (red arrow). Note that the $|\vec{B}_0|/|\vec{B}_{\mathrm{radio}}|$ is much higher in a real experiment.

$$\vec{\omega} = \vec{\omega}_0 + \vec{\omega}_1 = -\gamma(\vec{B}_0 + \vec{B}_1) = \begin{pmatrix} 0 \\ 0 \\ -\gamma|B_0| \end{pmatrix} + \begin{pmatrix} -\gamma|B_1|\cos(-\omega_{\mathrm{radio}}t + \phi_{\mathrm{rot}}) \\ -\gamma|B_1|\sin(-\omega_{\mathrm{radio}}t + \phi_{\mathrm{rot}}) \\ 0 \end{pmatrix} = \begin{pmatrix} -\gamma|B_1|\cos(-\omega_{\mathrm{radio}}t + \phi_{\mathrm{rot}}) \\ -\gamma|B_1|\sin(-\omega_{\mathrm{radio}}t + \phi_{\mathrm{rot}}) \\ -\gamma|B_0| \end{pmatrix} \tag{3.19}$$

in the laboratory frame, and by

$$\vec{\omega} = \vec{\omega}_1 = -\gamma\vec{B}_1 = \begin{pmatrix} -\gamma|B_1|\cos(\phi_{\mathrm{rot}}) \\ -\gamma|B_1|\sin(\phi_{\mathrm{rot}}) \\ 0 \end{pmatrix} \tag{3.20}$$

in the coordinate frame rotating with the angular frequency $\vec{\omega}_{\mathrm{rot}} = -\vec{\omega}_{\mathrm{radio}} = \vec{\omega}_0$.
What are the components of $\vec{B}_1$ in the rotating frame for different choices of ϕ_{rot}?
If $\phi_{\mathrm{rot}} = 0$, $\cos(0) = 1$, $\sin(0) = 0$, and

$$B_{1,x} = |B_1|, \tag{3.21}$$
$$B_{1,y} = 0, \tag{3.22}$$
$$B_{1,z} = 0. \tag{3.23}$$

If $\phi_{\mathrm{rot}} = \frac{\pi}{2}$, $\cos(\frac{\pi}{2}) = 0$, $\sin(\frac{\pi}{2}) = 1$, and

$$B_{1,x} = 0, \tag{3.24}$$
$$B_{1,y} = |B_1|, \tag{3.25}$$
$$B_{1,z} = 0. \tag{3.26}$$

If $\phi_{\mathrm{rot}} = \pi$, $\cos(\pi) = -1$, $\sin(\pi) = 0$, and

$$B_{1,x} = -|B_1|, \tag{3.27}$$
$$B_{1,y} = 0, \tag{3.28}$$
$$B_{1,z} = 0, \tag{3.29}$$

and so on.

The typical convention is to choose $\phi_{\mathrm{rot}} = \pi$ for nuclei with $\gamma > 0$ and $\phi_{\mathrm{rot}} = 0$ for nuclei with $\gamma < 0$. Then, the nutation frequency is $\omega_1 = +\gamma|B_1|$ (opposite convention to the precession frequency!) for nuclei with $\gamma > 0$ and $\omega_1 = -\gamma|B_1|$ (the same convention as the precession frequency) for nuclei with $\gamma < 0$.

If the radio waves are applied exactly for the time needed to rotate the magnetization by 90 °, they create a state with $\vec{M}$ perpendicular to $\vec{B}_0$. Such magnetization vector then rotates with the precession frequency, also known as the *Larmor frequency.* Such rotation corresponds to a coherent motion of nuclear dipoles polarized in the direction of $\vec{M}$ and generates measurable electromotoric force in the detector coil (Fig. 3.4).

3.2 Chemical shift

The description of the motions of the bulk nuclear magnetization presented in the previous section is simple but boring. What makes NMR useful for chemists and biologists

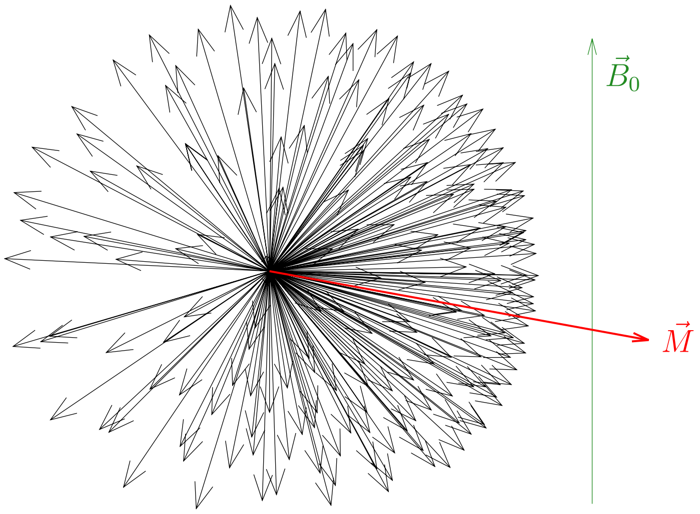

Figure 3.4: Distribution of magnetic moments after application of a 906○ radiofrequency pulse.

is the fact that the energy of the magnetic moment of the observed nucleus is influenced by magnetic fields associated with motions of nearby electrons. In order to understand this effect, we need to 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 $\vec{B}_{\mathrm{e}}$ is proportional to the inducing external field $\vec{B}_0$, the effective field can be described as

$$\vec{B} = \vec{B}_0 + \vec{B}_{\mathrm{e}} = (1+\delta)\vec{B}_0. \tag{3.30}$$

The constant δ is known as *chemical shift* and does not depend on the orientation of the molecule in such a case[4]. The precession frequency of the nucleus is equal[5] 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[6]. 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[7] constants δ_{jk} to describe the effect of electrons:

$$B_{\mathrm{e},x} = \delta_{xx}B_{0,x} + \delta_{xy}B_{0,y} + \delta_{xz}B_{0,z} \tag{3.31}$$
$$B_{\mathrm{e},y} = \delta_{yx}B_{0,x} + \delta_{yy}B_{0,y} + \delta_{yz}B_{0,z} \tag{3.32}$$
$$B_{\mathrm{e},z} = \delta_{zx}B_{0,x} + \delta_{zy}B_{0,y} + \delta_{zz}B_{0,z} \tag{3.33}$$

Eqs. 3.31–3.33 can be written in more compact forms

$$\begin{pmatrix} B_{\mathrm{e},x} \\ B_{\mathrm{e},y} \\ B_{\mathrm{e},z} \end{pmatrix} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix} \cdot \begin{pmatrix} B_{0,x} \\ B_{0,y} \\ B_{0,z} \end{pmatrix} \tag{3.34}$$

or

$$\vec{B}_\mathrm{e} = \underline{\delta} \cdot \vec{B}_0, \tag{3.35}$$

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 χ 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:

$$\begin{pmatrix} \delta_{XX} & 0 & 0 \\ 0 & \delta_{YY} & 0 \\ 0 & 0 & \delta_{ZZ} \end{pmatrix} = \delta_\mathrm{i} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \delta_\mathrm{a} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \delta_\mathrm{r} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{3.36}$$

where

---

[4] Instead of δ, a constant with the opposite sign defining the *chemical shielding* is sometimes used.

[5] The value of δ in Eq. 3.30 describes how much the frequency of nuclei deviates from a hypothetical frequency of free nuclei. Such a hypothetical frequency is difficult to measure. In practice, frequencies of nuclei in certain, readily accessible chemical compounds are used instead of the frequencies of free nuclei as the reference values of δ, as is described in Section 5.1.

[6] The currents induced in orbitals of other atoms may decrease or increase (shield or deshield) the effective magnetic field felt by the observed nucleus.

[7] There are nine constants in Eqs. 3.31–3.33, but $\delta_{xy} = \delta_{yx}$, $\delta_{xz} = \delta_{zx}$, and $\delta_{yz} = \delta_{zy}$.

$$\delta_{\rm i} = \frac{1}{3}{\rm Tr}\{\underline{\delta}\} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ}) \tag{3.37}$$

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

$$\delta_{\rm a} = \frac{1}{3}\Delta_\delta = \frac{1}{6}\left(2\delta_{ZZ} - (\delta_{XX} + \delta_{YY})\right) \tag{3.38}$$

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

$$\delta_{\rm r} = \frac{1}{3}\eta_\delta\Delta_\delta = \frac{1}{2}(\delta_{XX} - \delta_{YY}) \tag{3.39}$$

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 (i.e., $B_{0,z} = B_0$ and $B_{0,x} = B_{0,y} = 0$):

$$\vec{B}_{\rm e} = \delta_{\rm i}B_0\begin{pmatrix}0\\0\\1\end{pmatrix} + \delta_{\rm a}B_0\begin{pmatrix}3\sin\vartheta\cos\vartheta\cos\varphi\\3\sin\vartheta\cos\vartheta\sin\varphi\\3\cos^2\vartheta - 1\end{pmatrix} + \delta_{\rm r}B_0\begin{pmatrix}-(2\cos^2\chi - 1)\sin\vartheta\cos\vartheta\cos\varphi + 2\sin\chi\cos\chi\sin\vartheta\sin\varphi\\-(2\cos^2\chi - 1)\sin\vartheta\cos\vartheta\sin\varphi - 2\sin\chi\cos\chi\sin\vartheta\cos\varphi\\+(2\cos^2\chi - 1)\sin^2\vartheta\end{pmatrix}. \tag{3.40}$$

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 χ. 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:

$$\delta_{\rm a}\begin{pmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 2\end{pmatrix} \longrightarrow \delta_{\rm a}\begin{pmatrix}3a_x^2 - 1 & 3a_xa_y & 3a_xa_z\\3a_xa_y & 3a_y^2 - 1 & 3a_ya_z\\3a_xa_z & 3a_ya_z & 3a_z^2 - 1\end{pmatrix}, \tag{3.41}$$

where $a_x = \sin\vartheta\cos\varphi$, $a_y = \sin\vartheta\sin\varphi$, and $a_z = \cos\vartheta$.

We have derived a not very simple equation (Eq. 3.40) describing how electrons modify the external magnetic field. Do we really need it? When we analyze only the (average) value of the precession frequency, it is sufficient to consider only the isotropic component. The description of the effect of electrons then simplifies to Eq. 3.30, where δ now represents $\delta_{\rm i}$ of Eq. 3.40. When we analyze also the effect of stochastic motions, the other terms become important as well. The correct quantitative analysis requires full Eq. 3.40, but the basic principles can be discussed without using the rhombic component. Therefore, we will use the axially symmetric approximation of Eq. 3.40 when we discuss effects of molecular motions in Section 4.

3.2.1 Offset effects

The presence of electrons makes NMR a great method for chemical analysis. The measured precession frequency depends not only on the type of nucleus (e.g. ^{1}H) but also on the electronic environment: frequencies of protons in different chemical moieties differ and can be used to identify chemical groups in organic molecules. But how the electrons influence the physical description of the nuclear magnetization?

The effect of the isotropic component of the chemical shift on the precession frequency is simply introducing a small correction constant $1 + \delta$ modifying γ:

$$\vec{\omega}_0 = -\gamma\vec{B}_0 \quad \rightarrow \quad \vec{\omega}_0 = -\gamma(1+\delta)\vec{B}_0. \tag{3.42}$$

The trouble is that the correction is different for each proton (or carbon etc.) in the molecule. Therefore, the frequency of the radio waves can match $\omega_0 = -\gamma(1+\delta)|B_0|$ only for one proton in the molecule. For example, if the radio wave resonate with the frequency of the methyl proton in ethanol, it cannot resonate with the frequency of the proton in the OH or CH_2 group. In the rotating coordinate frame, only magnetization of the methyl protons rotates about $\vec{\omega}_1 = \gamma\delta(\text{methyl})\vec{B}_1$. Magnetizations of other protons rotate about other axes. Such rotations can be described by effective angular frequencies

$$\vec{\omega}_{\text{eff}} = \vec{\omega}_1 + \vec{\Omega}, \tag{3.43}$$

where

$$\vec{\Omega} = \vec{\omega}_0 - \vec{\omega}_{\text{rot}} = \vec{\omega}_0 - (-\vec{\omega}_{\text{radio}}) = \vec{\omega}_0 + \vec{\omega}_{\text{radio}} \tag{3.44}$$

is the angular frequency *offset*. As any vector in a 3D space, $\vec{\omega}_{\text{eff}}$ is characterized by three parameters: magnitude ω_{eff}, inclination ϑ, and azimuth φ.

The magnitude of the effective frequency is

$$\omega_{\text{eff}} = \sqrt{\omega_1^2 + \Omega^2}. \tag{3.45}$$

The inclination can be calculated from

$$\tan\vartheta = \frac{\omega_1}{\Omega}. \tag{3.46}$$

The azimuth is given by the phase of $\vec{B}_1$ ($\varphi = \varphi_{\text{rot}}$ in a single-pulse experiment).

As a result of the chemical shift, only the magnetization of the nucleus with $\Omega = 0$ (methyl protons in our case) rotates along the "meridian" in the rotating coordinate system. Magnetizations of other protons move in other circles. Therefore, if the radio transmitter is switched off when the methyl magnetization is pointing horizontally (and starts to rotate around the "equator" with the precession frequency of methyl protons), vectors of magnetizations of other protons point in different directions, and start to precess on cones with different inclinations and with different initial phases. Such effects, known as the *offset effects*, influence the measured signal.[8]

The discussed motion of the magnetization vector $\vec{M}$ is described by the following equations

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[8] The result is the same as if apparent effective fields of the magnitude $B_{\text{eff}} = \sqrt{B_1^2 + (\Omega/\gamma)^2}$ were applied in the direction in the directions of $\vec{\omega}_{\text{eff}}$. The apparent effective field $\vec{B}_{\text{eff}}$ is often used to describe the offset effects.

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = -\Omega M_y + \omega_1 \sin\varphi M_z, \tag{3.47}$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = +\Omega M_x - \omega_1 \cos\varphi M_z, \tag{3.48}$$

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = -\omega_1 \sin\varphi M_x + \omega_1 \cos\varphi M_y, \tag{3.49}$$

$$\tag{3.50}$$

where φ is the azimuth of $\vec{\omega}_{\text{eff}}$, which can be written in a compact form as

$$\frac{\mathrm{d}\vec{M}}{\mathrm{d}t} = \vec{\omega}_{\text{eff}} \times \vec{M}. \tag{3.51}$$

3.2.2 Evolution of magnetization in $\vec{B}_0$

Eqs. 3.47–3.49 are easy to solve in the absence of $\vec{B}_1$ (i.e., after turning off the radio waves):

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = -\Omega M_y \tag{3.52}$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = \Omega M_x \tag{3.53}$$

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = 0 \tag{3.54}$$

The trick is to multiply the second equation by i and add it to the first equation or subtract it from the first equation.

$$\frac{\mathrm{d}(M_x + \mathrm{i}M_y)}{\mathrm{d}t} = \Omega(-M_y + \mathrm{i}M_x) = +\mathrm{i}\Omega(M_x + \mathrm{i}M_y) \tag{3.55}$$

$$\frac{\mathrm{d}(M_x - \mathrm{i}M_y)}{\mathrm{d}t} = \Omega(-M_y - \mathrm{i}M_x) = -\mathrm{i}\Omega(M_x - \mathrm{i}M_y) \tag{3.56}$$

$$M_x + \mathrm{i}M_y = C_+ \mathrm{e}^{+\mathrm{i}\Omega t} \tag{3.57}$$

$$M_x - \mathrm{i}M_y = C_- \mathrm{e}^{-\mathrm{i}\Omega t} \tag{3.58}$$

where the integration constants $C_+ = M_x(0) + \mathrm{i}M_y(0) = \sqrt{M_x^2(0) + M_y^2(0)}\mathrm{e}^{\phi_0}$ and $C_- = M_x(0) - \mathrm{i}M_y(0) = \sqrt{M_x^2(0) + M_y^2(0)}\mathrm{e}^{-\phi_0}$ are given by the initial phase ϕ_0 of $\vec{M}$ in the coordinate system (in our case, $t = 0$ is defined by switching off the radio waves):

$$M_x + \mathrm{i}M_y = \sqrt{M_x^2(0) + M_y^2(0)}\mathrm{e}^{+(\mathrm{i}\Omega t + \phi_0)} = \sqrt{M_x^2(0) + M_y^2(0)}(\cos(\Omega t + \phi_0) + \mathrm{i}(\sin(\Omega t + \phi_0)) \tag{3.59}$$

$$M_x - \mathrm{i}M_y = \sqrt{M_x^2(0) + M_y^2(0)}\mathrm{e}^{-(\mathrm{i}\Omega t + \phi_0)} = \sqrt{M_x^2(0) + M_y^2(0)}(\cos(\Omega t + \phi_0) - \mathrm{i}(\sin(\Omega t + \phi_0)), \tag{3.60}$$

$$M_x = \sqrt{M_x^2(0) + M_y^2(0)}\cos(\Omega t + \phi_0) \tag{3.61}$$

$$M_y = \sqrt{M_x^2(0) + M_y^2(0)}\sin(\Omega t + \phi_0), \tag{3.62}$$

where

$$\tan\phi_0 = \frac{M_y(0)}{M_x(0)}. \tag{3.63}$$

In order to obtain ϕ_0 and $\sqrt{M_x^2(0) + M_y^2(0)}$, we must first solve Eqs. 3.47–3.49. This solution is not so easy, and we look only at the result:

$$\begin{aligned}
M_x(0) &= M_0 \sin(\omega_{\mathrm{eff}}\tau_{\mathrm{p}}) \sin\vartheta, && (3.64)\\
M_y(0) &= M_0(1 - \cos(\omega_{\mathrm{eff}}\tau_{\mathrm{p}})) \sin\vartheta \cos\vartheta, && (3.65)\\
M_z(0) &= M_0(\cos^2\vartheta + \cos(\omega_{\mathrm{eff}}\tau_{\mathrm{p}}) \sin^2\vartheta), && (3.66)
\end{aligned}$$

where M_0 is the magnitude of the bulk magnetization in the thermodynamic equilibrium, τ_{p} is duration of irradiation by the radio waves, and $\tan\vartheta = \omega_1/\Omega$.

Chapter 4

Relaxation

Literature: A nice introduction is in K9.1 and K9.3, more details can be found in L19 and L20.1–L20.3.

4.1 Relaxation due to chemical shift anisotropy

The Boltzmann law 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.* Relaxation 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.

Here, we introduce the basic idea by analyzing the effects of fluctuating magnetic fields in a classical manner.

4.2 Loss of coherence

Motion of a magnetic moment in a magnetic filed is described classically as (cf. Eq. 3.51)

$$\frac{\mathrm{d}\vec{\mu}}{\mathrm{d}t} = \vec{\omega} \times \vec{\mu} = -\gamma \vec{B} \times \vec{\mu}, \tag{4.1}$$

or for individual components:

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = \omega_y\mu_z - \omega_z\mu_y, \tag{4.2}$$
$$\frac{\mathrm{d}\mu_y}{\mathrm{d}t} = \omega_z\mu_x - \omega_x\mu_z, \tag{4.3}$$
$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = \omega_x\mu_y - \omega_y\mu_x. \tag{4.4}$$

Solving a set of three equations is not so easy. Therefore, we start with a simplified case. Remember what we learnt when we tried to rotate the magnetization away from the z direction by magnetic fields perpendicular to $\vec{B}_0$, i.e., fields with B_x and B_y components. Only B_x and B_y fields rotating with the frequency equal to the precession frequency of individual magnetic moments (*Larmor frequency*) have the desired effect. Let us start our analysis by assuming that the molecular motions are much slower than the Larmor frequency. Under such circumstances, the effects of $B_{\mathrm{e},x}$ and $B_{\mathrm{e},y}$ can be neglected and the equations of motion simplify to

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = -\omega_z\mu_y = \gamma B_z\mu_y \tag{4.5}$$
$$\frac{\mathrm{d}\mu_y}{\mathrm{d}t} = \omega_z\mu_x = -\gamma B_z\mu_x \tag{4.6}$$
$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = 0 \tag{4.7}$$

Eqs. 4.5–4.7 are very similar to Eqs. 3.52–3.54, so we try the same approach and calculate

$$\frac{\mathrm{d}\mu^+}{\mathrm{d}t} \equiv \frac{\mathrm{d}(\mu_x + \mathrm{i}\mu_y)}{\mathrm{d}t} = \mathrm{i}\omega_z(\mu_x + \mathrm{i}\mu_y) = -\mathrm{i}\gamma B_z(\mu_x + \mathrm{i}\mu_y) \tag{4.8}$$

According to Eq. 3.40,

$$B_z = B_0 + B_{\mathrm{e},z} = B_0(1 + \delta_{\mathrm{i}} + \delta_{\mathrm{a}}(3\cos^2\vartheta - 1) + \delta_{\mathrm{r}}(2\cos^2\chi - 1)\sin^2\vartheta). \tag{4.9}$$

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

$$\omega_z = -\gamma(B_0 + B_{\mathrm{e},z}) = -\gamma B_0(1 + \delta_{\mathrm{i}}) - \gamma B_0\delta_{\mathrm{a}}(3\cos^2\vartheta - 1) = \omega_0 + b\Theta^{\|}, \tag{4.10}$$

where

$$\omega_0 = -\gamma B_0(1 + \delta_{\mathrm{i}}) \tag{4.11}$$
$$b = -2\gamma B_0\delta_{\mathrm{a}} \tag{4.12}$$
$$\Theta^{\|} = \frac{3\cos^2\vartheta - 1}{2}. \tag{4.13}$$

This looks fine, but there is a catch here: Eq. 4.8 cannot be solved as easily as we solved 3.52–3.54 because ω_z is not constant but fluctuates in time. The value of ω_z is not only changing, is changing differently for each molecule in the sample and it is changing in a random, unpredictable way! Can we solve the equation of motion at all? The answer is "yes and no". The equation of motion cannot be solved for an individual magnetic moment. However, we can take advantage of *statistics* and solve the equation of motion for the *total magnetization* M^+, given by the statistical ensemble of magnetic moments.

We start by assuming that for a very short time Δt, shorter than the time scale of molecular motions, the orientation of the molecule does not change and $\Theta^{\|}$ remains constant. We try to describe the evolution of μ^+ in such small time steps, assuming

$$\frac{\Delta\mu^+}{\Delta t} \approx \frac{\mathrm{d}\mu^+}{\mathrm{d}t} \approx \mathrm{i}(\omega_0 + b\Theta^{\|})\mu^+ \tag{4.14}$$

If the initial value of μ^+ is μ_0^+ and if the values of $\omega_0, b, \Theta^{\|}$ during the first time step are $\omega_{0,1}, b_1, \Theta^{\|}_1$, respectively, the value of μ^+ after the first time step is

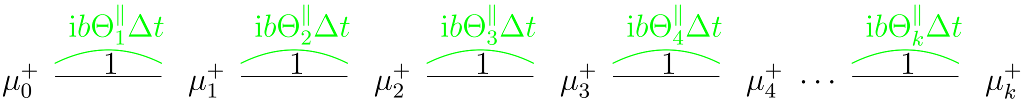

Figure 4.1: Evolution of magnetic moments due to longitudinal (parallel with $\vec{B}_0$) fluctuations of magnetic fields. The symbols μ_0^+ and μ_k^+ are connected by 2^k possible pathways composed of black and green segments. Each black segment represents multiplication by one, each green segment represents multiplication by $\mathrm{i}b\Theta_j^{\|}\Delta t$, where j ranges from 1 to k. The product of binomials in Eq. 4.21 is a sum of 2^k terms. In order to obtain one term of the series, we walk along the corresponding pathway and multiply all black and green numbers written above the individual steps. The pathway composed of the black segments only gives the result of multiplication equal to one, the pathways containing just one green segment give results of multiplication proportional to Δt, the pathways containing two green segments give results of multiplication proportional to $(\Delta t)^2$, etc. In order to get the complete product in Eq. 4.21, we must walk through all possible pathways (all possible combinations of the segments) and sum all results of the multiplication.

$$\mu_1^+ = \mu_0^+ + \Delta\mu_1^+ = \mu_0^+ + \mathrm{i}(\omega_{0,1} + b_1\Theta_1^{\|})\Delta t\mu_0^+ = [1 + \mathrm{i}(\omega_{0,1} + b_1\Theta_1^{\|})\Delta t]\mu_0^+. \tag{4.15}$$

After the second step,

$$\mu_2^+ = \mu_1^+ + \Delta\mu_2^+ = \mu_1^+ + \mathrm{i}(\omega_{0,2} + b_2\Theta_2^{\|})\Delta t\mu_1^+ = [1 + \mathrm{i}(\omega_{0,2} + b_2\Theta_2^{\|})\Delta t][1 + \mathrm{i}(\omega_{0,1} + b_1\Theta_1^{\|})\Delta t]\mu_0^+. \tag{4.16}$$

After k steps,

$$\mu_k^+ = [1 + \mathrm{i}(\omega_{0,k} + b_k\Theta_k^{\|})\Delta t][1 + \mathrm{i}(\omega_{0,k-1} + b_{k-1}\Theta_{k-1}^{\|})\Delta t]\cdots[1 + \mathrm{i}(\omega_{0,2} + b_2\Theta_2^{\|})\Delta t][1 + \mathrm{i}(\omega_{0,1} + b_1\Theta_1^{\|})\Delta t]\mu_0^+. \tag{4.17}$$

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, ω_0 and b are constant and the only time-dependent parameter is $\Theta^{\|}$, fluctuating as the orientation of the molecule (described by ϑ) changes. The parameter $\omega_0 = -\gamma B_0(1+\delta_\mathrm{i})$ represents a constant frequency of coherent rotation under such circumstances. The coherent rotation can be removed if we describe the evolution of μ^+ in a coordinate frame rotating with the frequency ω_0. The transformation of μ^+ to the rotating frame is given by

$$(\mu^+)_\mathrm{rot} = \mu^+\mathrm{e}^{-\mathrm{i}\omega_0 t}. \tag{4.18}$$

We also need to express the derivative of $(\mu^+)_\mathrm{rot}$, which is done easily by applying the chain rule:

$$\frac{\mathrm{d}(\mu^+)_\mathrm{rot}}{\mathrm{d}t} = \frac{\mathrm{d}(\mu^+\mathrm{e}^{-\mathrm{i}\omega_0 t})}{\mathrm{d}t} = \frac{\mathrm{d}\mu^+}{\mathrm{d}t}\mathrm{e}^{-\mathrm{i}\omega_0 t} - \mathrm{i}\omega_0\mu^+\mathrm{e}^{-\mathrm{i}\omega_0 t}. \tag{4.19}$$

Substituting $\mathrm{d}\mu^+/\mathrm{d}t$ from Eq. 4.14 results in

$$\frac{\mathrm{d}(\mu^+)_\mathrm{rot}}{\mathrm{d}t} = \mathrm{i}(\omega_0 + b\Theta^{\|})\mu^+\mathrm{e}^{-\mathrm{i}\omega_0 t} - \mathrm{i}\omega_0\mu^+\mathrm{e}^{-\mathrm{i}\omega_0 t} = \mathrm{i}b\Theta^{\|}\mu^+\mathrm{e}^{-\mathrm{i}\omega_0 t} = \mathrm{i}b\Theta^{\|}(\mu^+)_\mathrm{rot}. \tag{4.20}$$

When compared with Eq. 4.14, we see that ω_0 disappeared, which simplifies Eq. 4.17 to

$$(\mu_k^+)_\mathrm{rot} = [1 + \mathrm{i}b\Theta_k^{\|}\Delta t][1 + \mathrm{i}b\Theta_{k-1}^{\|}\Delta t]\cdots[1 + \mathrm{i}b\Theta_2^{\|}\Delta t][1 + \mathrm{i}b\Theta_1^{\|}\Delta t](\mu_0^+)_\mathrm{rot}. \tag{4.21}$$

The process of calculating the product of brackets in Eq. 4.21 is shown schematically in Figure 4.1. The final product is

$$(\mu_k^+)_\mathrm{rot} = [1 + \mathrm{i}b\Delta t(\Theta_k^{\|} + \Theta_{k-1}^{\|} + \cdots + \Theta_1^{\|}) - b^2\Delta t^2(\Theta_k^{\|}(\Theta_{k-1}^{\|} + \cdots\Theta_2^{\|} + \Theta_1^{\|}) + \cdots + \Theta_2^{\|}\Theta_1^{\|}) - \mathrm{i}b^3\Delta t^3(\ldots) + \cdots](\mu_0^+)_\mathrm{rot}. \tag{4.22}$$

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

$$\Delta(\mu_k^+)_{\mathrm{rot}} = (\mu_k^+)_{\mathrm{rot}} - (\mu_{k-1}^+)_{\mathrm{rot}} = [\mathrm{i}b\Delta t\Theta_k^{\|} - b^2\Delta t^2\Theta_k^{\|}(\Theta_{k-1}^{\|} + \cdots + \Theta_1^{\|}) - \mathrm{i}b^3\Delta t^3(\dots) + \cdots](\mu_0^+)_{\mathrm{rot}}. \tag{4.23}$$

Dividing both sides by Δt

$$\frac{\Delta(\mu_k^+)_{\mathrm{rot}}}{\Delta t} = [\mathrm{i}b\Theta_k^{\|} - b^2\Delta t\Theta_k^{\|}(\Theta_{k-1}^{\|} + \cdots + \Theta_1^{\|}) - \mathrm{i}b^3\Delta t^2(\dots) + \cdots](\mu_0^+)_{\mathrm{rot}} \tag{4.24}$$

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

$$\frac{\mathrm{d}(\mu^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = \left[\mathrm{i}b\Theta^{\|}(t_k) - b^2\int\limits_0^{t_k}\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)\mathrm{d}t_j\right](\mu_0^+)_{\mathrm{rot}}. \tag{4.25}$$

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 ($\Theta^{\|}(t_k - t_j)$). 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 other words, we should describe $\Theta^{\|}$ using *two* indices, k and m, where k describes the time step and m the orientation of the given molecule. Calculation of the evolution of M^+ then should include summation of $\Theta_{k,m}^{\|}$ for all k and m, or integration over the angles describing orientations of the molecule in addition to the time integration. As the magnetic moments move almost independently of the molecular motions, we can average $\Theta^{\|}$ and μ^+ separately. 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. In order to simplify averaging the orientations, we assume that all orientations are equally probable. This is a very dangerous assumption. It does not introduce any error in this section, but leads to wrong results when we analyze the effects of fluctuations of magnetic fields perpendicular to $\vec{B}_0$!

As the angle $\vartheta(t)$ is hidden in the function $\Theta^{\|}(t) = (3\cos\vartheta^2 - 1)/2$ in our equation, the ensemble averaging can be written as[1]

$$\frac{\mathrm{d}(M^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = \left[\mathrm{i}b\frac{1}{4\pi}\int\limits_0^{2\pi}\mathrm{d}\varphi\int\limits_0^{\pi}\Theta^{\|}(t_k)\sin\vartheta\mathrm{d}\vartheta - b^2\int\limits_0^{t_k}\mathrm{d}t_j\frac{1}{4\pi}\int\limits_0^{2\pi}\mathrm{d}\varphi\int\limits_0^{\pi}\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)\sin\vartheta\mathrm{d}\vartheta\right](M_0^+)_{\mathrm{rot}}, \tag{4.26}$$

where $\varphi \equiv \varphi(t_k)$ and $\vartheta \equiv \vartheta(t_k)$.

In order to avoid writing too many integration signs, we mark the averaging simply by a horizontal bar above the averaged function:

$$\frac{\mathrm{d}(M^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = -\left[\mathrm{i}b\overline{\Theta^{\|}(t_k)} + b^2\int\limits_0^{t_k}\overline{\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)}\mathrm{d}t_j\right](M_0^+)_{\mathrm{rot}}. \tag{4.27}$$

The average values of $a_z^2 = \cos^2\vartheta$, of $a_x^2 = \cos^2\varphi\sin^2\vartheta$, and of $a_y^2 = \sin^2\varphi\sin^2\vartheta$ must be the same because none of the directions x, y, z is preferred:

$$\overline{a_x^2} = \overline{a_y^2} = \overline{a_z^2}. \tag{4.28}$$

Therefore,

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[1] Two integrals in the following equation represent calculation of an average of a function depending on the orientation. Geometrically, it is summation of the values of the function for individual surface elements (defined by inclination ϑ and azimuth φ) of a unit sphere, divided by the complete surface of the sphere 4π. Note that the *current* orientation of each molecule at t_k is described by $\vartheta(t_k)$ and $\varphi(t_k)$, the values $\vartheta(t_j)$ hidden in the function $\Theta^{\|}(t_j)$ describe only *history* of each molecule. They are *somehow* related to $\vartheta(t_k)$ and $\varphi(t_k)$ and therefore treated as an unknown function of $\vartheta(t_k)$ and $\varphi(t_k)$ during the integration.

$$a_x^2 + a_y^2 + a_z^2 = 1 \Rightarrow \overline{a_x^2 + a_y^2 + a_z^2} = \overline{3a_z^2} \Rightarrow \overline{3a_z^2 - 1} = \overline{(3\cos^2\vartheta - 1)} = 2\overline{\Theta^{\|}} = 0 \Rightarrow \overline{\Theta^{\|}} = 0. \tag{4.29}$$

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).

We have derived that the equation describing the loss of coherence (resulting in a loss of transverse magnetization) is

$$\frac{\mathrm{d}(M^+(t_k))_{\mathrm{rot}}}{\mathrm{d}t} = -\left[b^2 \int\limits_0^{t_k} \overline{\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)}\mathrm{d}t_j\right](M_0^+)_{\mathrm{rot}}, \tag{4.30}$$

where the value of $\overline{\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)}$ is clearly defined statistically (by the averaging described above). Values of $\overline{\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)}$ can be determined easily for two limit cases:

- $t_j = 0$: If $t_j = 0$, $\overline{\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)} = \overline{(\Theta^{\|}(t_k))^2}$, i.e., $\Theta^{\|}(t_k)$ and $\Theta^{\|}(t_k - t_j)$ are *completely correlated.*

  The average value of $\overline{\Theta^{\|}(t_k)^2}$ is

$$\overline{\Theta^{\|}(t_k)^2} = \frac{1}{4}\overline{(3\cos^2\vartheta - 1)^2} = \frac{1}{16\pi}\int\limits_0^{2\pi}\mathrm{d}\varphi\int\limits_0^{\pi}\mathrm{d}\vartheta(\sin\vartheta)(3\cos^2\vartheta - 1)^2 = \frac{1}{5}. \tag{4.31}$$

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

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

$$\frac{\mathrm{d}(M^+)_{\mathrm{rot}}}{\mathrm{d}t} = -\left[b^2 \int\limits_0^{\infty} \overline{\Theta^{\|}(0)\Theta^{\|}(t)}\mathrm{d}t\right](M^+)_{\mathrm{rot}}, \tag{4.32}$$

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

$$R_0 = b^2 \int\limits_0^{\infty} \overline{\Theta^{\|}(0)\Theta^{\|}(t)}\mathrm{d}t. \tag{4.33}$$

In order to calculate the value of the rate constant R_0, we must be able to avaluate the averaged term $\overline{\Theta^{\|}(0)\Theta^{\|}(t)}$, known as the *time correlation function.* Note that statistics play the key role here: the whole analysis relies on the fact that although the product $\Theta^{\|}(0)\Theta^{\|}(t)$ changes randomly, the value of the time correlation function is defined statistically. If the structure of the molecule does not change (*rigid body rotational diffusion*), which is the case we analyze, the analytical form of $\overline{\Theta^{\|}(0)\Theta^{\|}(t)}$ can be derived.

4.2.1 Time correlation function

Analysis of the isotropic rotational diffusion in Section 2.2 allows us to calculate the time correlation function $\overline{\Theta^{\parallel}(0)\Theta^{\parallel}(t)}$ for this type of diffusion (with a spherical symmetry). The ensemble-averaged product of randomly changing $(3\cos^2\vartheta(t)-1)/2$, evaluated for a time difference t, can be expressed as

$$\overline{\left(\frac{3}{2}\cos^2\vartheta(0)-\frac{1}{2}\right)\left(\frac{3}{2}\cos^2\vartheta(t)-\frac{1}{2}\right)} \tag{4.34}$$

$$=\int\limits_0^{2\pi}\mathrm{d}\varphi(0)\int\limits_0^{\pi}\sin\vartheta(0)\mathrm{d}\vartheta(0)\rho_0\int\limits_0^{2\pi}\mathrm{d}\varphi(t)\int\limits_0^{\pi}\sin\vartheta(t)\mathrm{d}\vartheta(t)\left(\frac{3}{2}\cos^2\vartheta(0)-\frac{1}{2}\right)\left(\frac{3}{2}\cos^2\vartheta(t)-\frac{1}{2}\right)G(\vartheta(0),\varphi(0)|\vartheta(t),\varphi(t)), \tag{4.35}$$

where ρ_0 is the probability density of the original orientation described by $\vartheta(0)$ and $\varphi(0)$, and $G(\vartheta(0),\varphi(0)|\vartheta(t),\varphi(t))$ is the *conditional probability density* or *propagator* (also known as the *Green function*) describing what is the chance to find an orientation given by $\vartheta(t),\varphi(t)$ at time t, if the orientation at $t=0$ was given by $\vartheta(0),\varphi(0)$.

If the molecule is present in an isotropic environment[2], ρ_0 plays a role of a normalization constant and can be calculated easily from the condition that the overall probability of finding the molecule in *any* orientation is equal to one:

$$\int\limits_0^{2\pi}\mathrm{d}\varphi(0)\int\limits_0^{\pi}\sin\vartheta(0)\mathrm{d}\vartheta(0)\rho_0=4\pi\rho_0=1\quad\Rightarrow\quad\rho_0=\frac{1}{4\pi}. \tag{4.36}$$

Evaluation of $G(\vartheta(0),\varphi(0)|\vartheta(t),\varphi(t))$ requires to solve the diffusion equation Eq. 2.7. We again express G as a product of time-dependent and time-independent functions $g(t)P(\vartheta)$. The function $g(t)$ is defined by Eq. 2.6, the function $P(\vartheta)$ is a simplified version of function $f(\vartheta,\varphi)$ from Eq. 2.7. Since our correlation correlation function does not depend on φ, we can assume $\partial P/\partial\varphi=0$ and further simplify Eq. 2.7 to

$$\left((1-u^2)\frac{\mathrm{d}^2}{\mathrm{d}u^2}-2u\frac{\mathrm{d}}{\mathrm{d}u}\right)P=\lambda P, \tag{4.37}$$

$$(1-u^2)\frac{\mathrm{d}^2P}{\mathrm{d}u^2}-2u\frac{\mathrm{d}P}{\mathrm{d}u}-\lambda P=0. \tag{4.38}$$

We expand P in a Taylor series

$$P=\sum_{k=0}^{\infty}a_ku^k,\quad a_k=\frac{1}{k!}\frac{\mathrm{d}^kP(0)}{\mathrm{d}u^k}, \tag{4.39}$$

calculate its first and second derivatives

$$\frac{\mathrm{d}P}{\mathrm{d}u}=\sum_{k=0}^{\infty}ka_ku^{k-1}, \tag{4.40}$$

$$\frac{\mathrm{d}^2P}{\mathrm{d}u^2}=\sum_{k=0}^{\infty}k(k-1)a_ku^{k-2}, \tag{4.41}$$

and substitute them into Eq. 4.38

$$(1-u^2)\sum_{k=0}^{\infty}k(k-1)a_ku^{k-2}-2\sum_{k=0}^{\infty}ka_ku^k-\lambda\sum_{k=0}^{\infty}a_ku^k-2u=0 \tag{4.42}$$

$$\sum_{k=0}^{\infty}k(k-1)a_ku^{k-2}-\sum_{k=0}^{\infty}k(k-1)a_ku^k-2\sum_{k=0}^{\infty}ka_ku^k-\lambda\sum_{k=0}^{\infty}a_ku^k=0. \tag{4.43}$$

Note that the first two terms of the first sum are equal to zero (the first term includes multiplication by $k=0$ and the second term includes multiplication by $k-1=0$ for $k=1$). Therefore, we can start summation from $k=2$.

---

[2] Note that in the isotropic environment, where all orientations of the molecule are equally probable, the diffusion can be very anisotropic if the shape of the molecule greatly differs from a sphere.

$$\sum_{k=2}^{\infty} k(k-1)a_k u^{k-2} - \sum_{k=0}^{\infty} k(k-1)a_k u^k - 2\sum_{k=0}^{\infty} k a_k u^k - \lambda \sum_{k=0}^{\infty} a_k u^k = 0. \tag{4.44}$$

We shift the index in the first sum by two to get the first sum expressed in the same power of u as the other sums

$$\sum_{k=0}^{\infty}(k+2)(k+1)a_{k+2}u^k - \sum_{k=0}^{\infty} k(k-1)a_k u^k - 2\sum_{k=0}^{\infty} k a_k u^k - \lambda \sum_{k=0}^{\infty} a_k u^k = 0 \tag{4.45}$$

$$\sum_{k=0}^{\infty}\left((k+2)(k+1)a_{k+2} - (k(k-1)+2k+\lambda)a_k\right)u^k = \sum_{k=0}^{\infty}\left((k+2)(k+1)a_{k+2} - (k(k+1)+\lambda)a_k\right)u^k = 0. \tag{4.46}$$

This equation is true only if all terms in the sum are equal to zero

$$(k+2)(k+1)a_{k+2} - (k(k+1)+\lambda)a_k = 0, \tag{4.47}$$

which gives us a recurrence formula relating a_{k+2} and a_k:

$$a_{k+2} = \frac{k(k+1)+\lambda}{(k+2)(k+1)}a_k = 0. \tag{4.48}$$

We can use the recurrence formula to express the Taylor series in terms of a_0 and a_1:

$$P = a_0\left(1 + \frac{0\cdot 1+\lambda}{1\cdot 2}u^2 + \frac{0\cdot 1+\lambda}{1\cdot 2}\cdot\frac{2\cdot 3+\lambda}{3\cdot 4}u^4 + \dots\right) + a_1\left(u + \frac{1\cdot 2+\lambda}{2\cdot 3}u^3 + \frac{1\cdot 2+\lambda}{2\cdot 3}\cdot\frac{3\cdot 4+\lambda}{4\cdot 5}u^5 + \dots\right) = 0. \tag{4.49}$$

What is the value of λ? Note that $a_{k+2} = 0$ for each $\lambda = -k(k+1)$, which terminates one of the series in large parentheses, while the other series grows to infinity (for $u \neq 0$). To keep P finite, the coefficient before the large parentheses in the unterminated series must be set to zero. It tells us that we can find a possible solution for each even or odd k if $a_1 = 0$ or $a_0 0$, respectively.

$$k = 0 \quad a_1 = 0 \quad P = P_0 = 1 \qquad \lambda = -k(k+1) = 0 \tag{4.50}$$

$$k = 1 \quad a_0 = 0 \quad G = P_1 = u = \cos\vartheta \qquad \lambda = -k(k+1) = -2 \tag{4.51}$$

$$k = 2 \quad a_1 = 0 \quad G = P_2 = \frac{3u^2-1}{2} = \frac{3\cos^2\vartheta - 1}{2} \qquad \lambda = -k(k+1) = -6 \tag{4.52}$$

$$k = 3 \quad a_0 = 0 \quad G = P_3 = \frac{5u^3-3u}{2} = \frac{5\cos^3\vartheta - 3\cos\vartheta}{2} \qquad \lambda = -k(k+1) = -12 \tag{4.53}$$

$$\vdots \tag{4.54}$$

The value of a_0 or a_1 preceding the terminated series was chosen so that $P_k(u=1) = P_k(\vartheta=0) = 1$.
Which of the possible solutions is the correct one? It can be shown easily that

$$\int_{-1}^{1} P_k(u)P_{k'}(u)\mathrm{d}u = \int_{0}^{\pi} P_k(\vartheta)P_{k'}(\vartheta)\mathrm{d}\vartheta = \frac{2}{2k+1}\delta kk', \tag{4.55}$$

i.e., is equal to zero for each $k \neq k'$ (P_k are orthogonal). As we are going to use $G = g(t)P(\vartheta)$ to calculate a correlation function for functions having the same form as the solutions for $k = 2$ and as the calculation of the correlation function includes the same integration as in Eq. 4.55, it is clear that the only solution which gives us non-zero correlation function is that for $k = 2$, i.e. P_2. Our function G is therefore given by

$$G = g_0\frac{3\cos^2\vartheta - 1}{2}\mathrm{e}^{-6D^{\mathrm{rot}}t}. \tag{4.56}$$

Still, we need to evaluate the factor g_0. This value must be chosen so that we fulfill the following conditions:

$$\int_{0}^{2\pi} \mathrm{d}\varphi \int_{0}^{\pi} \sin\vartheta \mathrm{d}\vartheta G = 1 \tag{4.57}$$

and

$$G(t=0) = \delta(\theta - \theta_0), \tag{4.58}$$

where $\delta(\theta - \theta_0)$ is a so-called Dirac delta function, defined as

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0) = f(x_0). \tag{4.59}$$

The second condition says that ϑ must have its original value for $t = 0$. This is fulfilled for g_0 proportional to $(3\cos^2\vartheta_0 - 1)/2$:

$$g_0 = c_0 \frac{3}{2}\cos^2\vartheta(0) - \frac{1}{2}. \tag{4.60}$$

We can re-write our original definition of the correlation function with the evaluated G function and in a somewhat simplified form (omitting integration over φ and φ_0):

$$\overline{\left(\frac{3}{2}\cos^2\vartheta(0) - \frac{1}{2}\right)\left(\frac{3}{2}\cos^2\vartheta(t) - \frac{1}{2}\right)} = \int_{-1}^{1} \mathrm{d}u_0 \rho_0 c_0 \int_{-1}^{1} \mathrm{d}u \frac{(3u_0^2 - 1)^2}{4}\frac{(3u^2 - 1)^2}{4}\mathrm{e}^{-6D^{\mathrm{rot}}t}, \tag{4.61}$$

where ρ_0 can be evaluated from the normalization condition

$$\int_{-1}^{1} \mathrm{d}u_0 \rho_0 = 2\rho_0 = 1 \Rightarrow \rho_0 = \frac{1}{2} \tag{4.62}$$

and
c_0 from

$$\int_{-1}^{1} \mathrm{d}u_0 \int_{-1}^{1} c_0 \frac{3u_0^2 - 1}{2}\frac{3u^2 - 1}{2}\delta(u - u_0)\mathrm{d}u = \int_{-1}^{1} \mathrm{d}u_0 c_0 \frac{(3u_0^2 - 1)^2}{4} = \frac{2}{5}c_0 \Rightarrow c_0 = \frac{5}{2}. \tag{4.63}$$

Finally, the correlation function can be calculated

$$\overline{\left(\frac{3}{2}\cos^2\vartheta(0) - \frac{1}{2}\right)\left(\frac{3}{2}\cos^2\vartheta(t) - \frac{1}{2}\right)} = \frac{5}{4}\int_{-1}^{1} \mathrm{d}u_0 \int_{-1}^{1} \mathrm{d}u \frac{(3u_0^2 - 1)^2}{4}\frac{(3u^2 - 1)^2}{4}\mathrm{e}^{-6D^{\mathrm{rot}}t} = \frac{1}{5}\mathrm{e}^{-6D^{\mathrm{rot}}t}. \tag{4.64}$$

We have derived that the time correlation function for spherically symmetric rotational diffusion is a single exponential function. Analytical solutions are also available (but more difficult to derive) for axially symmetric and asymmetric rotational diffusion, with the time correlation function in a form of three and five exponential functions, respectively.

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

$$R_0 = b^2 \int_{0}^{\infty} \frac{1}{5}\mathrm{e}^{-t/\tau_{\mathrm{c}}}\mathrm{d}t = \frac{b^2}{5}\tau_{\mathrm{c}} = \frac{b^2}{5}\frac{1}{6D^{\mathrm{rot}}}, \tag{4.65}$$

where D^{rot} is the *rotational diffusion coefficient*, given by the Stokes' law

$$\frac{k_{\mathrm{B}}T}{8\pi\eta(T)r^3}, \tag{4.66}$$

where r is the radius of the spherical particle, T is the temperature, and $\eta(T)$ is the dynamic viscosity of the solvent, strongly dependent on the temperature.[3]

4.3 Return to equilibrium

After introducing the correlation function, we can repeat the analysis using the same simplifications (rigid molecule, isotropic liquid), but taking the transverse (perpendicular) field fluctuations into account.

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = \omega_y\mu_z - \omega_z\mu_y \tag{4.68}$$

$$\frac{\mathrm{d}\mu_y}{\mathrm{d}t} = \omega_z\mu_x - \omega_x\mu_z \tag{4.69}$$

$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = \omega_x\mu_y - \omega_y\mu_x \tag{4.70}$$

Expressing ω_x as $b\Theta^{\perp}\cos\varphi$ and ω_y as $b\Theta^{\perp}\sin\varphi$, where

$$b = -2\gamma B_0\delta_{\mathrm{a}} \tag{4.71}$$

$$\Theta^{\perp} = \frac{3}{2}\sin\vartheta\cos\vartheta, \tag{4.72}$$

gives

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = (b\Theta^{\perp}\sin\varphi)\mu_z - (\omega_0 + b\Theta^{\parallel})\mu_y \tag{4.73}$$

$$\frac{\mathrm{d}\mu_y}{\mathrm{d}t} = (\omega_0 + b\Theta^{\parallel})\mu_x - (b\Theta^{\perp}\cos\varphi)\mu_z \tag{4.74}$$

$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = (b\Theta^{\perp}\cos\varphi)\mu_y - (b\Theta^{\perp}\sin\varphi)\mu_x, \tag{4.75}$$

Introducing $\mu^+ = \mu_x + \mathrm{i}\mu_y$ and $\mu^- = \mu_x - \mathrm{i}\mu_y$ results in

$$\frac{\mathrm{d}\mu^+}{\mathrm{d}t} = -\mathrm{i}b\Theta^{\perp}\mathrm{e}^{\mathrm{i}\varphi}\mu_z + \mathrm{i}(\omega_0 + b\Theta^{\parallel})\mu^+ \tag{4.76}$$

$$\frac{\mathrm{d}\mu^-}{\mathrm{d}t} = \mathrm{i}b\Theta^{\perp}\mathrm{e}^{-\mathrm{i}\varphi}\mu_z - \mathrm{i}(\omega_0 + b\Theta^{\parallel})\mu^- \tag{4.77}$$

$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = \frac{\mathrm{i}}{2}b\Theta^{\perp}\left(\mathrm{e}^{-\mathrm{i}\varphi}\mu^+ - \mathrm{e}^{\mathrm{i}\varphi}\mu^-\right), \tag{4.78}$$

---

[3] Dynamic viscosity of water can be approximated by

$$\eta(T) = \eta_0 \times 10^{T_0/(T-T_1)}, \tag{4.67}$$

where $\eta_0 = 2.414\times10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, $T_0 = 247.8\,\mathrm{K}$, and $T_1 = 140\,\mathrm{K}$ (Al-Shemmeri, T., 2012. Engineering Fluid Mechanics. Ventus Publishing ApS. pp. 1718.).

In a coordinate frame rotating with ω_0,

$$\frac{\mathrm{d}(\mu^+)_{\mathrm{rot}}}{\mathrm{d}t} = -\mathrm{i}b\Theta^{\perp}\mathrm{e}^{\mathrm{i}(\varphi-\omega_0 t)}\mu_z + \mathrm{i}b\Theta^{\parallel}(\mu^+)_{\mathrm{rot}} \tag{4.79}$$

$$\frac{\mathrm{d}(\mu^-)_{\mathrm{rot}}}{\mathrm{d}t} = \mathrm{i}b\Theta^{\perp}\mathrm{e}^{-\mathrm{i}(\varphi-\omega_0 t)}\mu_z - \mathrm{i}b\Theta^{\parallel}(\mu^-)_{\mathrm{rot}} \tag{4.80}$$

$$\frac{\mathrm{d}\mu_z}{\mathrm{d}t} = \frac{\mathrm{i}}{2}b\Theta^{\perp}\left(\mathrm{e}^{-\mathrm{i}(\varphi-\omega_0 t)}(\mu^+)_{\mathrm{rot}} - \mathrm{e}^{\mathrm{i}(\varphi-\omega_0 t)}(\mu^-)_{\mathrm{rot}}\right), \tag{4.81}$$

Note that now the transformation to the rotating frame did not remove ω_0 completely, it survived in the exponential terms.

Again, the set of differential equations cannot be solved because $\Theta^{\parallel}$, $\Theta^{\perp}$, and φ fluctuate in time, but we can analyze the evolution in time steps short enough to keep $\Theta^{\parallel}$, $\Theta^{\perp}$, and φ constant.

$$\mu_1^+ = \mu_0^+ + \Delta\mu_1^+ = [1+\mathrm{i}(\omega_0 + b\Theta_1^{\parallel})\Delta t]\mu_0^+ - \mathrm{i}b\Theta_1^{\perp}\Delta t\mathrm{e}^{\mathrm{i}(\varphi_1-\omega_0 t_1)}\mu_{z,0} \tag{4.82}$$

$$\mu_1^- = \mu_0^- + \Delta\mu_1^- = [1-\mathrm{i}(\omega_0 + b\Theta_1^{\parallel})\Delta t]\mu_0^- + \mathrm{i}b\Theta_1^{\perp}\Delta t\mathrm{e}^{-\mathrm{i}(\varphi_1-\omega_0 t_1)}\mu_{z,0} \tag{4.83}$$

$$\mu_{z,1} = \mu_{z,0} + \Delta\mu_{z,1} = \mu_{z,0} - \frac{\mathrm{i}}{2}b\Theta_1^{\perp}\Delta t\mathrm{e}^{-\mathrm{i}(\varphi_1-\omega_0 t_1)}\mu_0^+ + \frac{\mathrm{i}}{2}b\Theta_1^{\perp}\Delta t\mathrm{e}^{\mathrm{i}(\varphi_1-\omega_0 t_1)}\mu_0^-. \tag{4.84}$$

The μ^+, μ^-, and $\mu_{z,0}$ are now coupled which makes the step-by-step analysis much more complicated. Instead of writing the equations, we just draw a picture (Figure 4.2) similar to Fig. 4.1. Derivation of the values of relaxation rates follows the procedure described for the parallel fluctuations (Eqs. 4.21–4.26). As the number of possible pathways in Fig. 4.2 is very high, already the list of the terms proportional to Δt and Δt^2 is very long. Fortunately, we are not interested in evolution of magnetic moments in individual molecules, described in Fig. 4.2. The values of $\Theta_1^{\parallel}$, $\Theta_1^{\perp}$, φ_1, etc. are different for each molecule and we are interested in what we get after averaging results of multiplications for all molecules (all possible orientations). In order to avoid writing the long expressions for magnetic moments of individual molecules, we skip steps corresponding to Eqs. 4.21–4.25 and jump directly to the calculation of the evolution of total magnetization (corresponding to Eq. 4.26).

Let us start with the terms proportional to Δt, which give us the imaginary term proportional to b when calculating $\mathrm{d}M^+/\mathrm{d}t$ (and $\mathrm{d}M^-/\mathrm{d}t$, $\mathrm{d}M_z/\mathrm{d}t$). We have already seen that the average of $\Theta^{\parallel}$ (the green segment) is zero. The terms containing $\Theta^{\perp}$ (red and blue segments) contain the exponential expression with the phase including φ. If the azimuth φ is random[4], the "red" and "blue" terms average to zero.

Let us now turn to the terms proportional to Δt^2, which give us the time integral multiplied by b^2 when calculating $\mathrm{d}M^+/\mathrm{d}t$ (and $\mathrm{d}M^-/\mathrm{d}t$, $\mathrm{d}M_z/\mathrm{d}t$). The pathways containing two red segments or two blue segments correspond to Δt^2 terms with a random phase in the exponent (random sums of $\varphi_j - \omega_0 t_j$). When averaged for all orientations, such phases tend to zero. The Δt^2 terms do not average to zero only in two cases: (i) if the pathway contains two green segments (effect of longitudinal fluctuations described above) or (ii) if the pathway contains a combination of one red and one blue segment. The former case is obvious, but the latter one is more subtle.

We can distinguish two combinations of one red and one blue segment:

$$\frac{1}{2}b^2\Delta t^2\Theta_k^{\perp}\mathrm{e}^{\mathrm{i}(\varphi_k-\omega_0 t_k)}\Theta_j^{\perp}\mathrm{e}^{-\mathrm{i}(\varphi_j-\omega_0 t_j)} = \frac{1}{2}b^2\Delta t^2\Theta_k^{\perp}\Theta_j^{\perp}\mathrm{e}^{\mathrm{i}(\varphi_k-\varphi_j-\omega_0(t_k-t_j))} \tag{4.85}$$

(with $-\omega_0(t_k - t_j)$ in the exponent) and

$$\frac{1}{2}b^2\Delta t^2\Theta_k^{\perp}\mathrm{e}^{-\mathrm{i}(\varphi_k-\omega_0 t_k)}\Theta_j^{\perp}\mathrm{e}^{\mathrm{i}(\varphi_j-\omega_0 t_j)} = \frac{1}{2}b^2\Delta t^2\Theta_k^{\perp}\Theta_j^{\perp}\mathrm{e}^{\mathrm{i}(-\varphi_k+\varphi_j+\omega_0(t_k-t_j))} \tag{4.86}$$

(with $-\omega_0(t_k - t_j)$ in the exponent). As discussed in Section 4.2, we can replace t_k by zero and t_j by t because the molecular motions are random:

$$\frac{1}{2}b^2\Delta t^2\Theta^{\perp}(0)\Theta^{\perp}(t)\mathrm{e}^{\mathrm{i}(-(\varphi(t)-\varphi(0))+\omega_0 t))} \tag{4.87}$$

(with $+\omega_0 t$ in the exponent) and

$$\frac{1}{2}b^2\Delta t^2\Theta^{\perp}(0)\Theta^{\perp}(t)\mathrm{e}^{\mathrm{i}(+(\varphi(0)-\varphi(t))+\omega_0 t))} \tag{4.88}$$

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[4] Note that this is true even in the presence of $\vec{B}_0$ and in molecules aligned along the direction of $\vec{B}_0$, for example in liquid crystals oriented by the magnetic field.

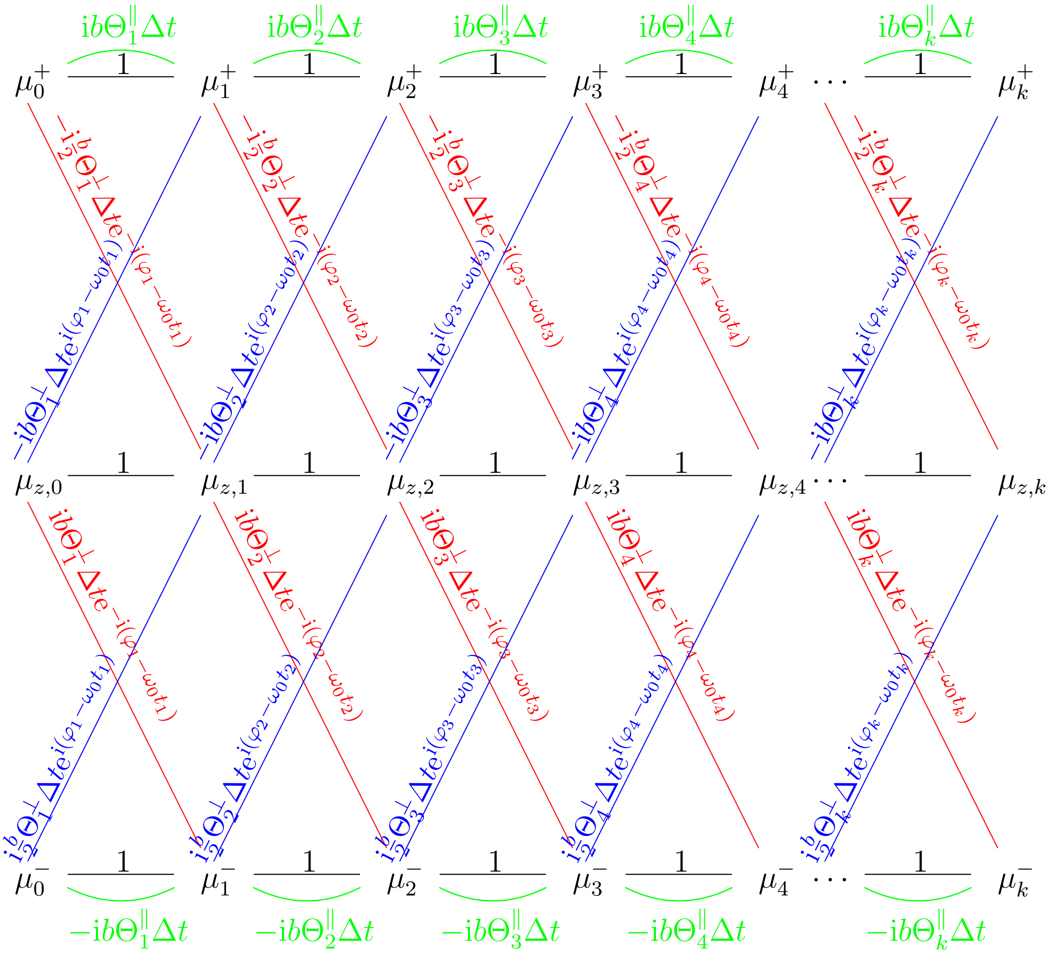

Figure 4.2: Evolution of magnetic moments due to longitudinal (parallel) and transverse (perpendicular) fluctuations of magnetic fields. The meaning of the diagram is the same as in Fig. 4.1, but additional segments (red and blue) interconnect μ_j^+, μ_j^-, and $\mu_{z,j}$., substantially increasing the number of possible pathways. The pathway composed of the black segments only gives the result of multiplication equal to one, the pathways containing just one segment of a different color give results of multiplication proportional to Δt, the pathways containing two segments of a color different than black segments give results of multiplication proportional to $(\Delta t)^2$, etc.

(with $-\omega_0 t$ in the exponent).

In both cases, the phase is not randomly distributed for different orientations only if $\varphi(0) - \varphi(t)$ is similar to $\omega_0 t$. The average value of $\overline{\Theta^{\perp}(0)^2}$ is 3/10:

$$\overline{\Theta^{\perp}(t)^2} = \frac{9}{4}\overline{\cos^2\vartheta\sin^2\vartheta} = \frac{9}{16\pi}\int\limits_0^{2\pi}\mathrm{d}\varphi\int\limits_0^{\pi}\mathrm{d}\vartheta(\sin^3\vartheta\cos^2\vartheta) = \frac{3}{10} \tag{4.89}$$

for any t.

The M_z component of magnetization is given by the average of the μ_z components at t_k. In order to get to $\mu_{z,k}$ through paths giving terms proportional to Δt^2, we must start at $\mu_{z,0}$ and pass one blue segment and one red segment in Figure 4.2. Eqs. 4.87 and 4.88 mathematically describe that orientations of magnetic moments are redistributed if the molecular motions (described by the azimuth φ) accidently resonate for a short time with the frequencies $\omega_0 t$ and $-\omega_0 t$. Then the magnetic energy of the magnetic moments is exchanged with the rotational kinetic energy of the molecules. This energy exchange must be taken into account when we average magnetic moments of individual molecules to calculate M_z. Let us call the total rotational energy of molecules E_0^{rot}. The exchange of the magnetic energy E_μ of a magnetic moment $\vec{\mu}$ with a small amount of rotational energy of molecules ΔE^{rot} can be described as

$$E_0^{\mathrm{rot}} \to E_0^{\mathrm{rot}} + \Delta E^{\mathrm{rot}} + E_\mu. \tag{4.90}$$

The molecular motions have much more degrees of freedom (both directions of rotational axes and rates of rotation vary) than the magnetic moments (size is fixed, only orientation changes). We can therefore assume that the exchange perturbs distribution of the magnetic moments, but the rotating molecules stay very close to the termodynamic equilibrium. At the equilibrium, the probability to find a molecule with the rotational kinetic energy $E_0^{\mathrm{rot}} + \Delta E^{\mathrm{rot}}$ is proportional to (Boltzmann law) to

$$\mathrm{e}^{-\Delta E^{\mathrm{rot}}} \approx 1 - \Delta E^{\mathrm{rot}}. \tag{4.91}$$

The conservation of energy requires

$$E_0^{\mathrm{rot}} + \Delta E^{\mathrm{rot}} + E_\mu = E_0^{\mathrm{rot}}, \tag{4.92}$$

showing that $\Delta E^{\mathrm{rot}} = -E_\mu$. Consequently, the population of molecules with the given rotational energy is proportional to $1 - \Delta E^{\mathrm{rot}} = 1 + E_\mu$. According to Eq. 3.3, the probability of finding a magnetic moment in the orientation described by a given $u = \cos\vartheta_\mu$ is

$$P^{\mathrm{eq}}(u) = \frac{w}{\mathrm{e}^{w} - \mathrm{e}^{-w}}\mathrm{e}^{uw} \approx \frac{w}{1 - w - 1 + w}(1 + uw) = \frac{1}{2}(1 + uw). \tag{4.93}$$

Consequently, $E_\mu = -uw = 1 - 2P^{\mathrm{eq}}(u)$ and the probability to find a molecule with the rotational kinetic energy $E_0^{\mathrm{rot}} + \Delta E^{\mathrm{rot}}$ is proportional to

$$1 - \Delta E^{\mathrm{rot}} = 1 + E_\mu = 2 - 2P^{\mathrm{eq}}(u) = 2(1 - P^{\mathrm{eq}}(u)), \tag{4.94}$$

where the factor of two can be absorbed to the normalization constant.

We have derived that the averaged values of μ_z are weigted by $1 - P^{\mathrm{eq}}(u)$. How does it affect calculation of M_z? In the expression $\mu_z - P^{\mathrm{eq}}(u)\mu_z$, μ_z in the first term is not weighted by anything and its average (multiplied by the number of magnetic moments per unit volume) is equal to M_z. The average value of the second term has been already calculated in Eqs. 3.7–3.12. It represents the quilibrium value of the magnetization, M^{eq}. Therefore, averaging of μ_z results in $M_z - M^{\mathrm{eq}}$, usually abbreviated as ΔM_z.

Using the same arguments as in Section 4.2,

$$\frac{\mathrm{d}\Delta M_z}{\mathrm{d}t} = -\left(\frac{1}{2}b^2\int\limits_0^{\infty}\overline{\Theta^{\perp}(0)\Theta^{\perp}(t)\mathrm{e}^{-\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \frac{1}{2}b^2\int\limits_0^{\infty}\overline{\Theta^{\perp}(0)\Theta^{\perp}(t)\mathrm{e}^{\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right)\Delta M_z \tag{4.95}$$

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

$$R_1 = b^2\Re\left\{\int\limits_0^{\infty}\overline{\Theta^{\perp}(0)\Theta^{\perp}(t)\mathrm{e}^{-\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \int\limits_0^{\infty}\overline{\Theta^{\perp}(0)\Theta^{\perp}(t)\mathrm{e}^{\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right\} \tag{4.96}$$

If the fluctuations are random and their statistical properties do not change in time, they are *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. Therefore,

$$\int_0^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{-\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{-\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \int_{-\infty}^0 \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{-\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right) \tag{4.97}$$

$$= \frac{1}{2}\int_{-\infty}^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{-\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t. \tag{4.98}$$

$$\int_0^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t + \int_{-\infty}^0 \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right) \tag{4.99}$$

$$= \frac{1}{2}\int_{-\infty}^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t. \tag{4.100}$$

In isotropic solutions, the motions of molecules are very little affected by magnetic fields. Therefore, the choice of the z axes is arbitrary form the point of the view of the molecule (not of the magnetic moment!). Therefore, the terms with $\Theta^\perp$ can be replaced by those with $\Theta^\parallel$, multiplied by 3/2 to match the difference between $\overline{\Theta^\parallel(0)^2} = 1/5$ with $\overline{\Theta^\perp(0)^2} = 3/10$:

$$\frac{1}{2}\int_{-\infty}^\infty \overline{\Theta^\perp(0)\Theta^\perp(t)\mathrm{e}^{\mp\mathrm{i}(\varphi(t)-\varphi(0))}}\mathrm{e}^{\pm\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{3}{4}\int_{-\infty}^\infty \overline{\Theta^\parallel(0)\Theta^\parallel(t)}\mathrm{e}^{\pm\mathrm{i}\omega_0 t}\mathrm{d}t. \tag{4.101}$$

Real parts of the integrals in the right-hand side of Eq. 4.101 are known as *spectral density functions* $J(\omega)$. Note that the integral in Eq. 4.32 in Section 4.2 can be also included in the definition of the spectral density function if we replace ω_0 by zero:

$$\int_0^\infty \overline{\Theta^\parallel(0)\Theta^\parallel(t)}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{\Theta^\parallel(0)\Theta^\parallel(t)}\mathrm{d}t + \int_{-\infty}^0 \overline{\Theta^\parallel(0)\Theta^\parallel(t)}\mathrm{d}t\right) = \frac{1}{2}\int_{-\infty}^\infty \overline{\Theta^\parallel(0)\Theta^\parallel(t)}\mathrm{e}^0\mathrm{d}t = \frac{1}{2}J(0). \tag{4.102}$$

The relaxation rate R_1 can be therefore written as

$$R_1 = \frac{3}{4}b^2\left(\frac{1}{2}J(\omega_0) + \frac{1}{2}J(-\omega_0)\right) \approx \frac{3}{4}b^2 J(\omega_0). \tag{4.103}$$

Let us now turn to M_+. Its value is given by the average of μ^+ components at t_k. The analysis of Figure 4.2 showed that the relaxation-relevant Δt^2 terms are obtained by walking through paths containing two green segments (leading to Eq. 4.32 in Section 4.2) or one blue segment and one red segment (which gave us Eq. 4.95 in this section). In any case, we must start at μ_0^+. As we have already analyzed both relevant types of pathways in Figure 4.2, we can directly write the result

$$R_2 = \frac{1}{2}b^2 J(0) + \frac{3}{8}b^2 J(-\omega_0). \tag{4.104}$$

Similarly, relaxation of M_- is given by

$$R_2 = \frac{1}{2}b^2 J(0) + \frac{3}{8}b^2 J(\omega_0). \tag{4.105}$$

The *longitudinal relaxation rate* R_1, describing the decay of ΔM_z due to the chemical shift anisotropy in randomly reorienting molecules, and the *transverse relaxation rate* R_2, describing the decay of transverse magnetization M_+ (or M_-) are given by

$$R_1 = \frac{3}{4}b^2 J(\omega_0), \tag{4.106}$$

$$R_2 = \frac{1}{2}b^2 J(0) + \frac{3}{8}b^2 J(\omega_0). \tag{4.107}$$

4.4 Internal motions, structural changes

So far, we analyzed only the rigid body motions of molecules, assuming that the structures of molecules are rigid. What happens if the structure of the molecule changes? Let us 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. 4.21 can be still used and R_0 is still given by Eq. 4.33, 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 $\Theta^{\|}(t_k)$ and $\Theta^{\|}(t_j)$ 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.

If the structural changes alter size and/or shape of the chemical shift tensor,[5] parameters ω_{0j} and b_j in Eq. 4.17 vary and cannot be treated as constants. E.g., the parameter ω_{0j} is not absorbed into the frequency of the rotating coordinate frame and terms $\overline{\omega_0(t_k)\omega_0(t_k - t_j)}$ contribute to R_0 even if $\overline{a(t_k)a(t_k - t_j)}$ decays much slower than $\overline{\Theta^{\|}(t_k)\Theta^{\|}(t_k - t_j)}$.

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[5] 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.

- 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 and consequently R_2.

4.5 Bloch equations

The effects of relaxation can be included in the equations describing evolution of the bulk magnetization (Eqs. 3.47–3.49). The obtained set of equations, known as *Bloch equations*, provides a general macroscopic description of NMR for proton and similar nuclei.

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = -R_2 M_x - \Omega M_y + \omega_1 \sin\varphi M_z, \tag{4.108}$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = +\Omega M_x - R_2 M_y - \omega_1 \cos\varphi M_z, \tag{4.109}$$

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = -\omega_1 \sin\varphi M_x + \omega_1 \cos\varphi M_y - R_1(M_z - M_z^{\mathrm{eq}}). \tag{4.110}$$

$$\tag{4.111}$$

How does the incorporation of the relaxation effects influence the solution of the Bloch equations? In the single-pulse experiment, irradiation by the radio waves is usually short and the relaxation can be neglected. Therefore the values $M_x(0)$ and $M_y(0)$ obtained by solving Eqs. 3.47–3.49 can be used as the initial conditions for solving the Bloch eqations. The evolution of magnetization during the relatively long period of signal acquisition in the absence of $\vec{B}_1$ (i.e., after turning off the radio waves), when the relaxation cannot be neglected, is given by

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = -R_2 M_x - \Omega M_y, \tag{4.112}$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = \Omega M_x - R_2 M_y, \tag{4.113}$$

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = 0. \tag{4.114}$$

The same trick can be applied as when solving Eqs. 3.52–3.54:

$$\frac{\mathrm{d}(M_x + \mathrm{i}M_y)}{\mathrm{d}t} = \Omega(-M_y + \mathrm{i}M_x) = (+\mathrm{i}\Omega - R_2)(M_x + \mathrm{i}M_y), \tag{4.115}$$

$$\frac{\mathrm{d}(M_x - \mathrm{i}M_y)}{\mathrm{d}t} = \Omega(-M_y - \mathrm{i}M_x) = (-\mathrm{i}\Omega - R_2)(M_x - \mathrm{i}M_y), \tag{4.116}$$

$$M_x + \mathrm{i}M_y = C_+\mathrm{e}^{(+\mathrm{i}\Omega - R_2)t} = \sqrt{M_x(0) + M_y(0)}\mathrm{e}^{-R_2 t}\mathrm{e}^{(+\mathrm{i}\Omega + \phi_0)t}, \tag{4.117}$$

$$M_x - \mathrm{i}M_y = C_-\mathrm{e}^{(-\mathrm{i}\Omega - R_2)t} = \sqrt{M_x(0) + M_y(0)}\mathrm{e}^{-R_2 t}\mathrm{e}^{(-\mathrm{i}\Omega + \phi_0)t}, \tag{4.118}$$

$$M_x = \sqrt{M_x(0) + M_y(0)}\mathrm{e}^{-R_2 t}\cos(\Omega t + \phi_0) \tag{4.119}$$

$$M_y = \sqrt{M_x(0) + M_y(0)}\mathrm{e}^{-R_2 t}\sin(\Omega t + \phi_0). \tag{4.120}$$

As a result of relaxation, the detected NMR signal does not oscillate as a cosine (or sine) function with a constant amplitude, but decays exponentially, with the rate constant of the decay equal to R_2. Such a signal is usually described as the *free induction decay* (*FID*).

Chapter 5

Signal acquisition and processing

Literature: Function of an NMR spectrometer is nicely described in L4, K13, or C3.1. More details are provided in B23. Experimental setup is discussed in C3.8.2. Signal averaging is described in L5.2, quadrature detection in L5.7 and LA.5, K13.6, and C3.2.3, Fourier transformation is introduced in K5.1–K5.3.1 and L5.8.1.–L5.8.3, and treated moro thoroughly in B8 and C3.3.1. Phase correction is described nicely in K5.3.2–K5.3.4 and discussed also in C3.3.2.3 and L5.8.4–L5.8.5, zero filling is discussed in C3.3.2.1 and K5.5, and apodization is explained in K5.4 and C3.3.2.2.

5.1 NMR experiment

The real NMR experiment closely resembles FM radio broadcast. The mega-hertz radio frequency ω_{radio} plays the role of the *carrier frequency*, and is *frequency-modulated* by the offset, which usually falls in the range of kilo-hertz *audio frequencies*. In the same fashion, the carrier frequency of the FM broadcast is modulated by the audio frequency of the transmitted signal (voice, music). Like when listening to the radio, we need to know the carrier frequency to tune the receiver, but its value is not interesting. The interesting information about the chemical environment is hidden in the audio-frequency offset. Note, however, that the numerical value of Ω is arbitrary as it depends on the actual choice of the carrier frequency. What can be interpreted unambiguously, is the constant δ, given just by the electron density. But in practice, the absolute value of δ is extremely difficult to obtain because the reference $\delta = 0$ represents nuclei with no electrons – definitely not a sample we are used to produce in our labs. Therefore, more accessible references (precession frequencies ω_{ref} of stable chemical compounds) are used instead of the vacuum frequency. The value of δ is than defined as $(\omega - \omega_{\mathrm{ref}})/\omega_{\mathrm{ref}}$ and usually presented in the units of ppm.

5.1.1 Setting up the experiment

- *Temperature control and calibration.* Temperature affects molecular motions and chemical shits, it should be controlled carefully to obtain reproducible spectra and to analyze them quantitatively. The sample temperature is controlled by a flow of pre-heated/cooled air or nitrogen gas. The exact temperature inside the sample is not so easy to measure. Usually, spectra of compounds with known temperature dependence of chemical shifts are recorded (e.g. methanol). The temperature is obtained by comparing a difference of two well defined chemical shifts (of methyl and hydroxyl protons in the case of methanol) with its values reported for various temperatures. Purity of the standard samples is a critical issue.

- *Field-frequency lock.* The external magnetic field should be *stationary.* It is achieved by a feedback system known as *field-frequency lock.* A deuterated compound (usually heavy water or other deuterated solvent) is added to the sample and the deuterium frequency is measured continually and kept constant by adjusting electric current in an auxiliary electromagnet. The lock parameters for the particular deuterium compound used are selected and the deuterium spectrometer is switched on before the measurement.

- *Shimming.* The external magnetic field should be also *homogeneous.* The inhomogeneities caused e.g. by the presence of the sample are compensated by adjusting electric current in a set of correction coils called *shims.* This is usually at least partially automated.

- *Tuning.* Each radio-frequency circuit in the probe consists of a receiver coil and two adjustable capacitors. The capacitors should be adjusted for each sample. The *tuning capacitor* of the capacitance C_T and the coil of the inductance L make an LC circuit, acting as a resonator. Adjusting the value of C_T defines the resonant frequency, which should be equal to the precession frequency of the measured nucleus ω_0. If we neglect the second capacitor, the resonant frequency is $\omega = 1/\sqrt{LC_\mathrm{T}}$. The second, *matching capacitor* of the capacitance C_M is used to adjust the impedance of the resonator. The radio waves do not travel from the transmitter to the coil through air but through co-axial cables. In order to have minimum of the wave reflected back to the transmitter, the impedance of the resonator should match the input impedance Z_in.

  The impedance of the coil circuit is given by

$$Z_\mathrm{c} = \frac{1}{\frac{1}{Z_\mathrm{M}} + \frac{1}{Z_\mathrm{T}+Z_\mathrm{L}+R}} = \frac{1}{\mathrm{i}\omega C_\mathrm{M} + \frac{1}{\frac{1}{\mathrm{i}\omega C_\mathrm{T}} + \mathrm{i}\omega L + R}}.$$

  In order to tune the circuit, C_T and C_M must be adjusted simultaneously to get (i) $Z_\mathrm{c} = Z_\mathrm{in}$ and (ii) $\omega = \omega_0$.

- *Calibration of pulse duration.* The magnitude of $\vec{B}_1$ cannot be set directly. Therefore, the duration of irradiation rotating $\vec{M}$ by 360 ° at the given strength of radio waves is searched for empirically. This duration is equal to $2\pi/\omega_1$ and can be used to calculate ω_1 or $|\vec{B}_1| = \omega_1/\gamma$. As $|\vec{B}_1|$ is proportional to the square root of power P, durations of pulses of radio waves of other strengths need not be calibrated, but can be recalculated.

Power is measured in the units of Watt, but the relative power is usually expressed on a logarithmic scale in decibells (dB). One Bell represents a ten-fold attenuation of power

$$\log_{10}\frac{P_2}{P_1} = \text{attenuation/B}. \tag{5.1}$$

Consequently,

$$10\log_{10}\frac{P_2}{P_1} = \text{attenuation/dB} \tag{5.2}$$

and

$$20\log_{10}\frac{P_2^2}{P_1^2} = 20\log_{10}\frac{|\vec{B}_1|_2^2}{|\vec{B}_1|_1^2} = 10\log_{10}\frac{|\vec{B}_1|_2}{|\vec{B}_1|_1} = \text{attenuation/dB}. \tag{5.3}$$

5.1.2 Quadrature detection

Precession of the magnetization vector in the sample induces a signal oscillating with the same frequency (Larmor frequency ω_0) in the coil of the NMR probe. The signal generated in the coil and amplified in the preamplifier is split into two channels. The signal in each channel is mixed with a reference wave supplied by the radio-frequency synthesizer. The reference waves have the same frequency ω_{ref} in both channels, but their phases are shifted by 90 °. Let us assume that the signal oscillates as a cosine function $\cos(\omega_0 t)$ and that the reference wave in the first channel is a cosine wave $\cos(\omega_{\text{ref}}t)$ and that the reference wave in the second channel is a sine wave $-\sin(\omega_{\text{ref}}t)$.

Mathematically, the procedure can be described as

$$\cos(\omega_0 t) \to \begin{cases} \frac{1}{2}\cos(\omega_0 t) \to \frac{1}{2}\cos(\omega_0 t)\cos(\omega_{\text{ref}}t) \\ \frac{1}{2}\cos(\omega_0 t) \to -\frac{1}{2}\cos(\omega_0 t)\sin(\omega_{\text{ref}}t) \end{cases} \tag{5.4}$$

Basic trigonometric identities show that the result of mixing in the first channel is a sum of a high-frequency cosine wave $\cos((\omega_0+\omega_{\text{ref}})t)$ and a low-frequency cosine wave $\cos((\omega_0-\omega_{\text{ref}})t)$, while the result of mixing in the second channel is a difference of the corresponding sine waves:

$$\frac{1}{2}\cos(\omega_0 t)\cos(\omega_{\text{ref}}t) = \frac{1}{4}\cos((\omega_0+\omega_{\text{ref}})t) + \frac{1}{4}\cos((\omega_0-\omega_{\text{ref}})t), \tag{5.5}$$

$$-\frac{1}{2}\cos(\omega_0 t)\sin(\omega_{\text{ref}}t) = -\frac{1}{4}\sin((\omega_0+\omega_{\text{ref}})t) + \frac{1}{4}\sin((\omega_0-\omega_{\text{ref}})t). \tag{5.6}$$

The high-frequency waves are filtered out by a low-pass filter, resulting in signals oscillating with a low frequency $\omega_0-\omega_{\text{ref}}$. If $\omega_{\text{ref}} = -\omega_{\text{radio}}$, then $\omega_0-\omega_{\text{ref}} = \Omega$. The procedure, similar to the demodulation in an ordinary radio receiver, thus produces audio signals in both channels

$$\cos(\omega_0 t) \to \begin{cases} \frac{1}{2}\cos(\omega_0 t) \to \frac{1}{2}\cos(\omega_0 t)\cos(\omega_{\text{ref}}t) \to \frac{1}{4}\cos(\Omega t) \\ \frac{1}{2}\cos(\omega_0 t) \to -\frac{1}{2}\cos(\omega_0 t)\sin(\omega_{\text{ref}}t) \to \frac{1}{4}\sin(\Omega t) \end{cases} \tag{5.7}$$

It is convenient to treat the signals in the individual channels as a real and imaginary component of a single complex number, denoted $y(t)$ in this text:

$$y(t) = \frac{1}{4}\cos(\Omega t) + \mathrm{i}\frac{1}{4}\sin(\Omega t) = \frac{1}{4}\mathrm{e}^{\mathrm{i}\Omega t}. \tag{5.8}$$

5.1.3 Analog-digital conversion

The output of the quadrature receiver is converted to a digital form. Therefore, the information obtained from an NMR experiment is a set of complex numbers describing the signal intensities at the time points $t \in \{0, \Delta t, 2\Delta t, \cdots, (N-1)\Delta t\}$.

5.1.4 Signal averaging and signal-to-noise ratio

The NMR signal induced by precession of the magnetization vector is very weak, comparable to the *noise*, generated mostly by random motions of electrons in the receiver coil. Therefore, the NMR experiments are usually repeating several times, adding the signal together. If the experiment is repeated in the same manner N-times, the evolution of the magnetization vector is identical in all repetitions (magnetization is evolving *coherently*), and the sum of the signals from the individual measurements, called *transients*, is simply $Ny(t)$. However, the absolute size of the signal is not important, what really matters is the *signal-to-noise* ratio. Therefore, it is also important how noise accumulates when adding signals of separate measurements.

The noise $n(t)$ is random and so its average[1] $\langle n(t)\rangle = 0$. The size of the noise is typically defined by the *root-mean-square* $\sqrt{\langle n(t)^2\rangle}$. Sum of the noise from N independent experiments is

$$\sqrt{\left\langle (n_1(t) + n_2(t) + \cdots + n_N(t))^2 \right\rangle}. \tag{5.9}$$

Because the random motions of electrons in the individual experiments are not correlated (are independent), all terms like $\langle 2n_1(t)n_2(t)\rangle$ are equal to zero. Therefore, calculation of the square in Eq. 5.9 simplifies to

$$\sqrt{\left\langle (n_1(t) + n_2(t) + \cdots + n_N(t))^2 \right\rangle} = \sqrt{\langle n_1(t)^2\rangle + \langle n_2(t)^2\rangle + \cdots + \langle n_N(t)^2\rangle}. \tag{5.10}$$

We can also assume that the root-mean-square is the same in all experiments, and write it as $\sqrt{\langle n(t)^2\rangle}$. The sum of the noise can be then calculated as

$$\sqrt{N\langle n(t)^2\rangle} = \sqrt{N}\sqrt{\langle n(t)^2\rangle}. \tag{5.11}$$

We can now calculate the signal-to-noise ratio as

$$\frac{Ny(t)}{\sqrt{N}\sqrt{\langle n(t)^2\rangle}} = \sqrt{N}\frac{y(t)}{\sqrt{\langle n(t)^2\rangle}}. \tag{5.12}$$

The signal-to-noise ratio is proportional to the square root of the number of summed transients.

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[1] To avoid writing the integrals defining averaging, we indicate the time average by the angled brackets.

5.2 Fourier transformation

The effect of electrons (chemical shift) makes NMR signal much more interesting but also much more complicated. Oscillation of the voltage induced in the receiver coil is not described by a cosine function, but represents a superposition (sum) of several cosine curves (phase-shifted and dumped). It is practically impossible to get the frequencies of the individual cosine functions just by looking at the recorded interferograms. Fortunately, the signal acquired as a function of time can be converted into a frequency dependence using a straightforward mathematical procedure, known as *Fourier transformation*.

It might be useful to present the basic idea of the Fourier transformation in a pictorial form before we describe details of Fourier transformation by mathematical equations. The oscillating red dots in Figure 5.1 represent an NMR signal defined by one frequency ν. Let us assume that the signal oscillates as a cosine function but we do not know the frequency. We generate a testing set of cosine functions of different known frequencies f_j (blue curves in Figure 5.1) and we multiply each blue testing function by the red signal. The resulting product is plotted as magenta dots in Figure 5.1. Then we sum the values of the magenta points for each testing frequency getting one number (the sum) for each blue function. Finally, we plot these numbers (the sums) as the function of the testing frequency. How does the plot looks like? If the testing frequency differs from ν, the magenta dots oscillate around zero and their sum is close to zero (slightly positive or negative, depending on how many points were summed). But if we are lucky and the testing frequency matches ν (f_3 in Figure 5.1), the result is always positive (we always multiply two positive numbers or two negative numbers). The sum is then also positive, the larger the more points are summed. Therefore, the sum for the matching frequency is much higher than the other sums, making a positive peak in the final green plot (the dependence on f_j). The final plot represents a *frequency spectrum* and the position of the peak immediately identifies the value of the unknown frequency. If the NMR signal is composed of two frequencies, the red dots oscillate in a wild interference patterns, not allowing to get the frequency simply by measuring the period of the oscillation. However, the individual components (if they are sufficiently different) just make several peaks in the final green plot and their frequencies can be easily obtained by reading the positions of the peaks.

Let us now try to describe the Fourier transformation in a bit more mathematical manner. We start with a special case of a signal which can be described by a sum of cosine functions with frequencies that are integer multiples of some small frequency increment $\Delta\omega$. All such cosine functions must have the same value at time t and $t + 2\pi/\Delta\omega$: the whole signal periodic with the period $2\pi/\Delta\omega$. If we record such a signal using quadrature detection, we obtain

$$y(t) = \sum_{k=-\infty}^{\infty} \mathcal{A}_k \mathrm{e}^{\mathrm{i}\omega_k t} = \sum_{k=-\infty}^{\infty} \mathcal{A}_k \mathrm{e}^{\mathrm{i}k\Delta\omega t}. \tag{5.13}$$

The mentioned periodicity allows us to determine $\mathcal{A}_k$ by calculating the integrals

$$\int\limits_0^{\frac{2\pi}{\Delta\omega}} y(t)\mathrm{e}^{-\mathrm{i}\omega_j t}\mathrm{d}t = \sum_{j=-\infty}^{\infty} \mathcal{A}_j \int\limits_0^{\frac{2\pi}{\Delta\omega}} \mathrm{e}^{\mathrm{i}(k-j)\Delta\omega t}\mathrm{d}t = \frac{2\pi}{\Delta\omega}\mathcal{A}_k \tag{5.14}$$

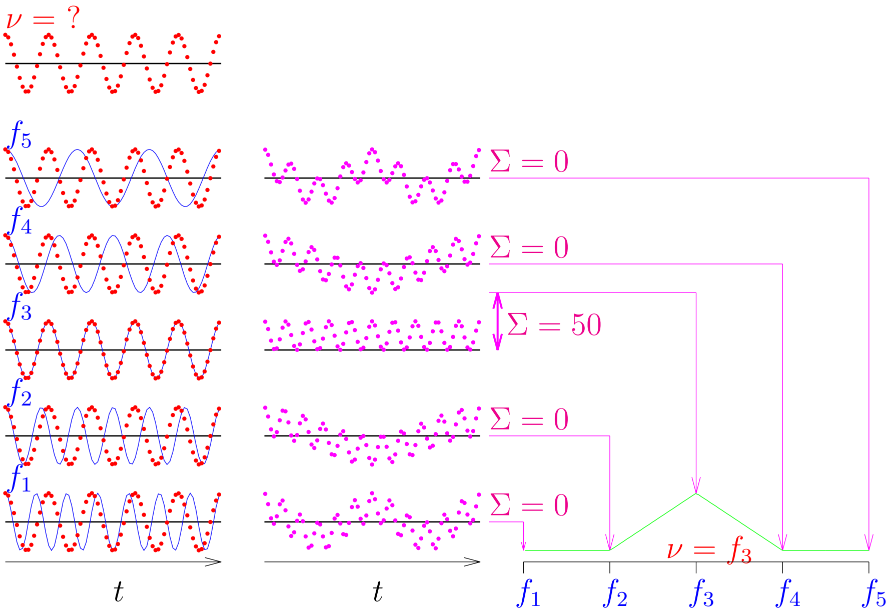

Figure 5.1: The basic idea of Fourier transformation.

(All integrated functions are periodic and their integrals are therefore equal to zero with the exception of the case when $k = j$, which is a constant function).

The same result is obtained for any integration limits which differ by $2\pi/\Delta\omega$, e.g.

$$\int\limits_{-\frac{\pi}{\Delta\omega}}^{+\frac{\pi}{\Delta\omega}} y(t)\mathrm{e}^{-\mathrm{i}\omega_j t}\mathrm{d}t = \sum_{j=-\infty}^{\infty} \mathcal{A}_j \int\limits_{-\frac{\pi}{\Delta\omega}}^{+\frac{\pi}{\Delta\omega}} \mathrm{e}^{\mathrm{i}(k-j)\Delta\omega t}\mathrm{d}t = \frac{2\pi}{\Delta\omega}\mathcal{A}_k \tag{5.15}$$

We can now continue in two different directions. We can describe the signal as it is actually measured, not as a continuous function of time, but as a discrete series of points sampled in time increments Δt. Then, the integral in Eq. 5.14 is replaced by summation of a finite number of measured signal points:

$$Y_k = \sum_{j=0}^{N-1} y_j \mathrm{e}^{-\mathrm{i}k\Delta\omega j\Delta t}\Delta t, \tag{5.16}$$

where $Y_k = \frac{2\pi}{\Delta\omega}\mathcal{A}_k$. As the time and frequency are treated in the same manner, we can also define the inverse operation

$$y_j = \sum_{k=0}^{N-1} Y_k \mathrm{e}^{\mathrm{i}k\Delta\omega j\Delta t}\Delta\omega. \tag{5.17}$$

This way of the signal analysis, discussed in more details in Section 5.2.4, handles the signal as it is measured in reality. It is also instructive to follow the other direction and to increase the period $2\pi/\Delta\omega$ by decreasing $\Delta\omega$. The series of ω_k becomes a continuous variable ω and $\pi/\Delta\omega \to \infty$ if $\Delta\omega \to 0$. The sum in Eq. 5.13 is replaced by the integral

$$\boxed{y(t) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} Y(\omega)\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega \qquad (5.18)}$$

and the integral in Eq. 5.15 becomes

$$\boxed{Y(\omega) = \int\limits_{-\infty}^{\infty} y(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t. \qquad (5.19)}$$

If we apply Eq. 5.19 to a function $y(t)$ and Eq. 5.18 to the obtained result, we should get back the function $y(t)$. Such a double transformation can be written as

$$y(t) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} Y(\omega)\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega \int\limits_{-\infty}^{\infty} y(t')\mathrm{e}^{-\mathrm{i}\omega t'}\mathrm{d}t' = \int\limits_{-\infty}^{\infty} y(t')\mathrm{d}t' \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega(t-t')}\mathrm{d}\omega. \tag{5.20}$$

This requires the second integral to be equal to 2π for $t' = t$ and to zero for $t' \neq t$. Therefore, the integral can be used to define the *delta* function

$$\delta(t-t') = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega(t-t')}\mathrm{d}\omega. \tag{5.21}$$

An alternative definition

$$Y(\omega) = \frac{1}{\sqrt{2\pi}}\int\limits_{-\infty}^{\infty} y(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t, \tag{5.22}$$

$$y(t) = \frac{1}{\sqrt{2\pi}}\int\limits_{-\infty}^{\infty} Y(\omega)\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}\omega. \tag{5.23}$$

is equally acceptable.

Although the actual NMR signal is not recorded and processed in a continuous manner, the idealized continuous Fourier transformation helps to understand the fundamental relation between the shapes of FID and frequency spectra and reveals important features of signal processing. Therefore, we discuss the continuous Fourier transformation before we proceed to the discrete analysis.

5.2.1 Fourier transformation of an ideal NMR signal

An "ideal signal" (see Figure 5.2) has the form $y(t) = 0$ for $t \leq 0$ and $y(t) = \mathcal{A}\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega t}$ for $t \geq 0$, where $\mathcal{A}$ can be a complex number (*complex amplitude*), including the real amplitude $|\mathcal{A}|$ and the initial phase ϕ_0:

$$\mathcal{A} = |\mathcal{A}|\mathrm{e}^{\phi_0}. \tag{5.24}$$

$$Y(\omega) = \int\limits_{-\infty}^{\infty} y(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t = \int\limits_{0}^{\infty} \mathcal{A}\mathrm{e}^{(\mathrm{i}(\Omega-\omega)-R_2)t}\mathrm{d}t = \frac{-\mathcal{A}}{\mathrm{i}(\Omega-\omega)-R_2} = \mathcal{A}\frac{1}{R_2-\mathrm{i}(\Omega-\omega)}\frac{R_2+\mathrm{i}(\Omega-\omega)}{R_2+\mathrm{i}(\Omega-\omega)} = \mathcal{A}\frac{R_2+\mathrm{i}(\Omega-\omega)}{R_2^2+(\Omega-\omega)^2} \tag{5.25}$$

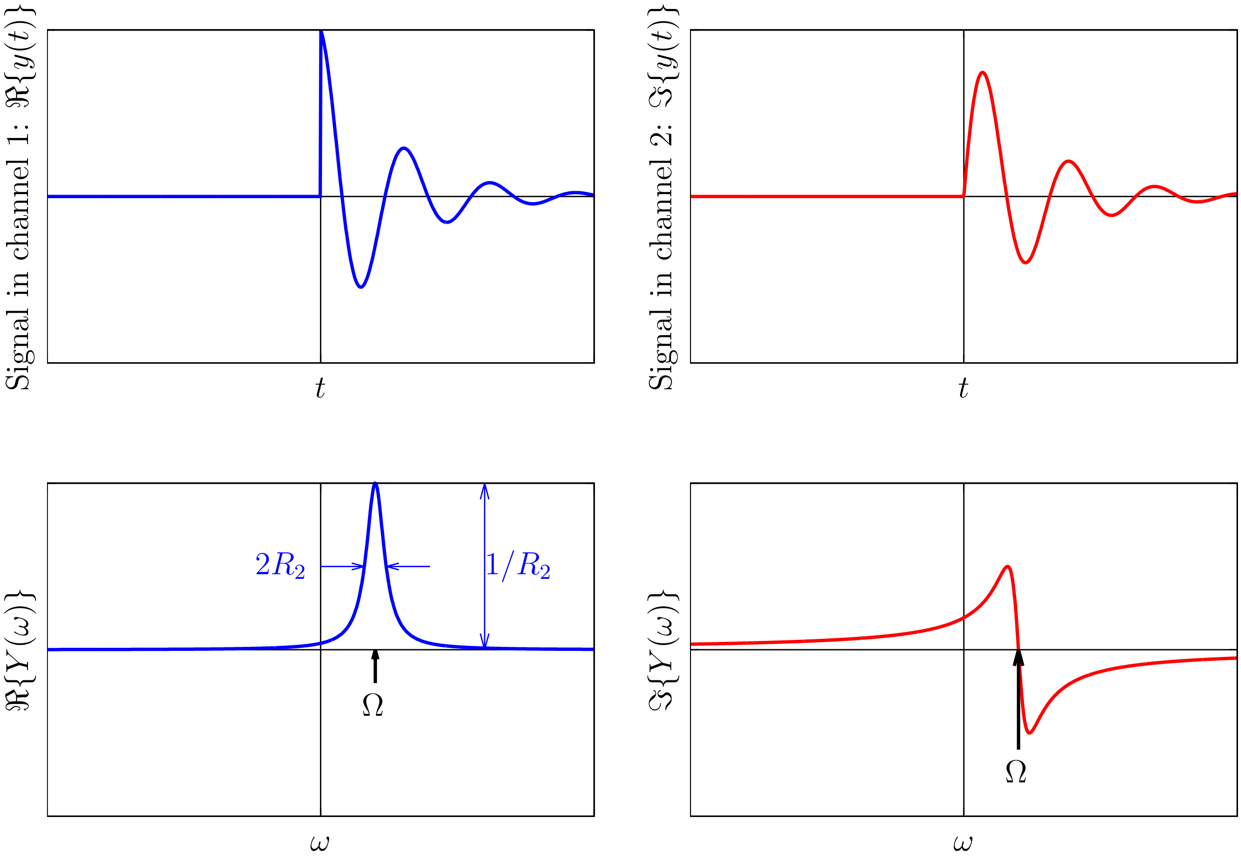

Figure 5.2: Ideal signal detected with a quadrature detection (top) and its Fourier transform (bottom).

Fourier transform of the "ideal" signal is

$$Y(\omega) = \int\limits_{-\infty}^{\infty} \mathcal{A}\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t = \mathcal{A}\frac{R_2}{R_2^2+(\Omega-\omega)^2} + \mathrm{i}\mathcal{A}\frac{\Omega-\omega}{R_2^2+(\Omega-\omega)^2} \tag{5.26}$$

If $\phi_0 = 0$, the blue term, known as the *absorption line* is a real function ($\Re\{Y(\omega)\}$) having a shape of the *Lorentz curve* (see Figure 5.2). The shape of the absorption line is given[2] by the relaxation rate R_2:

- Peak height $\propto 1/R_2$ ($Y = Y_{\max}$ at $\omega = \Omega \Rightarrow Y_{\max} = Y(\Omega) = \mathcal{A}/R_2$)
- Linewidth at the half-height $= 2R_2$ ($Y = Y_{\max}/2$ at $\Omega - \omega = \pm R_2$)

The red term, the *dispersion line*, is purely imaginary ($\Im\{Y(\omega)\}$) if $\phi_0 = 0$. Such shape is less convenient in real spectra containing several lines because the broad wings of the dispersion line distort the shape of the neighbouring lines (see Figure 5.2).

Figure 5.3 documents that Fourier transformation allows us to immediately determine several Larmor frequencies in spectra even if the signal in the time domain (FID) is very difficult to interpret, and that the real (absorption) part of the complex spectrum is much better for such purpose.

The discussed transformation of a continuous signal is extremely useful for understanding the relation between evolution of the magnetization vector and shape of the peaks observed in the frequency spectra. But in reality, the signal is finite ($t_{\max} < \infty$) and discrete ($\Delta t > 0$):

- $t \in \{0, \Delta t, 2\Delta t, \cdots, (N-1)\Delta t\}$ $\quad y(t) \in \{y_0, y_1, y_2, \cdots, y_{N-1}\}$
- $\omega \in \{0, \Delta\omega, 2\Delta\omega, \cdots, (N-1)\Delta\omega\}$ $\quad Y(t) \in \{Y_0, Y_1, Y_2, \cdots, Y_{N-1}\}$

The seemingly marginal difference between ideal and real (finite and discrete) signal has several practical consequences, discussed below.

Figures 5.4 and 5.5 document the advantage of recording the signal with the quadrature detection, as a complex number. If we take only the signal from the first channel, oscillating as the cosine function if $\phi = 0$, and stored as the real part if the quadrature detection is used (Figure 5.4), and perform the Fourier transformation, we get a spectrum with two peaks with the frequency offsets Ω and $-\Omega$. Such a spectrum does not tell us if the actual Larmor frequecy is $\omega_0 = \omega_{\text{radio}} - \Omega$ or $\omega_0 = \omega_{\text{radio}} + \Omega$. If we use the signal from the second channel only, oscillating as the sine function if $\phi = 0$ (Figure 5.5), a spectrum with two peaks is obtained again, the only difference is that the peaks have

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[2] In practice, it is also affected by inhomogeneities of the static magnetic field, increasing the apparent value of R_2. This effect is known as *inhomogeneous broadening*.

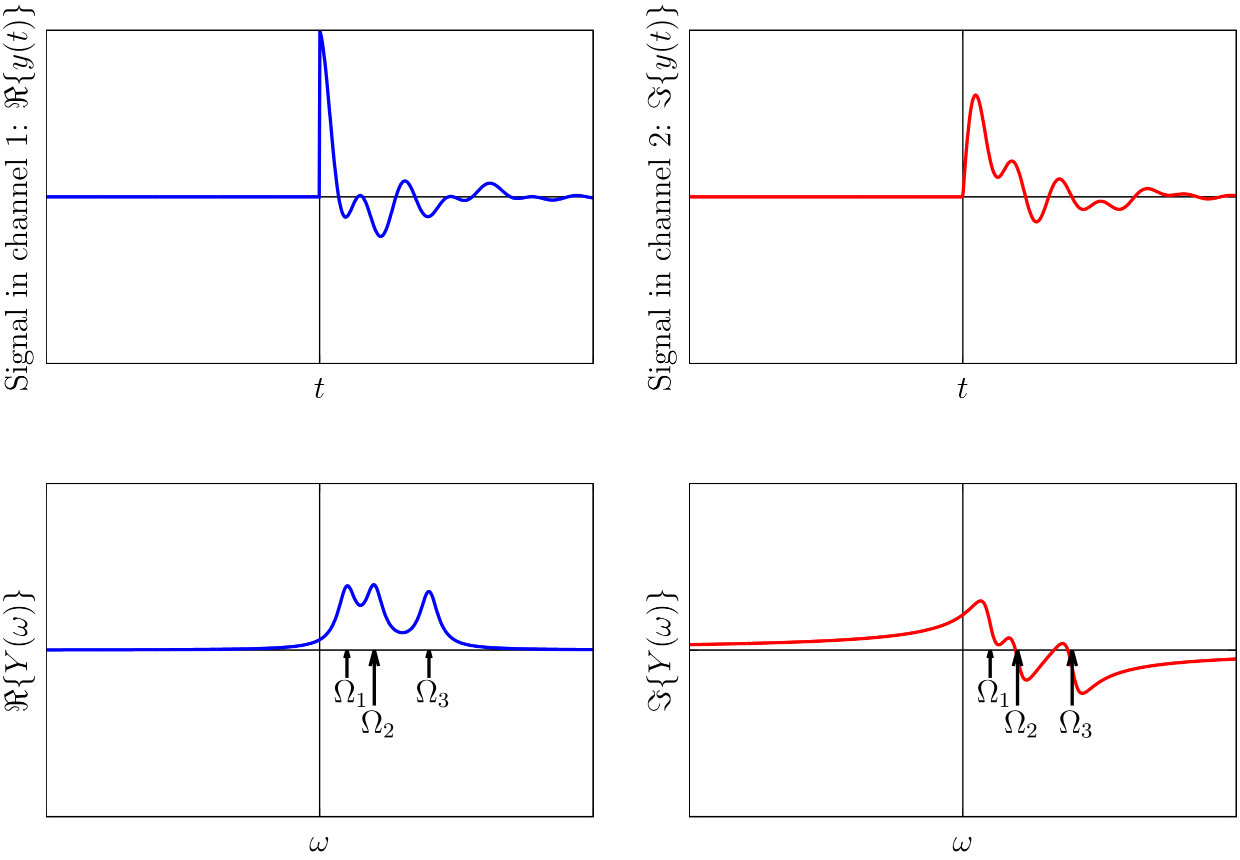

Figure 5.3: Signal (top) and frequency spectrum (bottom) with three Larmor frequencies.

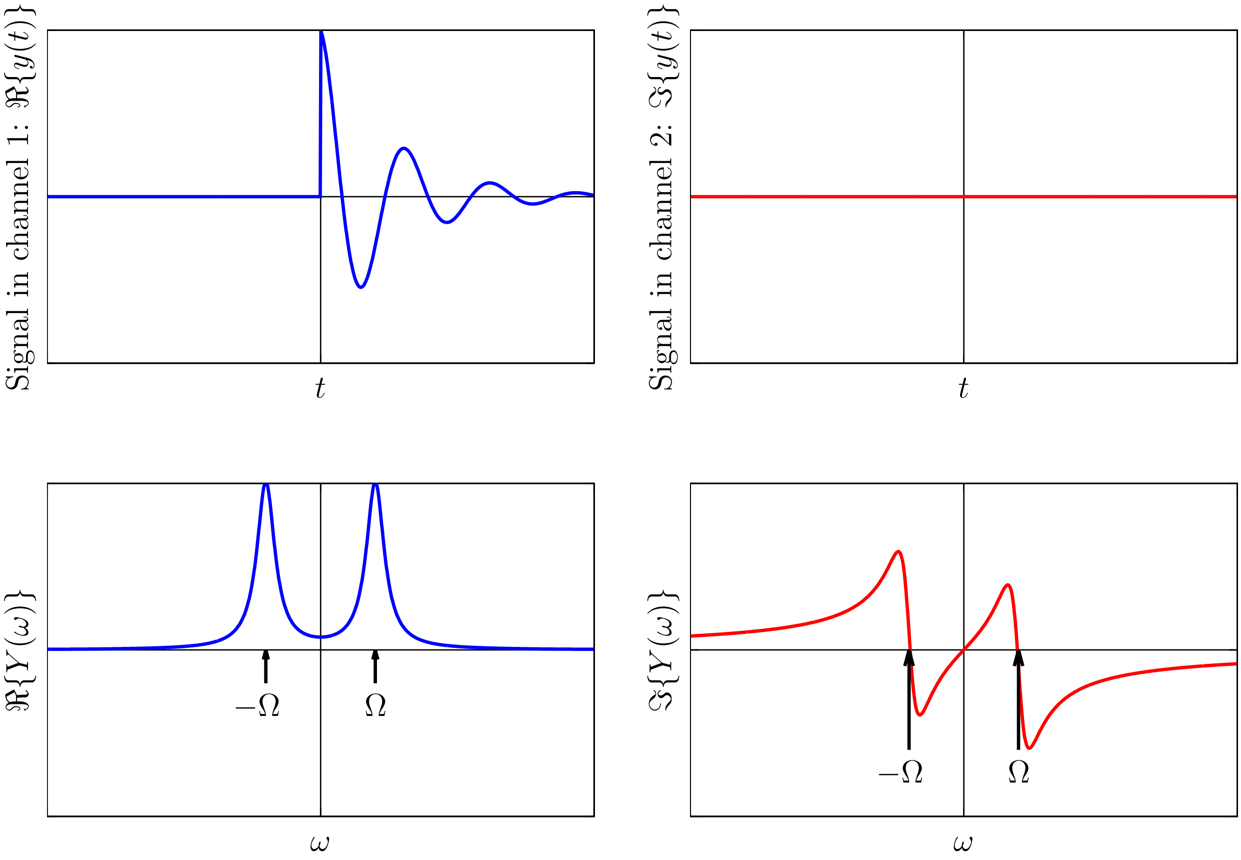

Figure 5.4: A signal detected in the first ("real") channel (top) and its Fourier transform (bottom).

opposite phase (i.e., their phases differ by 180 °). But if we combine both signals, the false peaks at $-\Omega$ disappear because they have opposite signs and cancel each other in the sum of the spectra.

5.2.2 Properties of continuous Fourier transformation

The continuous Fourier transformation has several important properties:

- *Parseval's theorem* $\int\limits_{-\infty}^{\infty} |y(t)|^2 \mathrm{d}t = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} |Y(\omega)|^2 \mathrm{d}\omega$

  A conservation law, documents that the signal energy (information content) is preserved by the Fourier transformation.

- *Linearity* $\int\limits_{-\infty}^{\infty} (y(t) + z(t)) \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{d}t = Y(\omega) + Z(\omega)$

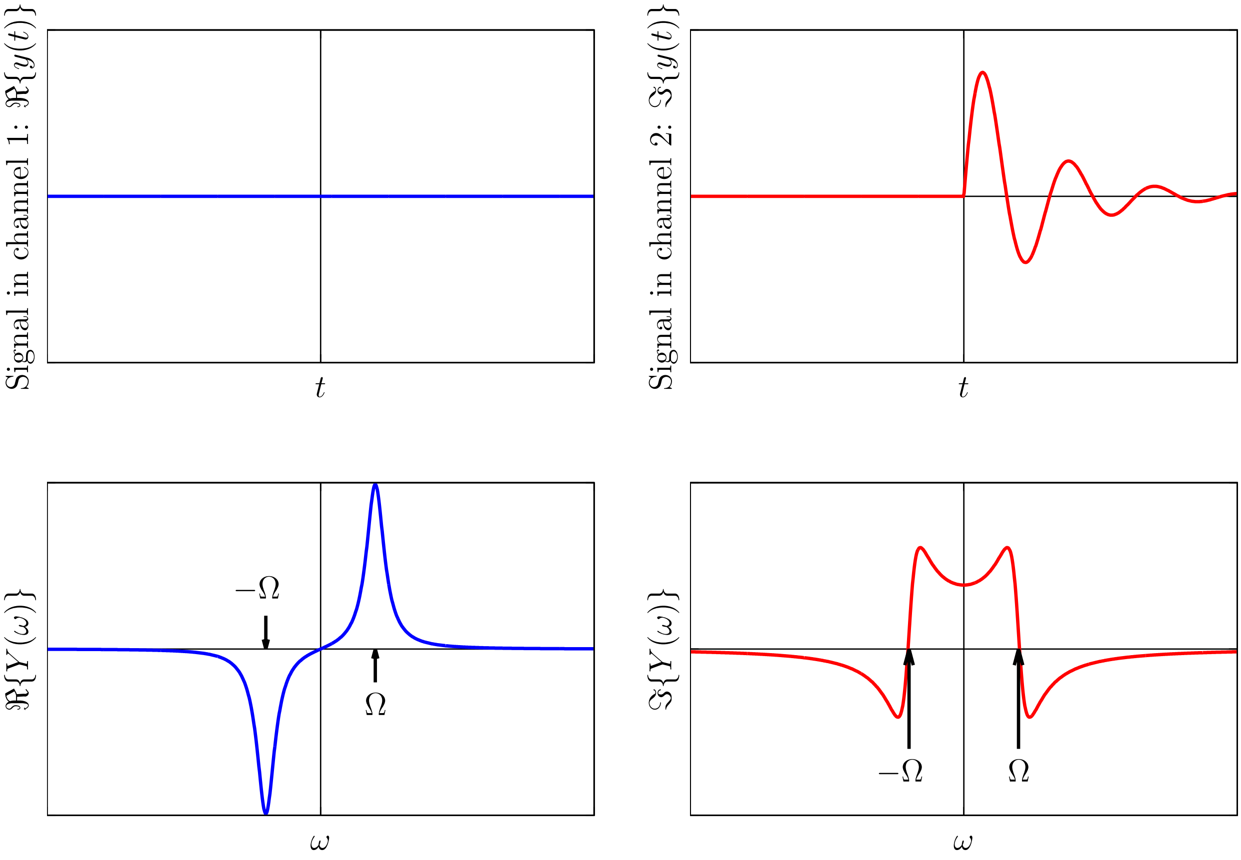

Figure 5.5: A signal detected in the second (”imaginary”) channel (top) and its Fourier transform (bottom).

It documents that a sum of periodic functions (difficult to be distinguished in the time domain) can be converted to a sum of resonance peaks (easily distinguishable in the frequency domain if the resonance frequencies differ).

- *Convolution* $\int\limits_{-\infty}^{\infty}(y(t)\cdot z(t))\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t=\int\limits_{-\infty}^{\infty}Y(\omega)Z(\omega-\omega')\mathrm{d}\omega'$

  It provides mathematical description of apodization (Section 5.5)

- *Time shift* $\int\limits_{-\infty}^{\infty}y(t-t_0)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t=Y(\omega)\mathrm{e}^{-\mathrm{i}\omega t_0}$

  It shows that time delays result in frequency-dependent phase shifts in the frequency domain (Section 5.3)

- *Frequency modulation* $\int\limits_{-\infty}^{\infty}y(t)\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t=Y(\omega-\omega_0)$

  It shows that the apparent frequencies can be shifted after acquisition.

- *Causality* $\int\limits_{-\infty}^{\infty}y(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t=\int\limits_{0}^{\infty}y(t)\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{d}t$

  It says that no signal is present before the radio-wave pulse (this is why we can start integration at $t=0$ or $t=-\infty$, $y(t)=0$ for $t<0$). This provides an extra piece of information allowing us to reconstruct the imaginary part of the signal from the real one and vice versa (Figure 5.6).

The mentioned consequence of causality is rather subtle. As mentioned above, the NMR signal is recorded in two channels, as a real and imaginary part of a complex number. It is because Fourier transformation of a cosine (or sine) function gives a symmetric (or antisymmetric) spectrum with two frequency peaks and thus does not allow us to distinguish frequencies higher than the carrier frequency from those lower than the carrier frequency. Once we have the transformed complex signal in the frequency domain, we can ask whether we need both its parts (real and imaginary). It looks like we do because the inverse Fourier transformation of just the real (imaginary) part produces a symmetric (antisymmetric) picture in the time domain (the second row in Figure 5.6). But the causality tells us that this is not a problem because we know that there is no signal left from the zero time – the symmetry does not bother us because we know that we can reconstruct the time signal simply by discarding the left half of the inverse Fourier image (the third row in Figure 5.6). The time signal reconstructed from the real part of the frequency spectrum only, can be then Fourier transformed to provide the missing imaginary part of the frequency spectrum.

5.2.3 Consequence of finite signal acquisition

In reality, the acquisition of signal stops at a finite time t_{max}:

$$Y(\omega)=\int\limits_{0}^{t_{\mathrm{max}}}\mathcal{A}\mathrm{e}^{(\mathrm{i}(\Omega-\omega)-R_2)t}\mathrm{d}t=\mathcal{A}\frac{1-\mathrm{e}^{-R_2t_{\mathrm{max}}}\mathrm{e}^{\mathrm{i}(\Omega-\omega)t_{\mathrm{max}}}}{R_2-\mathrm{i}(\Omega-\omega)}. \tag{5.27}$$

It has some undesirable consequences:
Leakage: Part of the signal is lost, peak height $Y(\Omega)<\mathcal{A}/R_2$.

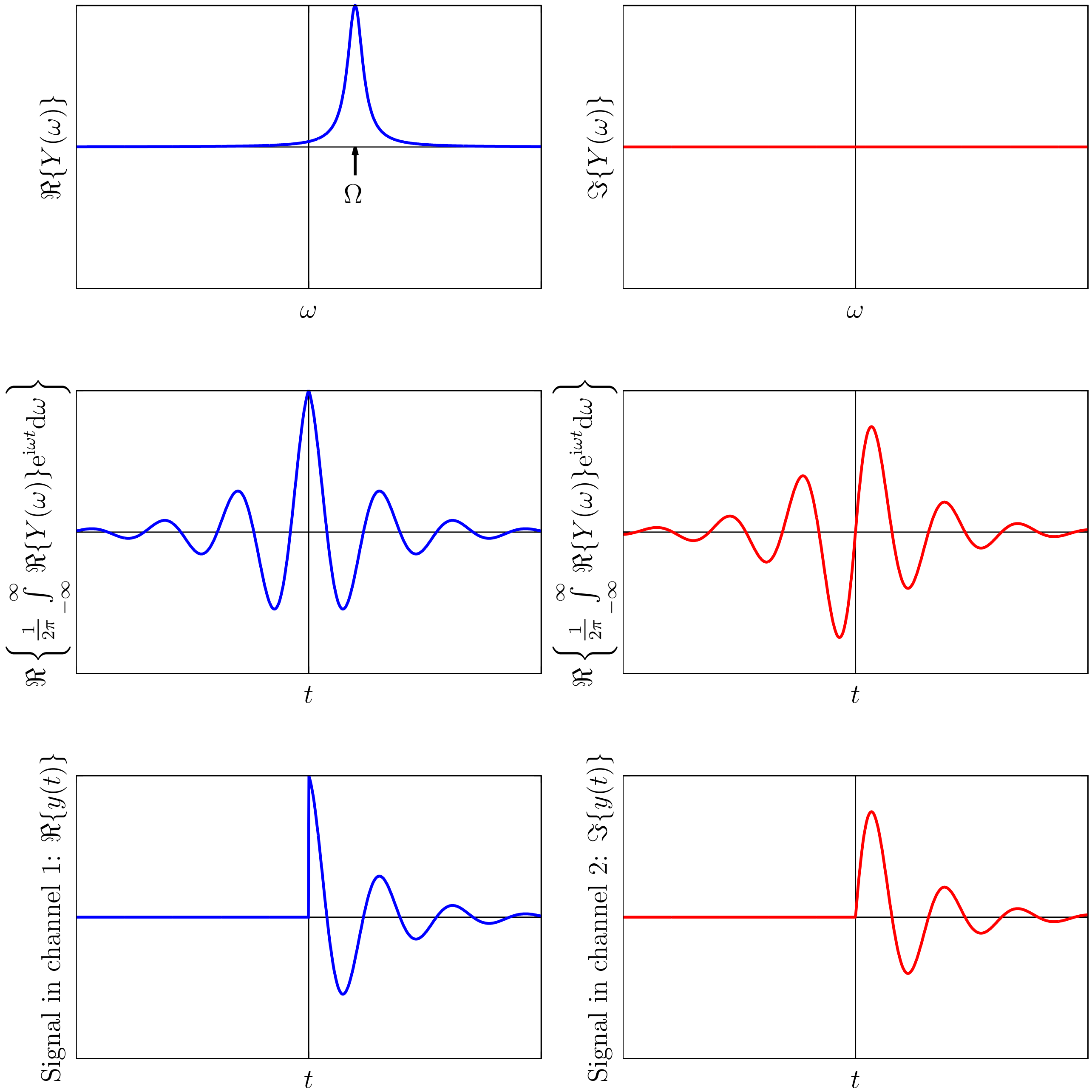

Figure 5.6: Causality of NMR signal. If we take a frequency spectrum, discard its imaginary part (the first row), and perform the inverse Fourier transformation, we do not get the original signal (starting at $t = 0$), but a set of symmetric (real part) and antisymmetric (imaginary part) functions predicting non-zero signal before $t = 0$ (the second row). However, we can apply our knowledge that no signal was present before $t = 0$ and multiply the left half of the predicted signal by zero. This recovers the actual signal (the third row). Fourier transformation of this signal provides both real and inmaginary parts of the spectrum, as shown in Figure 5.2.

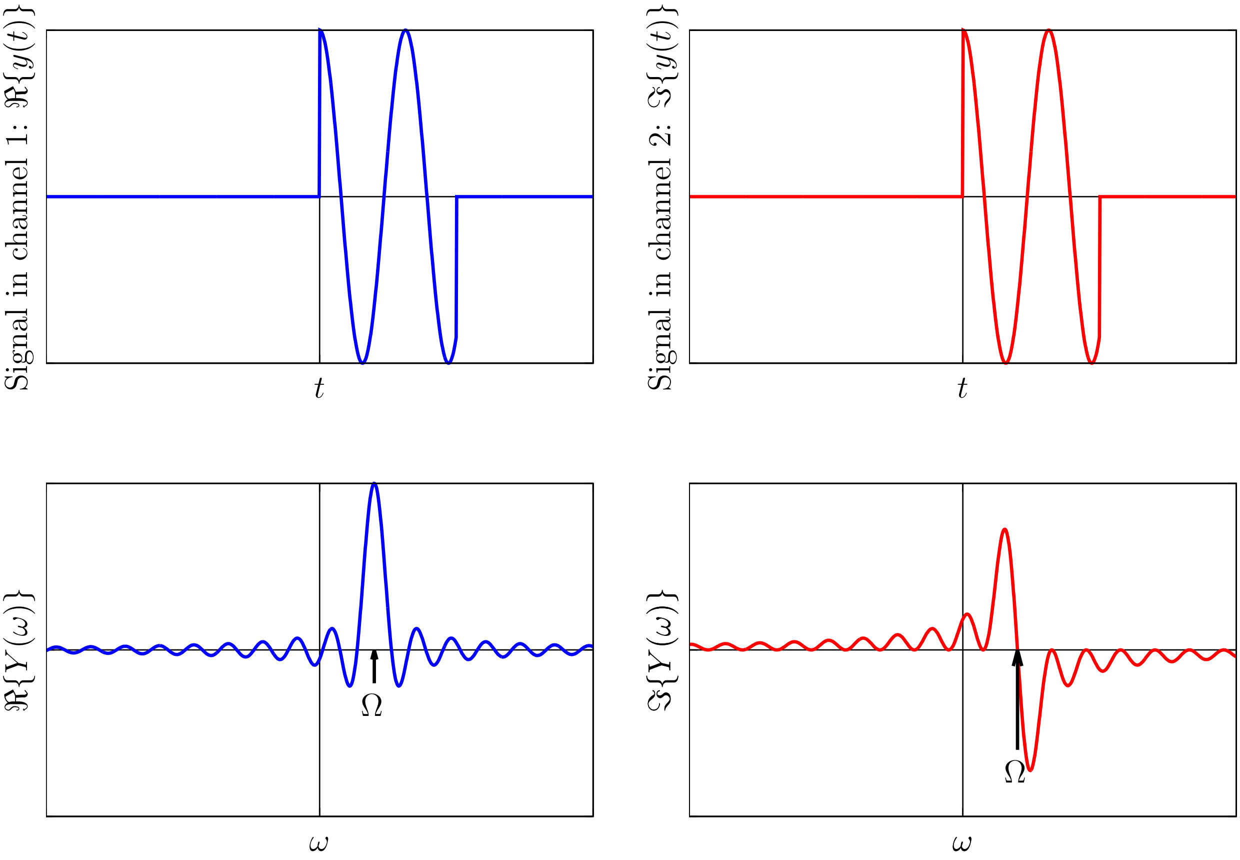

Figure 5.7: Effect of finite acqusition in the limit $R_2 \to 0$.

Truncation artifacts: For $R_2 \to 0$,

$$Y(\omega) = \int\limits_0^{t_{\max}} \mathcal{A}\mathrm{e}^{(\mathrm{i}(\Omega-\omega))t}\mathrm{d}t = \mathcal{A}\frac{1-\mathrm{e}^{\mathrm{i}(\Omega-\omega)t_{\max}}}{-\mathrm{i}(\Omega-\omega)} = \mathcal{A}\frac{\sin(\Omega-\omega)t_{\max}}{\Omega-\omega} + \mathrm{i}\mathcal{A}\frac{1-\cos(\Omega-\omega)t_{\max}}{\Omega-\omega}. \tag{5.28}$$

If the acquisition is stopped before the signal relaxes completely, artifacts (baseline oscillation) appear. In the limit of no relaxation, the real part of the Fourier-transformed signal does not have a pure absorption shape (Lorentz curve), but has a shape of the $\sin(\Omega-\omega)t_{\max}/(\Omega-\omega)t_{\max}$ function (*sinc function*).

5.2.4 Discrete Fourier transformation

In reality, the acquired signal is finite ($t_{\max} < \infty$) and discrete ($\Delta t > 0$):

- $t \in \{0, \Delta t, 2\Delta t, \cdots, (N-1)\Delta t\} \qquad y(t) \in \{y_0, y_1, y_2, \cdots, y_{N-1}\}$

- $\omega \in \{0, \Delta\omega, 2\Delta\omega, \cdots, (N-1)\Delta\omega\} \qquad Y(t) \in \{Y_0, Y_1, Y_2, \cdots, Y_{N-1}\}$

We may try to define the discrete Fourier transform as

$$Y_k = \sum_{j=0}^{N-1} y_j \mathrm{e}^{-\mathrm{i}k\Delta\omega j\Delta t}\Delta t = \sum_{j=0}^{N-1} y_j \mathrm{e}^{-\mathrm{i}2\pi\Delta f\Delta t kj}\Delta t, \tag{5.29}$$

$$y_j = \sum_{k=0}^{N-1} Y_k \mathrm{e}^{\mathrm{i}k\Delta\omega j\Delta t}\Delta t = \sum_{k=0}^{N-1} Y_k \mathrm{e}^{\mathrm{i}2\pi\Delta f\Delta t kj}\Delta f. \tag{5.30}$$

However, there is a catch here. It turns out that Δt and Δf are not independent, but closely related. The transformation can be written in a matrix form as

$$\begin{pmatrix} Y_0 \\ Y_1 \\ Y_2 \\ \vdots \\ Y_{N-1} \end{pmatrix} = \underbrace{\begin{pmatrix} F_{0,0} & F_{0,1} & F_{0,2} & \ldots F_{0,N-1} \\ F_{1,0} & F_{1,1} & F_{1,2} & \ldots F_{1,N-1} \\ F_{2,0} & F_{2,1} & F_{2,2} & \ldots F_{2,N-1} \\ \vdots & \vdots & \vdots & \ddots \vdots \\ F_{N-1,0} & F_{N-1,1} & F_{N-1,2} & \ldots F_{N-1,N-1} \end{pmatrix}}_{\hat{F}} \begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ \vdots \\ y_{N-1} \end{pmatrix} \Delta t, \tag{5.31}$$

where the elements of the matrix $\hat{F}$ are $F_{jk} = \mathrm{e}^{-\mathrm{i}2\pi\Delta f\Delta t\cdot k\cdot j}$.
Let us now try to transform Y_k back to the time domain:

$$\begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ \vdots \\ y_{N-1} \end{pmatrix} = \underbrace{\begin{pmatrix} F^{-1}_{0,0} & F^{-1}_{0,1} & F^{-1}_{0,2} & \ldots F^{-1}_{0,N-1} \\ F^{-1}_{1,0} & F^{-1}_{1,1} & F^{-1}_{1,2} & \ldots F^{-1}_{1,N-1} \\ F^{-1}_{2,0} & F^{-1}_{2,1} & F^{-1}_{2,2} & \ldots F^{-1}_{2,N-1} \\ \vdots & \vdots & \vdots & \ddots \vdots \\ F^{-1}_{N-1,0} & F^{-1}_{N-1,1} & F^{-1}_{N-1,2} & \ldots F^{-1}_{N-1,N-1} \end{pmatrix}}_{\hat{F}^{-1}} \begin{pmatrix} Y_0 \\ Y_1 \\ Y_2 \\ \vdots \\ Y_{N-1} \end{pmatrix} \Delta f, \tag{5.32}$$

where the elements of the matrix $\hat{F}^{-1}$ are $F^{-1}_{jk} = \mathrm{e}^{+\mathrm{i}2\pi\Delta f\Delta t\cdot k\cdot j}$. Substituting from Eq. 5.31,

$$\begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ \vdots \\ y_{N-1} \end{pmatrix} = \begin{pmatrix} F^{-1}_{0,0} & F^{-1}_{0,1} & F^{-1}_{0,2} & \ldots F^{-1}_{0,N-1} \\ F^{-1}_{1,0} & F^{-1}_{1,1} & F^{-1}_{1,2} & \ldots F^{-1}_{1,N-1} \\ F^{-1}_{2,0} & F^{-1}_{2,1} & F^{-1}_{2,2} & \ldots F^{-1}_{2,N-1} \\ \vdots & \vdots & \vdots & \ddots \vdots \\ F^{-1}_{N-1,0} & F^{-1}_{N-1,1} & F^{-1}_{N-1,2} & \ldots F^{-1}_{N-1,N-1} \end{pmatrix} \begin{pmatrix} F_{0,0} & F_{0,1} & F_{0,2} & \ldots F_{0,N-1} \\ F_{1,0} & F_{1,1} & F_{1,2} & \ldots F_{1,N-1} \\ F_{2,0} & F_{2,1} & F_{2,2} & \ldots F_{2,N-1} \\ \vdots & \vdots & \vdots & \ddots \vdots \\ F_{N-1,0} & F_{N-1,1} & F_{N-1,2} & \ldots F_{N-1,N-1} \end{pmatrix} \begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ \vdots \\ y_{N-1} \end{pmatrix} \Delta f\Delta t. \tag{5.33}$$

In order to get the original signal, the product of the transformation matrices,$\hat{F}^{-1}\hat{F}$ multiplied by $\Delta f\Delta t$, must be a unit matrix:

$$\begin{pmatrix} F^{-1}_{0,0} & F^{-1}_{0,1} & F^{-1}_{0,2} & \ldots F^{-1}_{0,N-1} \\ F^{-1}_{1,0} & F^{-1}_{1,1} & F^{-1}_{1,2} & \ldots F^{-1}_{1,N-1} \\ F^{-1}_{2,0} & F^{-1}_{2,1} & F^{-1}_{2,2} & \ldots F^{-1}_{2,N-1} \\ \vdots & \vdots & \vdots & \ddots \vdots \\ F^{-1}_{N-1,0} & F^{-1}_{N-1,1} & F^{-1}_{N-1,2} & \ldots F^{-1}_{N-1,N-1} \end{pmatrix} \begin{pmatrix} F_{0,0} & F_{0,1} & F_{0,2} & \ldots F_{0,N-1} \\ F_{1,0} & F_{1,1} & F_{1,2} & \ldots F_{1,N-1} \\ F_{2,0} & F_{2,1} & F_{2,2} & \ldots F_{2,N-1} \\ \vdots & \vdots & \vdots & \ddots \vdots \\ F_{N-1,0} & F_{N-1,1} & F_{N-1,2} & \ldots F_{N-1,N-1} \end{pmatrix} \Delta f\Delta t = \begin{pmatrix} 1 & 0 & 0 & \ldots 0 \\ 0 & 1 & 0 & \ldots 0 \\ 0 & 0 & 1 & \ldots 0 \\ \vdots & \vdots & \vdots & \ddots \vdots \\ 0 & 0 & 0 & \ldots 1 \end{pmatrix}. \tag{5.34}$$

According to the matrix multiplication rule, the jl-element of the product $\hat{F}^{-1}\hat{F}$ is given by

$$\sum_{k=0}^{N-1} \mathrm{e}^{-\mathrm{i}2\pi\Delta f\Delta t(jk-kl)}\Delta t. \tag{5.35}$$

Clearly, the exponential terms in the sums representing the diagonal elements ($j = l$) are equal to $\mathrm{e}^{-\mathrm{i}2\pi\Delta f\Delta t(jk-kj)}\Delta t = \mathrm{e}^{0} = 1$. Therefore, the diagonal elements (sums of N terms $\mathrm{e}^0 = 1$) are equal to N. Obviously, we need to set $N\Delta f\Delta t = 1$ to get the elements of the product $\hat{F}^{-1}\hat{F}$ equal to one.

What about the off-diagonal elements? For $N\Delta f\Delta t = 1$, the elements of $\hat{F}^{-1}\hat{F}$ are equal to

$$\sum_{k=0}^{N-1}\mathrm{e}^{-\mathrm{i}\frac{2\pi}{N}(j-l)k}\Delta t. \tag{5.36}$$

The complex numbers in the sum can be visualized as points in the Gauss plane (plane of complex numbers) with the phase of $2\pi k(l-j)/N$. Let us assume that N is an integer power of two ($N = 2^n$, a typical choice in discrete Fourier transform). Then all numbers in the series are symmetrically distributed in the Gauss plane. As a consequence, their sum is equal to zero (they cancel each other). We can therefore conclude that setting $N\Delta f\Delta t = 1$ ensures that the product $\hat{F}^{-1}\hat{F}$ is a unit matrix.

The consequences of the requirement $\Delta f\Delta t = 1/N$ are:

- spectral width $N\Delta f = 1/\Delta t$, it is defined by the choice of the time increment
- digital resolution $\Delta f = 1/N\Delta t$, it is defined by the choice of the maximum acquisition time

Possible definitions of the discrete Fourier transform with a correct normalization (so that $\Delta f\Delta t = 1/N$) are

$$Y_k = \sum_{j=0}^{N-1} y_j\mathrm{e}^{-\mathrm{i}\frac{2\pi}{N}kj} \qquad y_j = \frac{1}{N}\sum_{k=0}^{N-1} Y_k\mathrm{e}^{\mathrm{i}\frac{2\pi}{N}kj} \tag{5.37}$$

or

$$Y_k = \frac{1}{\sqrt{N}}\sum_{j=0}^{N-1} y_j\mathrm{e}^{-\mathrm{i}\frac{2\pi}{N}kj} \qquad y_j = \frac{1}{\sqrt{N}}\sum_{k=0}^{N-1} Y_k\mathrm{e}^{\mathrm{i}\frac{2\pi}{N}kj}. \tag{5.38}$$

5.2.5 Consequence of discrete signal acquisition

The "ideal" NMR signal converted to the digital form

$$y_j = \mathcal{A}\mathrm{e}^{-R_2 j\Delta t}\mathrm{e}^{\mathrm{i}2\pi\nu j\Delta t} \tag{5.39}$$

has a Fourier transform

$$Y_k = \sum_{j=0}^{N-1}\mathcal{A}\mathrm{e}^{-R_2 j\Delta t}\mathrm{e}^{\mathrm{i}2\pi\nu j\Delta t}\mathrm{e}^{-\mathrm{i}\frac{2\pi}{N}kj}\Delta t. \tag{5.40}$$

The summation formula

$$\sum_{j=0}^{N-1} z^j = \frac{1-z^N}{1-z} \tag{5.41}$$

helps us to evaluate the sum. For the sake of simplicity, let us assume that the carrier frequency is chosen so that the peak is in the middle of the spectrum

$$\nu = \frac{1}{2}N\Delta f = \frac{1}{2\Delta t}. \tag{5.42}$$

Then, z and z^N in the summation formula are

$$z = \mathrm{e}^{-R_2\Delta t}\mathrm{e}^{\mathrm{i}2\pi\left(\frac{1}{2}-\frac{k}{N}\right)} = \underbrace{\mathrm{e}^{-R_2\Delta t}}_{1-R_2\Delta t}\underbrace{\mathrm{e}^{\mathrm{i}\pi}}_{-1}\mathrm{e}^{-\mathrm{i}2\pi\frac{k}{N}} = -(1-R_2\Delta t)\mathrm{e}^{-\mathrm{i}2\pi\frac{k}{N}}, \tag{5.43}$$

$$z^N = \mathrm{e}^{-R_2N\Delta t}\mathrm{e}^{\mathrm{i}\pi(N-2k)}. \tag{5.44}$$

Therefore,

$$Y_k = \mathcal{A}\Delta t\frac{1-\mathrm{e}^{-R_2N\Delta t}\mathrm{e}^{\mathrm{i}\pi(N-2k)}}{1+(1-R_2\Delta t)\mathrm{e}^{-\mathrm{i}2\pi\frac{k}{N}}}. \tag{5.45}$$

- The signal is discrete ⇒ the spectral width is limited $\Delta t > 0 \Rightarrow N\Delta f = 1/\Delta t < \infty$

The consequences of the discrete sampling are:

Aliasing: If we add a value of $N\Delta f$ to the frequency which was originally in the middle of the frequency spectrum ($\frac{1}{2}N\Delta f = \frac{1}{2\Delta t}$), the second exponent in Eq. 5.40 changes from $\mathrm{i}\pi j$ to $\mathrm{i}3\pi j$, i.e. by one period (2π), and the transformed signal (the spectrum) does not change. In general, a peak of the real frequency $\nu+N\Delta f$ (outside the spectral width) appears at the apparent frequency ν in the spectrum (*Nyquist theorem*: frequencies ν and $\nu+1/\Delta t$ cannot be distinguished).

Offset: Peak height of the continuous Fourier transform $Y(f) = \mathcal{A}/R_2$ and offset of the continuous Fourier transform $Y(\pm\infty) = 0$. Peak height of the discrete Fourier transform.

$$Y_{\frac{N}{2}} = \mathcal{A}\Delta t\frac{1-\mathrm{e}^{-R_2N\Delta t}}{R_2\Delta t} \to \mathcal{A}/R_2 \tag{5.46}$$

for $N\Delta t \to \infty$, but offset of the discrete Fourier transform

$$Y_0 = \mathcal{A}\Delta t\frac{1-\mathrm{e}^{-R_2N\Delta t}\mathrm{e}^{\mathrm{i}N\pi}}{2-R_2\Delta t} \to \frac{1}{2}\mathcal{A}\Delta t = \frac{1}{2}y_0\Delta t \tag{5.47}$$

for $N\Delta t \to \infty$ and $\Delta t \to 0$. The offset of discrete Fourier transform is non-zero, equal to half of the intensity of the signal at the first time point $y(0)$ if the signal was acquired sufficiently long to relax completely ($N\Delta t \gg 1/R_2$).

Loss of causality: The algorithm of the discrete Fourier transform assumes that the signal is periodic. This contradicts the causality theorem: a periodic function cannot be equal to zero for $t < 0$ and different from zero $t > 0$. The causality must be introduced

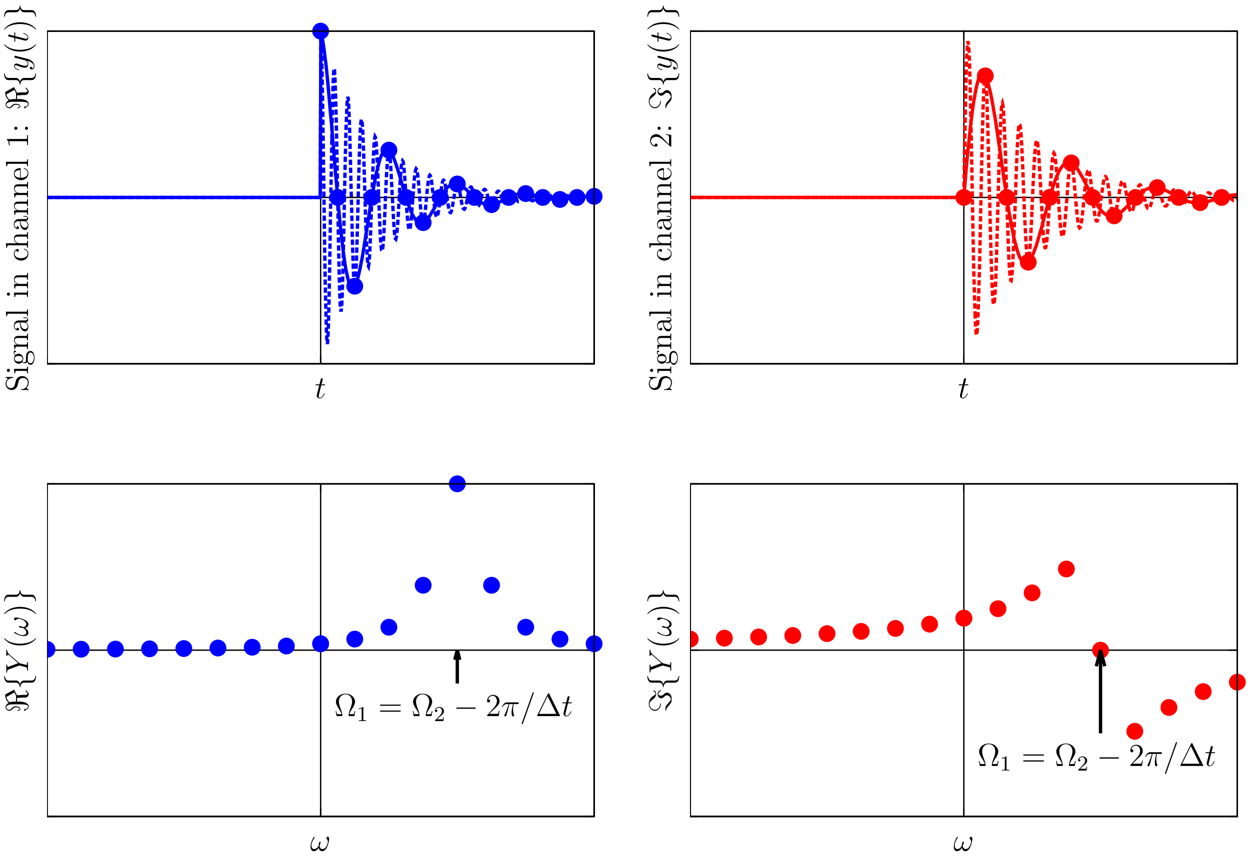

Figure 5.8: Aliasing. If the signal is acquired in discrete time intervals (dots in the top plots), the signals with frequencies different by an integer multiple of $2\pi/\Delta t$, shown by solid (Ω_1) and dotted (Ω_2) lines, cannot be distinguished. Both signals give a peak with the same frequency in the spectrum. This frequency is equal to Ω_1 and to $\Omega_2 - 2\pi/\Delta t$, where $2\pi/\Delta t$ is the width of the spectrum.

in a sort of artificial manner. After recording N time points, another N zeros should be added to the signal[3] (see Section 5.4).

5.3 Phase correction

So-far, we ignored the effect of the initial phase ϕ_0 and analyzed Fourier transforms of NMR signals consisting of a collection of (damped) cosine functions, with zero initial phase. In reality, the signal has a non-zero phase, difficult to predict

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[3] In practice, the zeros are added *after* the last point of the measured signal, not before the first one, as one may expect based on the fact that signal should be equal to zero for $t < 0$.

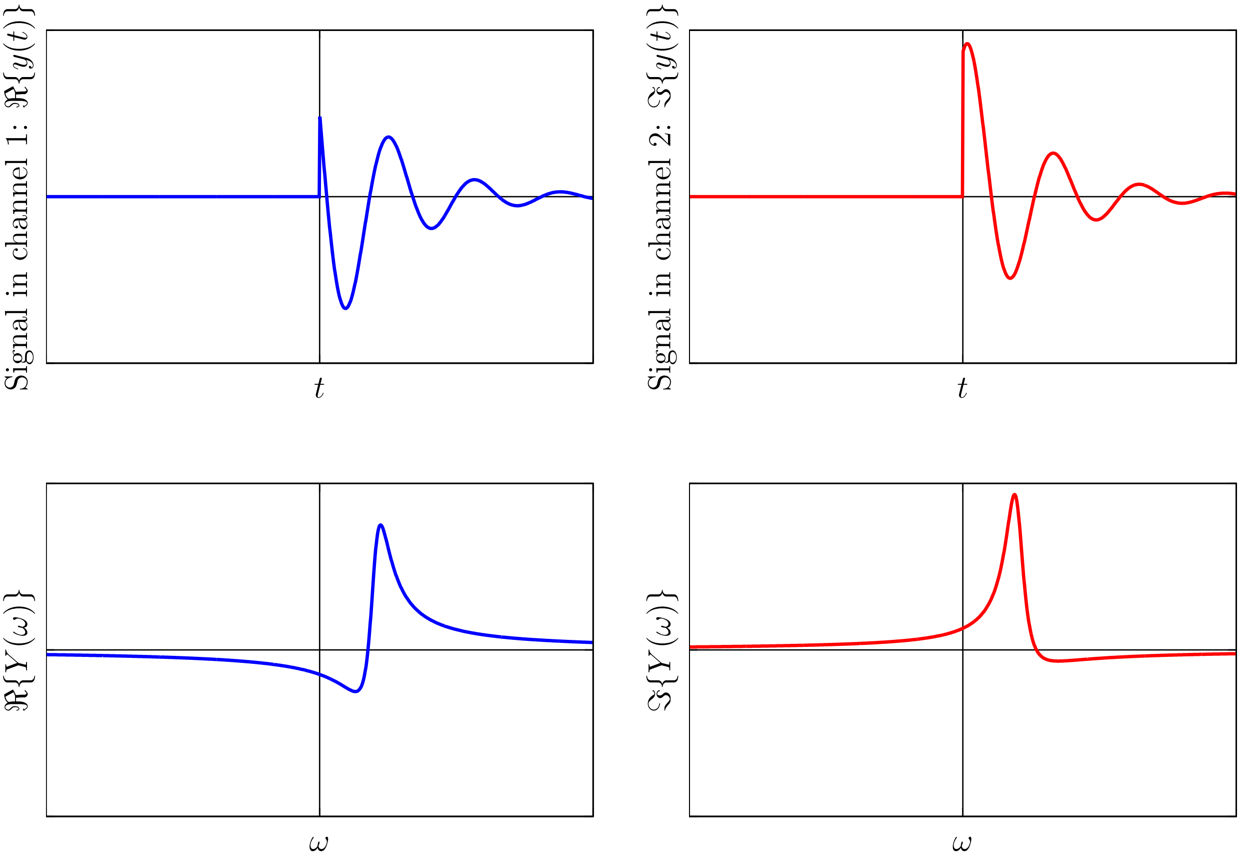

Figure 5.9: A signal with the initial phase of 60 ° (top) provides distorted spectra (bottom), unless a phase correction is applied.

$$y(t) = \mathcal{A}\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega(t+t_0)} = |\mathcal{A}|\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega(t+t_0)+\phi_0}. \tag{5.48}$$

The phase has a dramatic impact on the result of the Fourier transformation. Real and imaginary parts are mixtures of absorption and dispersion functions. If we plot the real part as a spectrum, it looks really ugly for a non-zero phase.

For a single frequency, the phase correction is possible (multiplication by the function $\mathrm{e}^{-(\mathrm{i}\Omega t_0+\phi_0)}$, where t_0 and ϕ_0 are found empirically):

$$|\mathcal{A}|\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega(t+t_0)+\phi_0}\mathrm{e}^{-(\mathrm{i}\Omega t_0+\phi_0)} = |\mathcal{A}|\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega t}. \tag{5.49}$$

In practice, phase corrections are applied also to signal with more frequencies – multiplication by a function $\mathrm{e}^{-\mathrm{i}(\vartheta_0+\vartheta_1\omega)}$, where ϑ_0 and ϑ_1 are zero-order and first-order phase corrections, respectively (we try to find ϑ_0 and ϑ_1 giving the best-looking spectra).

Note that phase correction is *always necessary*, but only approximative corrections are possible for a signal with multiple frequencies!

5.4 Zero filling

Routinely, a sequence of N_Z zeros is appended to the recorded signal, mimicking data obtained at time points $N\Delta t$ to $(N+N_Z-1)\Delta t$:

$$\begin{array}{l} \begin{array}{cccccc} 0, & \Delta t, & 2\Delta t, & \cdots, & (N-1)\Delta t \\ y_0, & y_1, & y_2, & \cdots, & y_{N-1} \end{array} \\ \downarrow \\ \begin{array}{cccccccccc} 0, & \Delta t, & 2\Delta t, & \cdots, & (N-1)\Delta t, & N\Delta t, & (N+1)\Delta t, & \cdots, & (N+N_Z-1)\Delta t \\ y_0, & y_1, & y_2, & \cdots, & y_{N-1}, & 0, & 0, & \cdots, & 0 \end{array} \end{array} \tag{5.50}$$

This may look like a completely artificial procedure, but there are several practical reasons to do it.

1. The very fast computational algorithm of calculating Fourier transform, known as *Cooley–Tukey FFT*, requires the number of time points to be an integer power of 2. If the number of collected time points N is not a power of 2, N_Z zeros are added to the data prior to Fourier transformation so that $N+N_Z$ is an integer power of 2.

2. In order to obtain a spectrum with the full content of information by discrete Fourier transformation, the collected data must be extended by a factor of 2 by zero-filling. As discussed in Section 5.2.5, this operation reintroduces causality and the full information content of N experimental complex points (i.e., N points of the real part and N points of the imaginary part, together $2N$ bits of information) is encoded in the spectrum (i.e., in the real part of the Fourier transform, which now consists of $2N$ frequency points because we artificially increased the maximum time from $N-1$ to $2N-1$ and therefore narrowed the frequency sampling step Δf from $1/N\Delta t$ to $1/2N\Delta t$).

3. The *digital resolution* $\Delta\nu$, given by $1/(N\Delta t)$, can be improved (narrowed) to $1/((N+N_Z)\Delta t)$ by zero-filling. In this manner, the visual appearance of spectra can be improved by interpolation between data points. Note, however, that adding more than N zeros does not improve the informational content of the spectrum. Although the digital resolution is improved, the real resolution is the same, zero-filling does not help to resolve frequencies that differ less than $1/(N\Delta t)$!

5.5 Apodization

The NMR signal is very often multiplied by a so-called *window function* prior to Fourier transformation.[4] This process is known as *apodization.* The goal is to

1. *improve resolution.* As the resolution is given by $1/(N\Delta t)$, resolution is improved if the signal is multiplied by a window function that amplifies the late data points.

2. *improve sensitivity.* Due to the relaxation, signal of data acquired at later time points is lower, but the noise is the same. Therefore, the late time points decrease the signal-to-noise ratio. The sensitivity can be improved by discarding or attenuating the late time points.

3. *suppress truncation artifacts.* We have seen that oscillations of the baseline appear if the data acquisition stops before the signal relaxes to zero (i.e., to the noise level). The desired effect of relaxation can be mimicked by a window function that smoothly converges to zero at $N\Delta t$.

Obviously, the three listed goals are in conflict, and only a compromise can been reached. There is no "best apodization". The choice of the optimal window function depends on the actual needs.

The simplest window function is a *rectangle*: multiplying the signal by a rectangular function equal to 1 for $j\Delta t \leq m\Delta t$ and to 0 for $j\Delta t > m\Delta t$ represents discarding data recorded for times longer than $m\Delta t$. It is a very useful way of improving signal-to-noise ratio if the signal relaxed before $m\Delta t$. Otherwise, it produces severe truncation artifacts.

The highest signal-to-noise ratio is provided by a *matched filter* window function. The matched filter has the shape of the envelope of the signal. The matched filter for our ideal signal is $\mathrm{e}^{-R_2 j\Delta t}$. The price paid for the signal-to-noise improvement is a lower resolution: Multiplying $\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega\Delta t}$ by $\mathrm{e}^{-R_2 t}$ obviously doubles the linewidth, given by the decay rate, which is now $2R_2$.

The best balance between resolution and truncation artifacts for an allowed extra line broadening λ is obtained with the *Dolph–Chebyshev* window, defined as

$$\frac{1}{\sqrt{N}}\sum_{k=0}^{N-1}\frac{\cos\left(2(N-1)\arccos\frac{\cos(\pi k/N)}{\cos(\pi\lambda\Delta t/2)}\right)}{\cosh\left(2(N-1)\mathrm{arccosh}\frac{1}{\cos(\pi\lambda\Delta t/2)}\right)}\mathrm{e}^{\mathrm{i}\frac{2\pi}{N}kj}, \tag{5.51}$$

which is, however, not used in practice due to its very complex form.

Instead, *sine-bell* windows $\sin^p\left(\frac{2\pi-\phi}{N}j+\phi\right)$ are used routinely, usually with the phase $\phi = \pi/2$ (i.e., cosine function) and with the power $p = 1$ or $p = 2$.

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[4] The mathematical expression describing the Fourier-transformed product of two functions, signal and window in our case, is given by the convolution theorem, presented in Section 5.2.2.

Summary of conventions

As mentioned in the preceding chapters, some of the conventions used in practical NMR spectroscopy do not follow directly from the physical analysis of NMR.

- The phase of the rotating coordinated system is chosen to be π for nuclei with $\gamma > 0$ and 0 for nuclei with $\gamma < 0$. As a consequence, $\vec{\omega}_1$ does not depend on the sign of γ. The exciting irradiation by radio waves, defining the rotating coordinate system, always rotates the magnetization vector about the $+x$ axis, from the z to the $-y$ direction (after 90° rotation), etc.

- The frequency axes of NMR spectra is plotted from left to right for nuclei with $\gamma > 0$, but from right to left for nuclei with $\gamma < 0$. As the nuclei with $\gamma > 0$ have negative $\omega_0 = -\gamma B_0$, peaks of $\gamma > 0$ nuclei precessing faster, i.e., having a higher positive chemical shift δ, are shifted to the left in the spectra. The nuclei with $\gamma < 0$ have positive $\omega_0 = -\gamma B_0$, but peaks of $\gamma < 0$ nuclei precessing faster, i.e., having a higher positive chemical shift δ, are also shifted to the left in the spectra because the spectrum is plotted in the opposite direction. The position of the peak in the spectrum does not depend on the sign of γ, it is only given by the value of its chemical shift, which increases from right to left.

- The zero value of the chemical shift is not given by the absence of shielding by electrons, but by the chosen reference compound. The zero value of the frequency offset Ω is given by the value of $-\omega_{\text{radio}}$, chosen by the operator in each NMR experiment. If the spectrum is plotted in Hertz, the position of zero is defined just by the experimental setup. If the spectrum is plotted in ppm and the zero value was correctly calculated based on a comparison with the reference compound, the position of zero and all values of chemical shifts are independent of the experimental conditions and unambiguously defined for the given chemical compound. Always report position of peaks in ppm!

Part II

Quantum description

Chapter 6

Spin

Literature: This chapter starts with a brief review of quantum mechanics. Textbooks covering this topic represent the best source of information. Brown presents in B9 a useful review of classical mechanics, usually missing in the quantum mechanics textbooks (assuming that students learnt the classical mechanics earlier, which is true in the case of students of physics, but not so often in the case of chemistry or biology students), and reviews quantum mechanics in B13, B15, and B16. B1–B5 provides overview of the relevant mathematical tools. NMR books also provide some introduction. Keeler reviews quantum mechanics in very understandable fashion, using the concept of spin from the very beginning (K3.2 and K6). Levitt proceeds more like us (L6–7). A condensed summary is presented in C2.1 (short, rigorous, but not a good start for a novice). Introduction to the special theory of relativity can be found in B10, but relativistic quantum mechanics is not discussed in the literature recommended for this course or in general physical chemistry textbooks (despite the important role of spin in chemistry). Therefore, more background information is presented here than in the other chapters. NMR can be correctly described if the spin is introduced *ad hoc*. The purpose of Section 6.8 is to show how the spin emerges naturally. Origin of nuclear magnetism is touched in L1.3 and L1.4. Quantum mechanics of spin angular momentum is reviewed in K6, L7, and L10.

6.1 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):

$$\Psi = C\mathrm{e}^{\mathrm{i}2\pi(\frac{x}{\lambda}-\frac{t}{T})} = C\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px-Et)}, \tag{6.1}$$

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 C (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 → integration).

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

$$\langle v|v\rangle = \vec{v}^\dagger\cdot\vec{v} = \sum_{j=1}^{N} v_j^*v_j, \tag{6.2}$$

$$\langle f|f\rangle = \int\limits_{-\infty}^{\infty} f^*(x)f(x)\mathrm{d}x. \tag{6.3}$$

6.2 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.

$$\Psi(x,t) = c_1\underbrace{A\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}}_{\psi_1} + c_2\underbrace{A\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)}}_{\psi_2} + \cdots \tag{6.4}$$

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*:

$$\int\limits_{-\infty}^{\infty} \mathcal{A}^* \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\mathcal{A}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)}\mathrm{d}x = |\mathcal{A}|^2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_1-E_2)t}\int\limits_{-\infty}^{\infty}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1-p_2)x}\mathrm{d}x =$$

$$|\mathcal{A}|^2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_1-E_2)t}\int\limits_{-\infty}^{\infty}\cos\frac{(p_1-p_2)x}{\hbar}\mathrm{d}x + \mathrm{i}|\mathcal{A}|^2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_1-E_2)t}\int\limits_{-\infty}^{\infty}\sin\frac{(p_1-p_2)x}{\hbar}\mathrm{d}x = 0 \tag{6.5}$$

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. 6.5 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

$$\int\limits_{-\infty}^{\infty}\Psi^*\Psi\mathrm{d}x = P = 1 \tag{6.6}$$

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

$$\int\limits_{-\infty}^{\infty}(c_1^*c_1 + c_2^*c_2 + \cdots)\mathrm{d}x = 1. \tag{6.7}$$

6.3 Operators and possible results of measurement

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.

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. 6.4? Calculation of $\partial\Psi/\partial x$ gives us a clue:

$$\frac{\partial\Psi}{\partial x} = c_1\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + c_2\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots = \frac{\mathrm{i}}{\hbar}p_1c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + \frac{\mathrm{i}}{\hbar}p_2c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots \tag{6.8}$$

It implies that

$$-\mathrm{i}\hbar\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} = p_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}, \quad -\mathrm{i}\hbar\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} = p_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)}, \ldots \tag{6.9}$$

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:

$$p_1 = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\left(-\mathrm{i}\hbar\frac{\partial}{\partial x}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\right) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}p_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} = p_1\underbrace{\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}}_{=1}. \tag{6.10}$$

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

$$\langle\psi_j|\hat{A}\psi_j\rangle = \langle\psi_j|A_j\cdot\psi_j\rangle = A_j\underbrace{\langle\psi_j|\psi_j\rangle}_{=1} = A_j. \tag{6.11}$$

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 $|\psi_j\rangle$.

6.4 Expected result of measurement

Eq. 6.11 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

$$\langle A\rangle = \langle\Psi|\hat{A}|\Psi\rangle. \tag{6.12}$$

There are three ways how to do the calculation described by Eq. 6.12:

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. 6.3

$$\langle A\rangle = \langle\Psi|\hat{A}|\Psi\rangle \equiv \langle\Psi|(\hat{A}\Psi)\rangle = \int_{-\infty}^{\infty}\cdots\left(\Psi^*(x,\ldots)\hat{A}\Psi(x,\ldots)\mathrm{d}x\ldots\right). \tag{6.13}$$

Three dots in Eq. 6.13 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. 6.13 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

$$\langle A\rangle = \begin{pmatrix} c_1^* \; c_2^* \cdots \end{pmatrix} \begin{pmatrix} A_1 & 0 & \cdots \\ 0 & A_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \tag{6.14}$$

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. 6.14 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 $\hat{A}$)

$$\Psi = c'_1\psi'_1 + c'_2\psi'_2 + \cdots \tag{6.15}$$

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

$$\hat{P}' = \begin{pmatrix} c'_1 c'^*_1 & c'_1 c'^*_2 & \cdots \\ c'_2 c'^*_1 & c'_2 c'^*_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{6.16}$$

Multiply the matrix $\hat{P}'$ by a matrix[1] $\hat{A}'$ representing the operator $\hat{A}$ in the basis

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[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. 6.15, 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 $\hat{A}$.

$\psi'_1, \psi'_1, \ldots$. The sum of the diagonal elements (called *trace*) of the resulting matrix $\hat{P}'\hat{A}'$ is equal to the expected value $\langle A\rangle$

$$\langle A\rangle = \mathrm{Tr}\{\hat{P}'\hat{A}'\}. \tag{6.17}$$

Why should we use such a bizarre way of calculating the expected value of A when it can be calculated easily from Eq. 6.14? The answer is that Eq. 6.17 is *more general.* We can use the same basis for operators with different sets of eigenfunctions.

6.5 Operators of position and momentum

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

6.5.1 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. 6.9). If a particle moves in a general direction, operators of components of the momentum tensor are derived in the same manner.

$$\hat{p}_x \equiv -\mathrm{i}\hbar\frac{\partial}{\partial x}, \tag{6.18}$$

$$\hat{p}_y \equiv -\mathrm{i}\hbar\frac{\partial}{\partial y}, \tag{6.19}$$

$$\hat{p}_z \equiv -\mathrm{i}\hbar\frac{\partial}{\partial z}. \tag{6.20}$$

6.5.2 Operator of position

The wave function $\Psi(x,t)$ defined by Eq. 6.4 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.

$$\hat{x} \equiv x\,\cdot \qquad \hat{y} \equiv y\,\cdot \qquad \hat{z} \equiv z\,\cdot \tag{6.21}$$

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:

$$x\Psi(x,t) = \begin{pmatrix} x_1c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x_1-E_1t)} + x_1c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x_1-E_2t)} + x_1c_3\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3x_1-E_3t)} + \cdots \\ x_2c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x_2-E_1t)} + x_2c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x_2-E_2t)} + x_2c_3\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3x_2-E_3t)} + \cdots \\ x_3c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x_3-E_1t)} + x_3c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x_3-E_2t)} + x_3c_3\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3x_3-E_3t)} + \cdots \\ \vdots \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \end{pmatrix}. \tag{6.22}$$

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

$$\Psi(x_2,t) = \begin{pmatrix} 0 \\ c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x_2-E_1t)} + c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x_2-E_2t)} + c_3\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3x_2-E_3t)} + \cdots \\ 0 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ \psi_2 \\ 0 \\ \vdots \end{pmatrix} \tag{6.23}$$

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

$$x_2\Psi(x_2,t) = \begin{pmatrix} 0 \\ x_2\left(c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x_2-E_1t)} + c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x_2-E_2t)} + c_3\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_3x_2-E_3t)} + \cdots\right) \\ 0 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ x_2\psi_2 \\ 0 \\ \vdots \end{pmatrix}. \tag{6.24}$$

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.

6.5.3 Commutators

If we apply two operators subsequently to the same wave function, order of the operators sometimes does not matter.

For example, $\hat{x}\hat{p}_y\Psi = \hat{p}_y\hat{x}\Psi$ ($\hat{x}$ 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

$$\hat{x}\hat{p}_x\Psi = -\mathrm{i}\hbar x\frac{\partial\Psi}{\partial x} \tag{6.25}$$

but

$$\hat{p}_x\hat{x}\Psi = -\mathrm{i}\hbar\frac{\partial(x\Psi)}{\partial x} = -\mathrm{i}\hbar\Psi - \mathrm{i}\hbar x\frac{\partial\Psi}{\partial x}. \tag{6.26}$$

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 reveals the basic commutation relations:

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

Written in a mathematically compact form,

$$[\hat{r}_j,\hat{p}_k] = \mathrm{i}\hbar\delta_{j,k} \qquad [\hat{r}_j,\hat{r}_k] = [\hat{r}_j,\hat{p}_k] = 0, \tag{6.27}$$

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. 6.4. However, we can also use Eq. 6.27 as the fundamental definition and Eq. 6.4 as its consequence:

We postulate that operators of position and momentum obey the relations

$$[\hat{r}_j, \hat{p}_k] = \mathrm{i}\hbar\delta_{j,k} \qquad [\hat{r}_j, \hat{r}_k] = [\hat{p}_j, \hat{p}_k] = 0. \tag{6.28}$$

Note that we only postulate relations between operators. Other choices are possible and correct as long as Eq. 6.27 holds.

6.6 Operator of energy and equation of motion

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

$$\frac{\partial\Psi}{\partial t} = c_1\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + c_2\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots = -\frac{\mathrm{i}}{\hbar}E_1c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} - \frac{\mathrm{i}}{\hbar}E_2c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} - \cdots \tag{6.29}$$

and consequently

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} = E_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)}, \quad \mathrm{i}\hbar\frac{\partial}{\partial t}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} = E_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)}, \quad \ldots \tag{6.30}$$

1. First, we obtain the *operator of energy* from Eq. 6.30, in analogy to Eq. 6.9.
2. The second achievement is Eq. 6.29 itself. Energy of free particles is just the kinetic energy (by definition). Therefore, all energies E_j in the right-hand side of Eq. 6.29 can be written as

$$E_j = \frac{mv_j^2}{2} = \frac{p_j^2}{2m}, \tag{6.31}$$

resulting in

$$\frac{\partial\Psi}{\partial t} = -\frac{\mathrm{i}}{\hbar}\left(\frac{p_1^2}{2m}c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + \frac{p_2^2}{2m}c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots\right). \tag{6.32}$$

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

$$\frac{1}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{2m}\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial x} = -\frac{1}{\hbar^2}\left(\frac{p_1^2}{2m}c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_1x-E_1t)} + \frac{p_2^2}{2m}c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_2x-E_2t)} + \cdots\right). \tag{6.33}$$

Comparison of Eqs. 6.32 and 6.33 gives us the *equation of motion*

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \cdots. \tag{6.34}$$

If we extend our analysis to particles experiencing a time-independent potential energy $E_{\mathrm{pot}}(x, y, z)$, the energy will be given by

$$E_j = \frac{p_j^2}{2m} + E_{\mathrm{pot}} \tag{6.35}$$

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

$$\frac{\partial\Psi}{\partial t} = -\frac{\mathrm{i}}{\hbar}\left(\frac{p_1^2}{2m}c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_1\vec{r}-E_1t)} + \frac{p_2^2}{2m}c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_2\vec{r}-E_2t)} + \cdots\right) - \frac{\mathrm{i}}{\hbar}E_{\mathrm{pot}}(\vec{r})\Psi \tag{6.36}$$

and

$$\left(\frac{p_1^2}{2m}c_1\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_1\vec{r}-E_1t)} + \frac{p_2^2}{2m}c_2\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\vec{p}_2\vec{r}-E_2t)} + \cdots\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial x^2}\right). \tag{6.37}$$

Substituting Eq. 6.37 into Eq. 6.36 gives us the famous Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = \underbrace{\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2}\right) + E_{\mathrm{pot}}(x,y,z)\right)}_{\hat{H}}\Psi. \tag{6.38}$$

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

In our case, the Hamiltonian is expressed in terms of linear momentum $\vec{p} = m\vec{v}$. In general, the *canonical* (or *generalized*) momentum should be used. The canonical momentum is defined by the Lagrange mechanics. Motions of objects can be described by the least action principle (nicely described in The Feynman lectures on physics, Vol. 2, Chapter 19), which can be formulated as

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}_j} = \frac{\partial\mathcal{L}}{\partial q_j}, \tag{6.39}$$

where q_j are generalized coordinates, the dot represents time derivative, and $\mathcal{L}$ is a scalar function of q_j and $\dot{q}_j$, known as *Lagrangian.* For example, for a free particle moving in one direction (x) in a field described by a potential energy $E_{\mathrm{pot}}(x)$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial v} = \frac{\partial\mathcal{L}}{\partial x}. \tag{6.40}$$

What $\mathcal{L}(x,v)$ gives the correct equation of motion? The equation of motion has the form

$$ma = m\frac{\mathrm{d}v}{\mathrm{d}t} = F = -\frac{\partial E_{\mathrm{pot}}(x)}{\partial x}. \tag{6.41}$$

Since

$$\frac{\partial E_{\mathrm{kin}}(v)}{\partial v} = \frac{\partial\frac{1}{2}mv^2}{\partial v} = mv \quad\Rightarrow\quad \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial E_{\mathrm{kin}}(v)}{\partial v} = m\frac{\mathrm{d}v}{\mathrm{d}t} = ma, \tag{6.42}$$

and

$$\frac{\partial E_{\mathrm{kin}}(v)}{\partial x} = 0, \qquad \frac{\partial E_{\mathrm{pot}}(x)}{\partial v} = 0, \tag{6.43}$$

we see that $\mathcal{L}(x,v)$ can be taken as a difference of the kinetic energy (depending on v, but not on x) and the potential energy (depending on x, but not on v)

$$ma = \frac{\mathrm{d}(mv)}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial(E_{\mathrm{kin}}(v) - E_{\mathrm{pot}}(x))}{\partial v} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial v} = F = -\frac{\partial(E_{\mathrm{kin}}(v) - E_{\mathrm{pot}}(x))}{\partial x} = \frac{\partial\mathcal{L}}{\partial x}. \tag{6.44}$$

Hamiltonian and Lagrangian are related by the Legendre transform[2]

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[2] Legendre transform has a simple graphical representation. If we plot a function of a variable x, e.g. $f(x)$, slope at a certain value of $x = x_0$ is equal to $s(x_0) = (\partial f/\partial x)_{x_0}$. A tangent line $y(x_0)$ touching the plotted f for $x = x_0$ is described by the slope $s(x_0)$ and intercept $a(x_0)$ as $y = a + s(x_0)x_0$. The value of the intercept for all possible values of x_0 can be expressed as a function of the slope $a(s(x_0)) = y(x_0) - s(x_0)x_0 = f(x_0) - s(x_0)x_0$ (y and f are equal at x_0 because they touch each other). If we identify x with q, f with $\mathcal{L}$, and $-a$ with H, we get Eq. 6.45 for a one-dimensional case ($i = 1$).

$$H(q_j,p_j)+\mathcal{L}(q_j,\dot{q}_j)=\sum_j(p_j\cdot\dot{q}_j), \tag{6.45}$$

where

$$p_j=\frac{\partial\mathcal{L}}{\partial\dot{q}_j} \tag{6.46}$$

is the canonical (generalized) momentum. In our example, $p_j=p_x=p$ is the linear momentum mv and the Hamiltonian is $pv-\mathcal{L}=mv^2-\frac{1}{2}mv^2+E_{\mathrm{pot}}=\frac{1}{2}mv^2+E_{\mathrm{pot}}$. The whole procedure may seem to be unnecessarily complicated, but it becomes useful when we analyze motions of magnetic particles in magnetic fields.

Derivation of the Hamiltonian (classical or quantum) for magnetic particles in magnetic fields is much more demanding because the canonical momentum is no longer identical with the linear momentum. We start our analysis by searching for a classical Lagrangian describing motion of a charged particle in a magnetic field. We know that the Lagrangian should give us the Lorentz force

$$\vec{F}=Q(\vec{E}+\vec{v}\times\vec{B}). \tag{6.47}$$

The information about $\vec{E}$ and $\vec{B}$ can be extracted from the following Maxwell equations

$$\vec{\nabla}\cdot\vec{B}=0 \tag{6.48}$$

$$\vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t}, \tag{6.49}$$

but we have to employ our knowledge of vector algebra to handle the divergence in Eq. 6.48 and the curl in Eq. 6.49. It may be unclear at the beginning why we go this way, but the purpose becomes evident when we combine the obtained expressions.

First, we notice that $\vec{a}\cdot(\vec{a}\times\vec{b})=0$ for any vectors $\vec{a}$ and $\vec{b}$ because $\vec{a}\times\vec{b}\perp\vec{a}$. As a consequence, we can replace $\vec{B}$ by a curl (rotation) of some vector $\vec{A}$ because $\vec{\nabla}\cdot(\vec{\nabla}\times\vec{A})=0$ as required by Eq. 6.48. The vector $\vec{A}$ is known as the *vector potential.* The first step gives us a new definition of $\vec{B}$

$$\vec{B}=\vec{\nabla}\times\vec{A} \tag{6.50}$$

which can be inserted into Eq. 6.47

$$\vec{F}=Q(\vec{E}+\vec{v}\times\vec{B})=Q(\vec{E}+\vec{v}\times(\vec{\nabla}\times\vec{A})). \tag{6.51}$$

Using the identity $\vec{a}\times(\vec{b}\times\vec{c})=\vec{b}(\vec{a}\cdot\vec{c})-(\vec{a}\cdot\vec{b})\vec{c}$,

$$\vec{F}=Q(\vec{E}+\vec{v}\times\vec{B})=Q(\vec{E}+\vec{v}\times(\vec{\nabla}\times\vec{A}))=Q(\vec{E}+\vec{\nabla}(\vec{v}\cdot\vec{A})-(\vec{v}\cdot\vec{\nabla})\vec{A}). \tag{6.52}$$

Second, we use our new definition of $\vec{B}$ and rewrite Eq. 6.49 as

$$0=\frac{\partial\vec{B}}{\partial t}+\vec{\nabla}\times\vec{E}=\vec{\nabla}\times\frac{\partial\vec{A}}{\partial t}+\vec{\nabla}\times\vec{E}=\vec{\nabla}\times\left(\frac{\partial\vec{A}}{\partial t}+\vec{E}\right). \tag{6.53}$$

Third, we notice that that for any vector $\vec{a}$ and constant c, $\vec{a}\times(c\vec{a})=0$ because $\vec{a}\parallel c\vec{a}$. As a consequence, we can replace $(\partial\vec{A}/\partial t+\vec{E})$ by a gradient of some scalar V because $\vec{\nabla}\times(\vec{\nabla}(\partial\vec{A}/\partial t+\vec{E}))=\vec{\nabla}\times(-\vec{\nabla}V)=0$ as required by Eq. 6.49. The scalar V is the well-known electric potential and allows us to express $\vec{E}$ as

$$\vec{E}=-\frac{\partial\vec{A}}{\partial t}-\vec{\nabla}V. \tag{6.54}$$

which can be also inserted into Eq. 6.47

$$\vec{F}=Q(\vec{E}+\vec{v}\times\vec{B})=Q\left(-\frac{\partial\vec{A}}{\partial t}-\vec{\nabla}V+\vec{\nabla}(\vec{v}\cdot\vec{A})-(\vec{v}\cdot\vec{\nabla})\vec{A}\right). \tag{6.55}$$

Finally, we notice that

$$\frac{\mathrm{d}\vec{A}}{\mathrm{d}t}=\frac{\partial\vec{A}}{\partial t}+\frac{\partial\vec{A}}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}t}+\frac{\partial\vec{A}}{\partial y}\frac{\mathrm{d}y}{\mathrm{d}t}+\frac{\partial\vec{A}}{\partial z}\frac{\mathrm{d}z}{\mathrm{d}t}=\frac{\partial\vec{A}}{\partial t}+\left(\vec{v}\cdot\vec{\nabla}\right)\vec{A}\quad\Rightarrow\quad\frac{\partial\vec{A}}{\partial t}=\frac{\mathrm{d}\vec{A}}{\mathrm{d}t}-\left(\vec{v}\cdot\vec{\nabla}\right)\vec{A}, \tag{6.56}$$

which shows that $\left(\vec{v}\cdot\vec{\nabla}\right)\vec{A}$ in Eq. 6.55 can be can be included into $\mathrm{d}\vec{A}/\mathrm{d}t$

$$\vec{F}=Q(\vec{E}+\vec{v}\times\vec{B})=Q\left(-\frac{\partial\vec{A}}{\partial t}-\vec{\nabla}V+\vec{\nabla}(\vec{v}\cdot\vec{A})-(\vec{v}\cdot\vec{\nabla})\vec{A}\right)=Q\left(-\frac{\mathrm{d}\vec{A}}{\mathrm{d}t}-\vec{\nabla}V+\vec{\nabla}(\vec{v}\cdot\vec{A})\right). \tag{6.57}$$

Let us now try to write $\mathcal{L}$ as

$$\mathcal{L}=E_{\mathrm{kin}}-E_{\mathrm{el}}+E_{\mathrm{magn}}=\frac{1}{2}mv^2-QV+E_{\mathrm{magn}}, \tag{6.58}$$

where E_{el} is a typical potential energy dependent on position but not on speed, and E_{magn} can depend on both position and speed.

For this Lagrangian,

$$\frac{\partial\mathcal{L}}{\partial x}=\frac{\partial E_{\mathrm{el}}}{\partial x}+\frac{\partial E_{\mathrm{magn}}}{\partial x}=-Q\frac{\partial V}{\partial x}+\frac{\partial E_{\mathrm{magn}}}{\partial x} \tag{6.59}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial v_x}=\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial E_{\mathrm{kin}}}{\partial v_x}+\frac{\partial E_{\mathrm{magn}}}{\partial v_x}\right)=ma_x+\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial E_{\mathrm{magn}}}{\partial v_x}. \tag{6.60}$$

If we use $E_{\mathrm{magn}}=Q\vec{v}\cdot\vec{A}$, Eqs. 6.59 and 6.60 give us

$$ma_x=-Q\left(\frac{\mathrm{d}A_x}{\mathrm{d}t}-\frac{\partial V}{\partial x}+\frac{\partial(\vec{v}\cdot\vec{A})}{\partial x}\right) \tag{6.61}$$

and a sum with similar y- and z-components is equal to the Lorentz force

$$m\vec{a}=F=Q\left(-\frac{\mathrm{d}\vec{A}}{\mathrm{d}t}-\vec{\nabla}V+\vec{\nabla}(\vec{v}\cdot\vec{A})\right)=Q(\vec{E}+\vec{v}\times\vec{B}). \tag{6.62}$$

We have found that our Lagrangian has the form

$$\mathcal{L}=\frac{1}{2}mv^2-QV+Q(\vec{v}\cdot\vec{A}). \tag{6.63}$$

According to Eq. 6.46, the canonical momentum has the following components

$$p_x=\frac{\partial\mathcal{L}}{\partial v_x}=mv_x+QA_x \qquad p_y=\frac{\partial\mathcal{L}}{\partial v_y}=mv_y+QA_y \qquad p_z=\frac{\partial\mathcal{L}}{\partial v_z}=mv_y+QA_z. \tag{6.64}$$

The Hamiltonian can be obtained as usually by the Legendre transform

$$H=\sum_{j=x,y,z}p_jv_j-\mathcal{L}=\vec{p}\cdot\vec{v}-\mathcal{L}. \tag{6.65}$$

In order to express H as a function of $\vec{p}$, we express $\vec{v}$ as $(\vec{p}-Q\vec{A})/m$:

$$H=\frac{2\vec{p}\cdot(\vec{p}-Q\vec{A})-(\vec{p}-Q\vec{A})^2-2Q(\vec{p}-Q\vec{A})\cdot\vec{A}}{2m}+QV=\frac{(\vec{p}-Q\vec{A})^2}{2m}+QV. \tag{6.66}$$

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:

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t}=\hat{H}\Psi. \tag{6.67}$$

Eq.6.67 can be also written for matrix representation of Ψ and $\hat{H}$. If eigenfunctions of $\hat{H}$ are used as a basis ($\Psi=c_1(t)\psi_1+c_2(t)\psi_2+\cdots$), the time-independent eigenfunctions

ψ_j can be factored out from $\partial\Psi/\partial t$ (left-hand side) and Ψ (right-hand side), and canceled, giving

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1 & 0 & \cdots \\ 0 & E_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}, \tag{6.68}$$

which is simply a set of independent differential equations

$$\frac{\mathrm{d}c_j}{\mathrm{d}t} = -\mathrm{i}\frac{E_j}{\hbar}c_j \quad \Rightarrow \quad c_j = a_j\mathrm{e}^{-\mathrm{i}\frac{E_j}{\hbar}t}, \tag{6.69}$$

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.

- States corresponding to the eigenfunctions of the Hamiltonian are *stationary* (do not vary in time).
- Only stationary states can be described by the *energy level diagram.*

6.7 Operator of angular momentum

In order to understand NMR experiments, we also need to describe *rotation* in space. The fundamental quantity related to the rotation is *angular momentum.* In a search for its operator, 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.

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

$$\vec{L} = \vec{r} \times \vec{p}. \tag{6.70}$$

The vector product represents the following set of equations:

$$L_x = r_yp_z - r_zp_y, \tag{6.71}$$

$$L_y = r_zp_x - r_xp_z, \tag{6.72}$$

$$L_z = r_xp_y - r_yp_x. \tag{6.73}$$

Going to the operators

$$\hat{L}_x = \hat{r}_y\hat{p}_z - \hat{r}_z\hat{p}_y = -\mathrm{i}\hbar y\frac{\partial}{\partial z} + \mathrm{i}\hbar z\frac{\partial}{\partial y}, \tag{6.74}$$
$$\hat{L}_y = \hat{r}_z\hat{p}_x - \hat{r}_x\hat{p}_z = -\mathrm{i}\hbar z\frac{\partial}{\partial x} + \mathrm{i}\hbar x\frac{\partial}{\partial z}, \tag{6.75}$$
$$\hat{L}_z = \hat{r}_x\hat{p}_y - \hat{r}_y\hat{p}_x = -\mathrm{i}\hbar x\frac{\partial}{\partial y} + \mathrm{i}\hbar y\frac{\partial}{\partial x}, \tag{6.76}$$
$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \tag{6.77}$$

It follows from Eq. 6.27 that

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z, \tag{6.78}$$
$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x, \tag{6.79}$$
$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y, \tag{6.80}$$

but

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0. \tag{6.81}$$

- Two components of angular momentum cannot be measured exactly at the same time
- Eqs. 6.78–6.81 can be used as a definition of angular momentum operators if the position and momentum operators are not available.

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

Eigenvalues and eigenfunctions are defined by

$$\hat{L}_z\psi_j = L_{z,j}\psi_j, \tag{6.82}$$
$$-\mathrm{i}\hbar\frac{\partial(QR_j)}{\partial\varphi} = L_{z,j}(QR_j), \tag{6.83}$$
$$-\mathrm{i}\hbar Q\frac{\mathrm{d}R_j}{\mathrm{d}\varphi} = L_{z,j}QR_j, \tag{6.84}$$
$$-\mathrm{i}\hbar\frac{\mathrm{d}\ln R_j}{\mathrm{d}\varphi} = L_{z,j}, \tag{6.85}$$
$$R_j = \mathrm{e}^{\mathrm{i}\frac{L_{z,j}}{\hbar}\varphi}. \tag{6.86}$$

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

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

There is a close relation between the angular momentum operators and description of rotation in quantum mechanics. Rotation about an axis given by the angular frequency vector $\vec{\omega}$

$$\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} = \vec{\omega} \times \vec{r}, \tag{6.87}$$

or more explicitly

$$\frac{\mathrm{d}r_x}{\mathrm{d}t} = \omega_y r_z - \omega_z r_y, \tag{6.88}$$
$$\frac{\mathrm{d}r_y}{\mathrm{d}t} = \omega_z r_x - \omega_x r_z, \tag{6.89}$$
$$\frac{\mathrm{d}r_z}{\mathrm{d}t} = \omega_x r_y - \omega_y r_x. \tag{6.90}$$

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

$$\frac{\mathrm{d}r_x}{\mathrm{d}t} = -\omega r_y, \tag{6.91}$$
$$\frac{\mathrm{d}r_y}{\mathrm{d}t} = \omega r_x, \tag{6.92}$$
$$\frac{\mathrm{d}r_z}{\mathrm{d}t} = 0. \tag{6.93}$$

We already know that such a set of equation can be solved easily: multiply the second equation by i and add it to the first equation or subtract it from the first equation.

$$\frac{\mathrm{d}(r_x + \mathrm{i}r_y)}{\mathrm{d}t} = \omega(-r_y + \mathrm{i}r_x) = +\mathrm{i}\omega(r_x + \mathrm{i}r_y), \tag{6.94}$$
$$\frac{\mathrm{d}(r_x - \mathrm{i}r_y)}{\mathrm{d}t} = \omega(-r_y - \mathrm{i}r_x) = -\mathrm{i}\omega(r_x - \mathrm{i}r_y), \tag{6.95}$$

$$r_x + \mathrm{i}r_y = C_+ \mathrm{e}^{+\mathrm{i}\omega t}, \tag{6.96}$$
$$r_x - \mathrm{i}r_y = C_- \mathrm{e}^{-\mathrm{i}\omega t}, \tag{6.97}$$

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

$$r_x + \mathrm{i}r_y = r\mathrm{e}^{+\mathrm{i}(\omega t + \phi_0)} = r(\cos(\omega t + \phi_0) + \mathrm{i}(\sin(\omega t + \phi_0)), \tag{6.98}$$
$$r_x - \mathrm{i}r_y = r\mathrm{e}^{-\mathrm{i}(\omega t + \phi_0)} = r(\cos(\omega t + \phi_0) - \mathrm{i}(\sin(\omega t + \phi_0)). \tag{6.99}$$

The angle of rotation φ is obviously given by $\omega t + \phi_0$.

$$r_x + \mathrm{i}r_y = r\mathrm{e}^{+\mathrm{i}\varphi} = r(\cos(\varphi) + \mathrm{i}(\sin(\varphi)), \tag{6.100}$$
$$r_x - \mathrm{i}r_y = r\mathrm{e}^{-\mathrm{i}\varphi} = r(\cos(\varphi) - \mathrm{i}(\sin(\varphi)). \tag{6.101}$$

Comparison with Eq. 6.86 documents the relation between $\hat{L}_z$ and rotation:

- Eigenfunction of $\hat{L}_z$ describes rotation about z.

Knowing the operator of the angular momentum, we can easily define the operators of the 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

$$\vec{\mu} = \frac{Q}{2}(\vec{r} \times \vec{v}) = \frac{Q}{2m}(\vec{r} \times \vec{p}) = \frac{Q}{2m}\vec{L} = \gamma\vec{L}, \tag{6.102}$$

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)*.[3]

Therefore, we can write the operators

$$\hat{\mu}_x = \gamma\hat{L}_x \qquad \hat{\mu}_y = \gamma\hat{L}_y \qquad \hat{\mu}_z = \gamma\hat{L}_z \qquad \hat{\mu}^2 = \gamma^2\hat{L}^2. \tag{6.103}$$

Finally, we can define the operator of energy (Hamiltonian) of a magnetic moment in a 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

$$\hat{H} = -B_x\hat{\mu}_x - B_y\hat{\mu}_y - B_z\hat{\mu}_z = -\gamma\left(B_x\hat{\mu}_x + B_y\hat{\mu}_y + B_z\hat{\mu}_z\right) = -\frac{Q}{2m}\left(B_x\hat{L}_x + B_y\hat{L}_y + B_z\hat{L}_z\right). \tag{6.104}$$

6.8 Relativistic quantum mechanics

The angular momentum discussed in Section 6.7 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 possess 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. In order to describe spin, we need a relativistic theory, i.e., a theory which in agreement with two fundamental postulates of the special theory of relativity:

- The laws of physics are invariant (i.e. identical) in all inertial systems (non-accelerating frames of reference).
- The speed of light in a vacuum is the same for all observers, regardless of the motion of the light source.

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:

$$t = \frac{t_0}{\sqrt{1 - v^2/c^2}} \qquad m = \frac{m_0}{\sqrt{1 - v^2/c^2}} \qquad E_t = mc^2 = \frac{m_0c^2}{\sqrt{1 - v^2/c^2}}, \tag{6.105}$$

where m_0 is the rest mass, m_0c^2 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 first equation can be used to express $\mathrm{d}t^2$

$$t^2 = \frac{\mathrm{d}t_0^2}{1 - v^2/c^2} = \frac{m^2c^4\mathrm{d}t_0^2}{m^2c^4 - m^2c^2v^2}, \tag{6.106}$$

where numerator and denominator were multiplied by $E_t^2 = m^2c^4$ in the second step. Eqs. 6.105 show that $t_0/t = m_0/m$. Therefore

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

$$\begin{aligned} \mathrm{d}t^2 &= \frac{m_0^2c^4\mathrm{d}t^2}{m^2c^4-m^2c^2v^2}, &(6.107)\\ m_0^2c^4 &= m^2c^4-(mcv_x)^2-(mcv_y)^2-(mcv_z)^2, &(6.108)\\ m_0^2c^4 &= E_t^2-c^2p_x^2-c^2p_y^2-c^2p_z^2. &(6.109)\end{aligned}$$

We see that the special theory of relativity requires that the quantity $m_0^2c^4-E_t^2+c^2p_x^2+c^2p_y^2+c^2p_z^2$ is equal to zero. Let us look for an operator which represents the quantity $m_0^2c^4-E_t^2+c^2p_x^2+c^2p_y^2+c^2p_z^2$. We know that for a monochromatic wave function

$$\psi=\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_xx+p_yy+p_zz-E_tt)}, \tag{6.110}$$

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

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial x}=-p_x\psi \qquad \mathrm{i}\hbar\frac{\partial\psi}{\partial y}=-p_y\psi \qquad \mathrm{i}\hbar\frac{\partial\psi}{\partial z}=-p_z\psi \qquad \mathrm{i}\hbar\frac{\partial\psi}{\partial t}=E_t\psi. \tag{6.111}$$

Therefore, the operator of $m_0^2c^4-E_t^2+c^2p_x^2+c^2p_y^2+c^2p_z^2$ should have a form

$$\hbar^2\frac{\partial^2}{\partial t^2}-c^2\hbar^2\frac{\partial^2}{\partial z^2}-c^2\hbar^2\frac{\partial^2}{\partial x^2}-c^2\hbar^2\frac{\partial^2}{\partial y^2}+(m_0c^2)^2. \tag{6.112}$$

Let us look for equation(s) of motion leading to such operator. As this problem is not easy to solve, we will proceed step by step. Let us first assume that particles do not move, i.e., $\vec{p}=0$. Then, Eq. 6.109 simplifies to

$$m_0^2c^4-E_t^2=0, \tag{6.113}$$

which can be written as

$$(m_0c^2+E_t)(m_0c^2-E_t)=0, \tag{6.114}$$

Using the operator of energy,

$$\hbar^2\frac{\partial^2\psi}{\partial t^2}+(m_0c^2)^2\psi=\left(m_0^2c^4-E_t^2\right)\psi=0 \tag{6.115}$$

if ψ is an eigenfunction of the energy operator. The operator of $m_0^2c^4-E_t^2$ (let us call it $\hat{O}^2$) can be obtained by a subsequent application of operators $\hat{O}^+$ and $\hat{O}^-$ in the following equations of motion:

$$\begin{aligned} \left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\psi &= \hat{O}^+\psi=0, &(6.116)\\ \left(-i\hbar\frac{\partial}{\partial t}-m_0c^2\right)\psi &= \hat{O}^-\psi=0. &(6.117)\end{aligned}$$

The operators $\hat{O}^-$ and $\hat{O}^+$ can be viewed as "square roots" of $\hat{O}^2$:

$$\hat{O}^2\psi\equiv\hbar^2\frac{\partial^2\psi}{\partial t^2}+(m_0c^2)^2\psi=\hat{O}^+\left(\hat{O}^-\psi\right)=\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\left(-i\hbar\frac{\partial}{\partial t}-m_0c^2\right)\psi=0. \tag{6.118}$$

What are the eigenfuctions? One solution is the monochromatic wave described by Eq. 6.110 (with $p_x=p_y=p_z=0$):

$$\begin{aligned} &\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\left(-i\hbar\frac{\partial}{\partial t}-m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(-E_tt)}=\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\left(-E_t-m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(-E_tt)}\\ &=\left(-E_t-m_0c^2\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(-E_tt)}=\left(-E_t-m_0c^2\right)\left(E_t-m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(-E_tt)}=\left(m_0^2c^4-E_t^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(-E_tt)}=0.\end{aligned} \tag{6.119}$$

But the complex conjugate of the monochromatic wave described by Eq. 6.110 is another possible solution:

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\left(-i\hbar\frac{\partial}{\partial t}-m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_tt)}=\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-m_0c^2\right)\left(E_t-m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_tt)}$$

$$= \left(E_t - m_0c^2\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_t t)} = \left(E_t - m_0c^2\right)\left(-E_t - m_0c^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_t t)} = \left(m_0^2c^4 - E_t^2\right)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(E_t t)} = 0. \tag{6.120}$$

The second eigenfunction can be interpreted as a particle with a positive energy moving backwards in time, or as an *antiparticle* moving forward in time.

Let us now turn our attention to particles that can move ($\vec{p} \neq 0$). For the most interesting particles as electron or quarks, the operator $\hat{O}^2$ should have the form described by Eq. 6.112

$$\hbar^2\frac{\partial^2}{\partial t^2} - c^2\hbar^2\frac{\partial^2}{\partial z^2} - c^2\hbar^2\frac{\partial^2}{\partial x^2} - c^2\hbar^2\frac{\partial^2}{\partial y^2} + (m_0c^2)^2\psi. \tag{6.121}$$

Let us try to find "square roots" of the operator $\hat{O}^2$ for a particle with a momentum $\vec{p}$. In Eq. 6.118, $\hat{O}^+$ and $\hat{O}^+$ were complex conjugates. A similar choice for a particle with a momentum $\vec{p}$, i.e.,

$$\hat{O}^+\psi = \left(\mathrm{i}\hbar\frac{\partial}{\partial t} + \mathrm{i}c\hbar\frac{\partial}{\partial x} + \mathrm{i}c\hbar\frac{\partial}{\partial y} + \mathrm{i}c\hbar\frac{\partial}{\partial z} - m_0c^2\right)\psi \tag{6.122}$$

$$\hat{O}^-\psi = \left(-\mathrm{i}\hbar\frac{\partial}{\partial t} - \mathrm{i}c\hbar\frac{\partial}{\partial x} - \mathrm{i}c\hbar\frac{\partial}{\partial y} - \mathrm{i}c\hbar\frac{\partial}{\partial z} - m_0c^2\right)\psi \tag{6.123}$$

gives

$$\begin{array}{rlllll}
\hat{O}^-\hat{O}^+\psi = \hat{O}^2\psi = & \hbar^2\frac{\partial^2\psi}{\partial t^2} & +c\hbar^2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial x} & +c\hbar^2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial y} & +c\hbar^2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial z} & -\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial t} \\
& +c\hbar^2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial t} & +\hbar^2\frac{\partial^2\psi}{\partial x^2} & +c\hbar^2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial y} & +c\hbar^2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial z} & -\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial x} \\
& +c\hbar^2\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial t} & +c\hbar^2\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial x} & +\hbar^2\frac{\partial^2\psi}{\partial y^2} & +c\hbar^2\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial z} & -\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial y} \\
& +c\hbar^2\frac{\partial\psi}{\partial z}\frac{\partial\psi}{\partial t} & +c\hbar^2\frac{\partial\psi}{\partial z}\frac{\partial\psi}{\partial x} & +c\hbar^2\frac{\partial\psi}{\partial z}\frac{\partial\psi}{\partial y} & +\hbar^2\frac{\partial^2\psi}{\partial z^2} & -\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial z} \\
& +\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial t} & +\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial x} & +\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial y} & +\mathrm{i}m_0c^2\hbar\frac{\partial\psi}{\partial z} & +(m_0c^2)^2\psi
\end{array} \tag{6.124}$$

with the correct five square terms along the "diagonal", but also with additional twenty unwanted mixed terms.

As the second trial, let us try (naïvely) to get rid of the unwanted mixed terms by introducing coefficients γ_j that hopefully cancel them:

$$\hat{O}^+\psi = \left(\mathrm{i}\hbar\frac{\partial}{\partial t}\gamma_0 + \mathrm{i}c\hbar\frac{\partial}{\partial x}\gamma_1 + \mathrm{i}c\hbar\frac{\partial}{\partial y}\gamma_2 + \mathrm{i}c\hbar\frac{\partial}{\partial z}\gamma_3 - m_0c^2\right)\psi \tag{6.125}$$

$$\hat{O}^-\psi = \left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\gamma_0 - \mathrm{i}c\hbar\frac{\partial}{\partial x}\gamma_1 - \mathrm{i}c\hbar\frac{\partial}{\partial y}\gamma_2 - \mathrm{i}c\hbar\frac{\partial}{\partial z}\gamma_3 - m_0c^2\right)\psi. \tag{6.126}$$

Then,

$$\begin{array}{rlllll}
\hat{O}^-\hat{O}^+\psi = \hat{O}^2\psi = & \gamma_0^2\hbar^2\frac{\partial^2\psi}{\partial t^2} & +\gamma_0\gamma_1c\hbar^2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial x} & +\gamma_0\gamma_2c\hbar^2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial y} & +\gamma_0\gamma_3c\hbar^2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial z} & -\mathrm{i}\gamma_0m_0c^2\hbar\frac{\partial\psi}{\partial t} \\
& +\gamma_1\gamma_0c\hbar^2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial t} & +\gamma_1^2\hbar^2\frac{\partial^2\psi}{\partial x^2} & +\gamma_1\gamma_2c\hbar^2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial y} & +\gamma_1\gamma_3c\hbar^2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial z} & -\mathrm{i}\gamma_1m_0c^2\hbar\frac{\partial\psi}{\partial x} \\
& +\gamma_2\gamma_0c\hbar^2\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial t} & +\gamma_2\gamma_1c\hbar^2\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial x} & +\gamma_2^2\hbar^2\frac{\partial^2\psi}{\partial y^2} & +\gamma_2\gamma_3c\hbar^2\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial z} & -\mathrm{i}\gamma_2m_0c^2\hbar\frac{\partial\psi}{\partial y} \\
& +\gamma_3\gamma_0c\hbar^2\frac{\partial\psi}{\partial z}\frac{\partial\psi}{\partial t} & +\gamma_3\gamma_1c\hbar^2\frac{\partial\psi}{\partial z}\frac{\partial\psi}{\partial x} & +\gamma_3\gamma_2c\hbar^2\frac{\partial\psi}{\partial z}\frac{\partial\psi}{\partial y} & +\gamma_3^2\hbar^2\frac{\partial^2\psi}{\partial z^2} & -\mathrm{i}\gamma_3m_0c^2\hbar\frac{\partial\psi}{\partial z} \\
& +\mathrm{i}\gamma_0m_0c^2\hbar\frac{\partial\psi}{\partial t} & +\mathrm{i}\gamma_1m_0c^2\hbar\frac{\partial\psi}{\partial x} & +\mathrm{i}\gamma_2m_0c^2\hbar\frac{\partial\psi}{\partial y} & +\mathrm{i}\gamma_3m_0c^2\hbar\frac{\partial\psi}{\partial z} & +(m_0c^2)^2\psi.
\end{array} \tag{6.127}$$

Obviously, the terms with $-\mathrm{i}\gamma_jm_0c^2\hbar$ cancel each other, which removes six unwanted terms. Can we also remove the remaining dozen of unwanted mixed derivative terms? In order to do it, we need the following conditions to be fulfilled:

$$\gamma_0^2 = 1 \tag{6.128}$$

$$\gamma_1^2 = -1 \tag{6.129}$$

$$\gamma_2^2 = -1 \tag{6.130}$$

$$\gamma_3^2 = -1 \tag{6.131}$$

$$\gamma_j\gamma_k + \gamma_k\gamma_j = 0 \text{ for } j \neq k. \tag{6.132}$$

These conditions are clearly in conflict. The first four condition require γ_j to be ±1 or ±i, but the last condition requires them to be zero. There are no complex numbers that allow us to get the correct operator $\hat{O}^2$. However, there are mathematical objects, that can fulfil the listed conditions simultaneously. Such objects are *matrices*.

6.8.1 Finding the matrices

Let us replace the coefficients γ_j in Eqs. 6.125–6.125 by matrices[4] $\hat{\gamma}^j$:

$$\hat{O}^+\Psi = \left(\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0 + \mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1 + \mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2 + \mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3 - m_0c^2\hat{1}\right)\Psi = 0 \tag{6.133}$$

$$\hat{O}^-\Psi = \left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0 - \mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1 - \mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2 - \mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3 - m_0c^2\hat{1}\right)\Psi = 0. \tag{6.134}$$

We need a set of four matrices $\hat{\gamma}^j$ with the following properties:

$$\hat{\gamma}^0\cdot\hat{\gamma}^0 = 1, \tag{6.135}$$

$$\hat{\gamma}^1\cdot\hat{\gamma}^1 = -1 \qquad \hat{\gamma}^2\cdot\hat{\gamma}^2 = -1 \qquad \hat{\gamma}^3\cdot\hat{\gamma}^3 = -1 \tag{6.136}$$

and

$$\hat{\gamma}^j\cdot\hat{\gamma}^k + \hat{\gamma}^k\cdot\hat{\gamma}^j = 0 \text{ for } j\neq k. \tag{6.137}$$

In addition, there is a physical restriction. We know that the operator of energy (Hamiltonian) is

$$\hat{H} = \mathrm{i}\hbar\frac{\partial}{\partial t} \tag{6.138}$$

We can get the *Dirac Hamiltonian* by multiplying Eq. 6.133 by $\hat{\gamma}^0$ from left:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{1}\Psi = \left(-\mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^0\cdot\hat{\gamma}^1 - \mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^0\cdot\hat{\gamma}^2 - \mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^0\cdot\hat{\gamma}^3 + m_0c^2\hat{\gamma}^0\right)\Psi = 0. \tag{6.139}$$

Operator of any measurable quantity must be *Hermitian* ($\langle\psi|\hat{O}\psi\rangle = \langle\hat{O}\psi|\psi\rangle$) in order to give real values of the measured value. Since the terms in the Hamiltonian are proportional to $\hat{\gamma}^0$ or to $\hat{\gamma}^0\cdot\hat{\gamma}^j$, all these matrices must be Hermitian (the elements in the j-th row and k-th column must be equal to the complex conjugates of the elements in the k-th row and j-th column for each j and k.).

We have a certain liberty in choosing the matrices. A matrix equation is nothing else than a set of equations. One of the matrices can be always chosen to be diagonal. Let us assume that $\hat{\gamma}^0$ is diagonal.[5] How should the diagonal elements of $\hat{\gamma}^0$ look like? In order to fulfill Eq. 6.135, the elements must be $+1$ or -1.

Another requirement follows from a general property of matrix multiplication: Trace of the matrix product $\hat{A}\cdot\hat{B}$ is the same as that of $\hat{B}\cdot\hat{A}$. Let us assume that $\hat{A} = \hat{\gamma}^j$ and $\hat{B} = \hat{\gamma}^0\cdot\hat{\gamma}^j$. Then,

$$\mathrm{Tr}\{\hat{\gamma}^j\cdot\hat{\gamma}^0\cdot\hat{\gamma}^j\} = \mathrm{Tr}\{\hat{\gamma}^j\cdot\hat{\gamma}^j\cdot\hat{\gamma}^0\}. \tag{6.140}$$

But Eq. 6.137 tells us that $\hat{\gamma}^0\cdot\hat{\gamma}^j = -\hat{\gamma}^j\cdot\hat{\gamma}^0$. Therefore, the left-hand side of Eq. 6.140 can be written as $\mathrm{Tr}\{\hat{\gamma}^j\cdot(-\hat{\gamma}^j)\cdot\hat{\gamma}^0\}$, resulting in

$$-\mathrm{Tr}\{\hat{\gamma}^j\cdot\hat{\gamma}^j\cdot\hat{\gamma}^0\} = \mathrm{Tr}\{\hat{\gamma}^j\cdot\hat{\gamma}^j\cdot\hat{\gamma}^0\}, \tag{6.141}$$

and using Eq. 6.137

$$\mathrm{Tr}\{\hat{\gamma}^0\} = -\mathrm{Tr}\{\hat{\gamma}^0\}. \tag{6.142}$$

It can be true only if the trace is equal to zero. Consequently, the diagonal of $\hat{\gamma}^0$ must contain the same number of $+1$ and -1 elements. It also tells us that the dimension of the $\hat{\gamma}^j$ matrices must be even. Can they be two-dimensional?

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[4] In relativistic quantum mechanics, these matrices can be treated as four components of a *four-vector*. There are two types of four-vectors (contravariant and covariant) which transform differently. There is a convention to distinguish these two types by writing components of covariant vectors with lower indices and components of contravariant vectors with upper indices. To keep this convention, we label the gamma matrices with upper indices, do not confuse them with power!

[5] This is a good choice because it results in a diagonal matrix representing the Hamiltonian, which is convenient.

No, for the following reason. The four $\hat{\gamma}^j$ matrices must be linearly independent, and it is impossible to find four linearly independent 2×2 matrices so that all fulfill Eq. 6.137.[6]

Is it possible to find four-dimensional $\hat{\gamma}^j$ matrices? Yes. We start by choosing

$$\hat{\gamma}^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{6.143}$$

(the diagonal must contain two $+1$ elements and two -1 elements, their order is arbitrary, but predetermines forms of the other matrices).

Being diagonal, $\hat{\gamma}^0$ is of course Hermitian. The $\hat{\gamma}^0 \cdot \hat{\gamma}^j$ products

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} \gamma^j_{1,1} & \gamma^j_{1,2} & \gamma^j_{1,3} & \gamma^j_{1,4} \\ \gamma^j_{2,1} & \gamma^j_{2,2} & \gamma^j_{2,3} & \gamma^j_{2,4} \\ \gamma^j_{3,1} & \gamma^j_{3,2} & \gamma^j_{3,3} & \gamma^j_{3,4} \\ \gamma^j_{4,1} & \gamma^j_{4,2} & \gamma^j_{4,3} & \gamma^j_{4,4} \end{pmatrix} = \begin{pmatrix} \gamma^j_{1,1} & \gamma^j_{1,2} & \gamma^j_{1,3} & \gamma^j_{1,4} \\ \gamma^j_{2,1} & \gamma^j_{2,2} & \gamma^j_{2,3} & \gamma^j_{2,4} \\ -\gamma^j_{3,1} & -\gamma^j_{3,2} & -\gamma^j_{3,3} & -\gamma^j_{3,4} \\ -\gamma^j_{4,1} & -\gamma^j_{4,2} & -\gamma^j_{4,3} & -\gamma^j_{4,4} \end{pmatrix} \tag{6.144}$$

must be also Hermitian, i.e.,

$$\begin{pmatrix} \gamma^j_{1,1} & \gamma^j_{1,2} & \gamma^j_{1,3} & \gamma^j_{1,4} \\ \gamma^j_{2,1} & \gamma^j_{2,2} & \gamma^j_{2,3} & \gamma^j_{2,4} \\ -\gamma^j_{3,1} & -\gamma^j_{3,2} & -\gamma^j_{3,3} & -\gamma^j_{3,4} \\ -\gamma^j_{4,1} & -\gamma^j_{4,2} & -\gamma^j_{4,3} & -\gamma^j_{4,4} \end{pmatrix} = \begin{pmatrix} (\gamma^j_{1,1})^* & (\gamma^j_{2,1})^* & -(\gamma^j_{3,1})^* & -(\gamma^j_{4,1})^* \\ (\gamma^j_{1,2})^* & (\gamma^j_{2,2})^* & -(\gamma^j_{3,2})^* & -(\gamma^j_{4,2})^* \\ (\gamma^j_{1,3})^* & (\gamma^j_{2,3})^* & -(\gamma^j_{3,3})^* & -(\gamma^j_{4,3})^* \\ (\gamma^j_{1,4})^* & (\gamma^j_{2,4})^* & -(\gamma^j_{3,4})^* & -(\gamma^j_{4,4})^* \end{pmatrix}. \tag{6.145}$$

At the same time, Eq. 6.137 requires $\hat{\gamma}^0 \cdot \hat{\gamma}^j = -\hat{\gamma}^j \cdot \hat{\gamma}^0$

$$\begin{pmatrix} \gamma^j_{1,1} & \gamma^j_{1,2} & \gamma^j_{1,3} & \gamma^j_{1,4} \\ \gamma^j_{2,1} & \gamma^j_{2,2} & \gamma^j_{2,3} & \gamma^j_{2,4} \\ -\gamma^j_{3,1} & -\gamma^j_{3,2} & -\gamma^j_{3,3} & -\gamma^j_{3,4} \\ -\gamma^j_{4,1} & -\gamma^j_{4,2} & -\gamma^j_{4,3} & -\gamma^j_{4,4} \end{pmatrix} = - \begin{pmatrix} \gamma^j_{1,1} & \gamma^j_{1,2} & \gamma^j_{1,3} & \gamma^j_{1,4} \\ \gamma^j_{2,1} & \gamma^j_{2,2} & \gamma^j_{2,3} & \gamma^j_{2,4} \\ \gamma^j_{3,1} & \gamma^j_{3,2} & \gamma^j_{3,3} & \gamma^j_{3,4} \\ \gamma^j_{4,1} & \gamma^j_{4,2} & \gamma^j_{4,3} & \gamma^j_{4,4} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -\gamma^j_{1,1} & -\gamma^j_{1,2} & \gamma^j_{1,3} & \gamma^j_{1,4} \\ -\gamma^j_{2,1} & -\gamma^j_{2,2} & \gamma^j_{2,3} & \gamma^j_{2,4} \\ -\gamma^j_{3,1} & -\gamma^j_{3,2} & \gamma^j_{3,3} & \gamma^j_{3,4} \\ -\gamma^j_{4,1} & -\gamma^j_{4,2} & \gamma^j_{4,3} & \gamma^j_{4,4} \end{pmatrix}, \tag{6.146}$$

which is possible only if the red elements are equal to zero. Eq. 6.145 shows that the blue elements form two adjoint 2×2 matrices for each $j > 0$:

$$\hat{\gamma}^j = \begin{pmatrix} 0 & 0 & \gamma^j_{1,3} & \gamma^j_{1,4} \\ 0 & 0 & \gamma^j_{2,3} & \gamma^j_{2,4} \\ \gamma^j_{3,1} & \gamma^j_{3,2} & 0 & 0 \\ \gamma^j_{4,1} & \gamma^j_{4,2} & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & \gamma^j_{1,3} & \gamma^j_{1,4} \\ 0 & 0 & \gamma^j_{2,3} & \gamma^j_{2,4} \\ -(\gamma^j_{1,3})^* & -(\gamma^j_{2,3})^* & 0 & 0 \\ -(\gamma^j_{1,4})^* & -(\gamma^j_{2,4})^* & 0 & 0 \end{pmatrix} = \begin{pmatrix} \hat{0} & \hat{\sigma}^j \\ -(\hat{\sigma}^j)^\dagger & \hat{0} \end{pmatrix}. \tag{6.147}$$

Now we use Eqs. 6.136 and 6.137 to find the actual forms of three $\hat{\sigma}^j$ (and consequently $\hat{\gamma}^j$) matrices for $j > 0$. Eq. 6.136 requires

$$\begin{pmatrix} \hat{0} & \hat{\sigma}^j \\ -(\hat{\sigma}^j)^\dagger & \hat{0} \end{pmatrix} \cdot \begin{pmatrix} \hat{0} & \hat{\sigma}^j \\ -(\hat{\sigma}^j)^\dagger & \hat{0} \end{pmatrix} = \begin{pmatrix} -\hat{\sigma}^j \cdot (\hat{\sigma}^j)^\dagger & \hat{0} \\ \hat{0} & -(\hat{\sigma}^j)^\dagger \cdot \hat{\sigma}^j \end{pmatrix} = - \begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}, \tag{6.148}$$

---

[6] If the $\hat{\gamma}^j$ matrices are linearly independent, they can be used as a basis. If they constitute a basis, there must exist a linear combination of $\hat{\gamma}^j$ giving any 2×2 matrix, e.g., the unit matrix $\hat{1}$: $\hat{1} = c_0\hat{\gamma}^0 + c_1\hat{\gamma}^1 + c_2\hat{\gamma}^2 + c_3\hat{\gamma}^3$. Let us now multiply this equation by $\hat{\gamma}^0$ from left (and use Eq. 6.135)

$$\hat{\gamma}^0 = c_0\hat{1} + c_1\hat{\gamma}^0 \cdot \hat{\gamma}^1 + c_2\hat{\gamma}^0 \cdot \hat{\gamma}^2 + c_3\hat{\gamma}^0 \cdot \hat{\gamma}^3,$$

then from right

$$\hat{\gamma}^0 = c_0\hat{1} + c_1\hat{\gamma}^1 \cdot \hat{\gamma}^0 + c_2\hat{\gamma}^2 \cdot \hat{\gamma}^0 + c_3\hat{\gamma}^3 \cdot \hat{\gamma}^0,$$

and sum both equations. If the matrices fulfill Eq. 6.137, the result must be $2\hat{\gamma}^0 = 2c_0\hat{1}$, but this cannot be true for our choice of $\hat{\gamma}^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

i.e.,

$$\hat{\sigma}^j \cdot (\hat{\sigma}^j)^\dagger = (\hat{\sigma}^j)^\dagger \cdot \hat{\sigma}^j = \hat{1} \tag{6.149}$$

Eq. 6.149 is obviously true if the $\hat{\sigma}^j$ matrices are Hermitian ($\hat{\sigma}^j = (\hat{\sigma}^j)^\dagger$), i.e. $\sigma^j_{m,n} = (\sigma^j_{n,m})^*$. It implies that the $\hat{\sigma}^j$ matrices have the following form:

$$\hat{\sigma}^j = \begin{pmatrix} a_j & c_j \\ c_j^* & b_j \end{pmatrix}, \tag{6.150}$$

where a_j and b_j are real, and c_j is complex. Eq. 6.149 can be then written as

$$\hat{\sigma}^j \cdot (\hat{\sigma}^j)^\dagger = \hat{\sigma}^j \cdot \hat{\sigma}^j = \begin{pmatrix} a_j & c_j \\ c_j^* & b_j \end{pmatrix} \cdot \begin{pmatrix} a_j & c_j \\ c_j^* & b_j \end{pmatrix} = \begin{pmatrix} a_j^2 + |c_j|^2 & (a_j+b_j)c_j \\ (a_j+b_j)c_j^* & b_j^2 + |c_j|^2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{6.151}$$

The off-diagonal terms of the product matrix must be equal to zero, which is true if $a_j = -b_j$ or $|c_j| = 0$. In the former case, matrices $\hat{\sigma}^j$ can be written as

$$\hat{\sigma}^j = \begin{pmatrix} \sqrt{1-|c_j|^2} & c_j \\ c_j^* & -\sqrt{1-|c_j|^2} \end{pmatrix}, \tag{6.152}$$

in the latter case, there are only two possibilities how to construct the $\hat{\sigma}^j$ matrix:

$$\hat{\sigma}^j = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{or} \quad \hat{\sigma}^j = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{6.153}$$

(note that $|c_j|^2 = 0 \Rightarrow a_j^2 = b_j^2 = 1$.) Eq. 6.137 shows that the second option is correct. Eq. 6.137 requires

$$\begin{pmatrix} \hat{0} & \hat{\sigma}^j \\ -(\hat{\sigma}^j)^\dagger & \hat{0} \end{pmatrix} \cdot \begin{pmatrix} \hat{0} & \hat{\sigma}^k \\ -(\hat{\sigma}^k)^\dagger & \hat{0} \end{pmatrix} + \begin{pmatrix} \hat{0} & \hat{\sigma}^k \\ -(\hat{\sigma}^k)^\dagger & \hat{0} \end{pmatrix} \cdot \begin{pmatrix} \hat{0} & \hat{\sigma}^j \\ -(\hat{\sigma}^j)^\dagger & \hat{0} \end{pmatrix} = -\begin{pmatrix} \hat{\sigma}^j \cdot (\hat{\sigma}^k)^\dagger + \hat{\sigma}^k \cdot (\hat{\sigma}^j)^\dagger & \hat{0} \\ \hat{0} & (\hat{\sigma}^j)^\dagger \cdot \hat{\sigma}^k + (\hat{\sigma}^k)^\dagger \cdot \hat{\sigma}^j \end{pmatrix} = \begin{pmatrix} \hat{0} & \hat{0} \\ \hat{0} & \hat{0} \end{pmatrix}, \tag{6.154}$$

therefore no $\hat{\sigma}^j$ can be a unit matrix.

As Eq. 6.153 unambiguously defines one sigma matrix (let us call it $\hat{\sigma}^3$), the other two ($\hat{\sigma}^1$ and $\hat{\sigma}^2$) are given by Eq. 6.152. According to Eq. 6.137,

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} \sqrt{1-|c_j|^2} & c_j \\ c_j^* & -\sqrt{1-|c_j|^2} \end{pmatrix} + \begin{pmatrix} \sqrt{1-|c_j|^2} & c_j \\ c_j^* & -\sqrt{1-|c_j|^2} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 2\sqrt{1-|c_j|^2} & 0 \\ 0 & -2\sqrt{1-|c_j|^2} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \tag{6.155}$$

showing that $|c_j|^2 = 1$ and the diagonal elements of $\hat{\sigma}^1$ and $\hat{\sigma}^2$ are equal to zero. Therefore, these equations can be written as

$$\hat{\sigma}^1 = \begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}\phi_1} \\ \mathrm{e}^{-\mathrm{i}\phi_1} & 0 \end{pmatrix} \qquad \hat{\sigma}^2 = \begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}\phi_2} \\ \mathrm{e}^{-\mathrm{i}\phi_2} & 0 \end{pmatrix} \tag{6.156}$$

According to Eq. 6.137,

$$\begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}\phi_1} \\ \mathrm{e}^{-\mathrm{i}\phi_1} & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}\phi_2} \\ \mathrm{e}^{-\mathrm{i}\phi_2} & 0 \end{pmatrix} + \begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}\phi_2} \\ \mathrm{e}^{-\mathrm{i}\phi_2} & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}\phi_1} \\ \mathrm{e}^{-\mathrm{i}\phi_1} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \mathrm{e}^{\mathrm{i}(\phi_1-\phi_2)} + \mathrm{e}^{-\mathrm{i}(\phi_1-\phi_2)} \\ \mathrm{e}^{-\mathrm{i}(\phi_1-\phi_2)} + \mathrm{e}^{\mathrm{i}(\phi_1-\phi_2)} & 0 \end{pmatrix} =$$

$$\begin{pmatrix} 0 & 2\cos(\phi_1-\phi_2) \\ 2\cos(\phi_1-\phi_2) & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{6.157}$$

The off-diagonal elements of the sum of the matrix products are equal to zero if the phases differ by $\pi/2$. Choosing $\phi_1 = 0$, the set of three sigma matrices is

$$\hat{\sigma}^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{\sigma}^2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad \hat{\sigma}^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{6.158}$$

and the set of the four gamma matrices is

$$\hat{\gamma}^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad \hat{\gamma}^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \qquad \hat{\gamma}^2 = \begin{pmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & \mathrm{i} & 0 \\ 0 & \mathrm{i} & 0 & 0 \\ -\mathrm{i} & 0 & 0 & 0 \end{pmatrix} \qquad \hat{\gamma}^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \tag{6.159}$$

6.8.2 Dirac equation

With the help of the $\hat{\gamma}^j$ matrices, we can modify our definition of $\hat{O}^+$ and $\hat{O}^-$ to get the correct operator $\hat{O}^2$:

$$\begin{aligned}&\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix}0&0&1&0\\0&0&0&-1\\-1&0&0&0\\0&1&0&0\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix}0&0&0&-\mathrm{i}\\0&0&\mathrm{i}&0\\0&\mathrm{i}&0&0\\-\mathrm{i}&0&0&0\end{pmatrix}\right.\\&\qquad\left.-m_0c^2\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\right)\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{pmatrix}=\hat{O}^+\Psi=0,\end{aligned}\tag{6.160}$$

$$\begin{aligned}&\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix}0&0&1&0\\0&0&0&-1\\-1&0&0&0\\0&1&0&0\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix}0&0&0&-\mathrm{i}\\0&0&\mathrm{i}&0\\0&\mathrm{i}&0&0\\-\mathrm{i}&0&0&0\end{pmatrix}\right.\\&\qquad\left.-m_0c^2\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\right)\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{pmatrix}=\hat{O}^-\Psi=0.\end{aligned}\tag{6.161}$$

Introducing matrices means that we do not have a single equation of motion, but a set of four equations for four coupled wave functions. The complete wave function Ψ is therefore a vector consisting of four components. The operators $\hat{O}^+$ and $\hat{O}^-$ consist of partial derivative operators summarized in Eq. 6.111, and Eq. 6.111 also shows that a monochromatic wave $\psi=\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_xx+p_yy+p_zz-E_tt)}$ is eigenfunction of the partial derivative operators, with the eigenvalues equal to E_t,p_x,p_y,p_z. Also note that the 2×2 sub-matrices, which form the $\hat{\gamma}^j$ matrices, always appear with the opposite sign on the first and last two lines, except for the unit matrix associated with the m_0c^2 term. It is therefore useful to use a complex conjugate of the aforementioned monochromatic wave as eigenfuction on the last two lines, in order to get eigenvalues with opposite signs. Possible solutions of the Dirac equation can be than assumed to have a form

$$\Psi=\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix},\tag{6.162}$$

where u_1,u_2,v_1,v_2 are coefficients to be determined. The Dirac equation[7] can be written as

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[7] Actually, two equations, one for $\hat{O}+$ and another one for $\hat{O}-$.

$$\begin{aligned}&\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix}0&0&1&0\\0&0&0&-1\\-1&0&0&0\\0&1&0&0\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}+\mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix}0&0&0&-\mathrm{i}\\0&0&\mathrm{i}&0\\0&\mathrm{i}&0&0\\-\mathrm{i}&0&0&0\end{pmatrix}\right.\\&\qquad\left.-m_0c^2\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^+\Psi=0,\end{aligned}\tag{6.163}$$

$$\begin{aligned}&\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial z}\begin{pmatrix}0&0&1&0\\0&0&0&-1\\-1&0&0&0\\0&1&0&0\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial x}\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}-\mathrm{i}c\hbar\frac{\partial}{\partial y}\begin{pmatrix}0&0&0&-\mathrm{i}\\0&0&\mathrm{i}&0\\0&\mathrm{i}&0&0\\-\mathrm{i}&0&0&0\end{pmatrix}\right.\\&\qquad\left.-m_0c^2\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^-\Psi=0,\end{aligned}\tag{6.164}$$

or shortly

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0+\mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1+\mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2+\mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3-m_0c^2\hat{1}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^+\Psi=0\tag{6.165}$$

$$\left(-\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0-\mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1-\mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2-\mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3-m_0c^2\hat{1}\right)\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=\hat{O}^-\Psi=0.\tag{6.166}$$

For our wavefunctions,

$$\hat{O}^+\Psi=\begin{pmatrix}E_tu_1\psi+cp_xv_2\psi^*-\mathrm{i}cp_yv_2\psi^*+cp_zv_1\psi^*-m_0c^2u_1\psi\\E_tu_2\psi+cp_xv_1\psi^*+\mathrm{i}cp_yv_1\psi^*-cp_zv_2\psi^*-m_0c^2u_2\psi\\E_tv_1\psi^*+cp_xu_2\psi^*-\mathrm{i}cp_yu_2\psi^*+cp_zu_1\psi^*-m_0c^2v_1\psi^*\\E_tv_2\psi^*+cp_xu_1\psi^*+\mathrm{i}cp_yu_1\psi^*-cp_zu_2\psi^*-m_0c^2v_2\psi^*\end{pmatrix}=0\tag{6.167}$$

and

$$\hat{O}^2\Psi=\hat{O}^-\hat{O}^+\Psi=\begin{pmatrix}E_t^2-c^2p^2-(m_0c^2)^2\\E_t^2-c^2p^2-(m_0c^2)^2\\E_t^2-c^2p^2-(m_0c^2)^2\\E_t^2-c^2p^2-(m_0c^2)^2\end{pmatrix}\begin{pmatrix}u_1\psi\\u_2\psi\\v_1\psi^*\\v_2\psi^*\end{pmatrix}=(E_t^2-c^2p^2-(m_0c^2)^2)\Psi\tag{6.168}$$

in agreement with Eq.6.109.

Eq. 6.167 can be also used to find four explicit solutions of the Dirac equation, treating u_1,u_2,v_1,v_2 as unknown variables to be determined. The solutions are found by setting one of the coefficients u_1,u_2,v_1,v_2 to zero, and calculating the other coefficients so that the following normalization condition is fulfilled

$$\int_0^L\int_0^L\int_0^L\Psi^*\Psi\mathrm{d}x\mathrm{d}y\mathrm{d}z=1\tag{6.169}$$

(other normalizations could be used as well). The solutions have the following form.

$$\Psi_1 = \sqrt{\frac{E_t + m_0c^2}{2E_tL^3}} \begin{pmatrix} \psi \\ 0 \\ \frac{cp_z}{E_t+m_0c^2}\psi^* \\ \frac{c(p_x+\mathrm{i}p_y)}{E_t+m_0c^2}\psi^* \end{pmatrix}, \qquad \Psi_2 = \sqrt{\frac{E_t + m_0c^2}{2E_tL^3}} \begin{pmatrix} 0 \\ \psi \\ \frac{c(p_x-\mathrm{i}p_y)}{E_t+m_0c^2}\psi^* \\ \frac{-cp_z}{E_t+m_0c^2}\psi^* \end{pmatrix},$$

$$\Psi_3 = \sqrt{\frac{E_t + m_0c^2}{2E_tL^3}} \begin{pmatrix} \frac{cp_z}{E_t+m_0c^2}\psi \\ \frac{c(p_x+\mathrm{i}p_y)}{E_t+m_0c^2}\psi \\ \psi^* \\ 0 \end{pmatrix}, \qquad \Psi_4 = \sqrt{\frac{E_t + m_0c^2}{2E_tL^3}} \begin{pmatrix} \frac{c(p_x-\mathrm{i}p_y)}{E_t+m_0c^2}\psi \\ \frac{-cp_z}{E_t+m_0c^2}\psi \\ 0 \\ \psi^* \end{pmatrix}, \tag{6.170}$$

where $\psi = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(p_xx+p_yy+p_zz-E_tt)}$.

Eq. 6.133

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\hat{\gamma}^0 + \mathrm{i}c\hbar\frac{\partial}{\partial x}\hat{\gamma}^1 + \mathrm{i}c\hbar\frac{\partial}{\partial y}\hat{\gamma}^2 + \mathrm{i}c\hbar\frac{\partial}{\partial z}\hat{\gamma}^3 - m_0c^2\hat{1}\right)\Psi = \hat{O}^+\Psi = 0 \tag{6.171}$$

is known as the *Dirac equation.* When postulated by Dirac, Eq. 6.133 naturally explained the behavior of particles with spin number 1/2 and predicted existence of antiparticles, discovered a few years later.

How is the Dirac equation related to the 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. 6.109:

$$\begin{aligned} &(m_0c^2)^2 = (m_0c^2 + E)^2 - c^2p^2 = (m_0c^2)^2 + 2E(m_0c^2) + E^2 - c^2p^2 \approx (m_0c^2)^2 + 2E(m_0c^2) - c^2p^2 \\ &\Rightarrow \qquad E = \frac{p^2}{2m_0}. \end{aligned} \tag{6.172}$$

6.9 Hamiltonian of spin magnetic moment

Our goal is to find Hamiltonian for a relativistic charged particle in a magnetic field. When we compare the classical Hamiltonian of a particle in an electromagnetic (Eq. 6.66) with the classical Hamiltonian of a free particle $H = (\vec{p})^2/(2m)$ outside the field, we see that the presence of an electromagnetic field requires the following modifications:

$$H \to H - QV \qquad \vec{p} \to \vec{p} - Q\vec{A}, \tag{6.173}$$

Accordingly, the operators of energy and momentum in the quantum description change to

$$\mathrm{i}\hbar\frac{\partial}{\partial t} \to \mathrm{i}\hbar\frac{\partial}{\partial t} - QV \qquad -\mathrm{i}\hbar\frac{\partial}{\partial x} \to -\mathrm{i}\hbar\frac{\partial}{\partial x} - QA_x \qquad -\mathrm{i}\hbar\frac{\partial}{\partial y} \to -\mathrm{i}\hbar\frac{\partial}{\partial y} - QA_y \qquad -\mathrm{i}\hbar\frac{\partial}{\partial z} \to -\mathrm{i}\hbar\frac{\partial}{\partial z} - QA_z. \tag{6.174}$$

This modifies Eq. 6.139 to

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - QV\right)\hat{1}\Psi = \left(-c\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)\hat{\gamma}^0\hat{\gamma}^1 - c\left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)\hat{\gamma}^0\hat{\gamma}^2 - c\left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)\hat{\gamma}^0\hat{\gamma}^3 + m_0c^2\hat{\gamma}^0\right)\Psi \tag{6.175}$$

In order to obtain the Hamiltonian describing energy of our particle in a magnetic field, we apply the operator $(\mathrm{i}\hbar\partial/\partial t - QV)$ twice

$$
\begin{aligned}
&\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-QV\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-QV\right)\hat{1}\Psi=\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-QV\right)^2\Psi\\
=\;&\left(c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)^2\hat{\gamma}^0\hat{\gamma}^1\hat{\gamma}^0\hat{\gamma}^1+c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)^2\hat{\gamma}^0\hat{\gamma}^2\hat{\gamma}^0\hat{\gamma}^2+c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)^2\hat{\gamma}^0\hat{\gamma}^3\hat{\gamma}^0\hat{\gamma}^3+m_0^2c^4\hat{\gamma}^0\hat{\gamma}^0\right)\Psi\\
&-m_0c^3\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\hat{\gamma}^0\hat{\gamma}^1\hat{\gamma}^0+\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\hat{\gamma}^0\hat{\gamma}^2\hat{\gamma}^0+\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\hat{\gamma}^0\hat{\gamma}^3\hat{\gamma}^0\right)\Psi\\
&-m_0c^3\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\hat{\gamma}^0\hat{\gamma}^0\hat{\gamma}^1+\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\hat{\gamma}^0\hat{\gamma}^0\hat{\gamma}^2+\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\hat{\gamma}^0\hat{\gamma}^0\hat{\gamma}^3\right)\Psi\\
&+c^2\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\hat{\gamma}^0\hat{\gamma}^1\hat{\gamma}^0\hat{\gamma}^2+\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\hat{\gamma}^0\hat{\gamma}^2\hat{\gamma}^0\hat{\gamma}^1\right)\Psi\\
&+c^2\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\hat{\gamma}^0\hat{\gamma}^2\hat{\gamma}^0\hat{\gamma}^3+\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\hat{\gamma}^0\hat{\gamma}^3\hat{\gamma}^0\hat{\gamma}^2\right)\Psi\\
&+c^2\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\hat{\gamma}^0\hat{\gamma}^3\hat{\gamma}^0\hat{\gamma}^1+\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\hat{\gamma}^0\hat{\gamma}^1\hat{\gamma}^0\hat{\gamma}^3\right)\Psi=0.
\end{aligned}
\tag{6.176}
$$

We use the properties of the gamma matrices (Eqs. 6.135–6.137) to simplify the equation. In particular, we invert of the order of matrices in the products

$$
\begin{aligned}
\hat{\gamma}^0\hat{\gamma}^j\hat{\gamma}^0 &= -(\hat{\gamma}^0\hat{\gamma}^0)\hat{\gamma}^j=\hat{\gamma}^j, &(6.177)\\
\hat{\gamma}^0\hat{\gamma}^j\hat{\gamma}^0\hat{\gamma}^j &= -(\hat{\gamma}^0\hat{\gamma}^0)(\hat{\gamma}^j\hat{\gamma}^j)=-(\hat{1})(-\hat{1})=\hat{1}, &(6.178)\\
\hat{\gamma}^0\hat{\gamma}^j\hat{\gamma}^0\hat{\gamma}^k &= -(\hat{\gamma}^0\hat{\gamma}^0)(\hat{\gamma}^j\hat{\gamma}^k)=-(\hat{1})(\hat{\gamma}^j\hat{\gamma}^k)=-\hat{\gamma}^j\hat{\gamma}^k=\hat{\gamma}^k\hat{\gamma}^j &(6.179)
\end{aligned}
$$

and obtain

$$
\begin{aligned}
\left(\mathrm{i}\hbar\frac{\partial}{\partial t}-QV\right)^2\hat{1}\Psi=&\left(c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)^2\hat{1}+c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)^2\hat{1}+c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)^2\hat{1}+m_0^2c^4\hat{1}\right)\Psi\\
&-m_0c^3\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\hat{\gamma}^1+\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\hat{\gamma}^2+\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\hat{\gamma}^3\right)\Psi\\
&+m_0c^3\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\hat{\gamma}^1+\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\hat{\gamma}^2+\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\hat{\gamma}^3\right)\Psi\\
&-c^2\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)-\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\right)\hat{\gamma}^1\hat{\gamma}^2\Psi\\
&-c^2\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)-\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\right)\hat{\gamma}^2\hat{\gamma}^3\Psi\\
&-c^2\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)-\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)\right)\hat{\gamma}^3\hat{\gamma}^1\Psi=0,
\end{aligned}
\tag{6.180}
$$

where the second line and the third line cancel each other. To proceed, we need to evaluate the products of operators on the last three lines (we must be very careful with differentiation).

$$
\begin{aligned}
&\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)-\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)\right)\psi=\\
&-\hbar^2\left(\frac{\partial}{\partial x}\frac{\partial\psi}{\partial y}-\frac{\partial}{\partial y}\frac{\partial\psi}{\partial x}\right)+Q^2(A_xA_y-A_yA_x)\psi+\mathrm{i}\hbar Q\left(\frac{\partial(A_y\psi)}{\partial x}+A_x\frac{\partial\psi}{\partial y}-\frac{\partial(A_x\psi)}{\partial y}-A_y\frac{\partial\psi}{\partial x}\right)=\\
&\mathrm{i}\hbar Q\left(\frac{\partial A_y}{\partial x}\psi+A_y\frac{\partial\psi}{\partial x}+A_x\frac{\partial\psi}{\partial y}-\frac{\partial A_x}{\partial y}\psi-A_x\frac{\partial\psi}{\partial y}-A_y\frac{\partial\psi}{\partial x}\right)=\mathrm{i}\hbar Q\left(\frac{\partial A_y}{\partial x}-\frac{\partial A_x}{\partial y}\right)\psi=\mathrm{i}\hbar QB_z\psi
\end{aligned}
\tag{6.181}
$$

because $\partial^2\psi/\partial x\partial y=\partial^2\psi/\partial y\partial x$. The combinations on the last two lines of Eq. 6.180 are obtained in the same manner. The products $\hat{\gamma}^1\hat{\gamma}^2$, $\hat{\gamma}^2\hat{\gamma}^3$, and $\hat{\gamma}^3\hat{\gamma}^1$ can be calculated from Eq. 6.147

$$\hat{\gamma}^1\hat{\gamma}^2 = \begin{pmatrix} \hat{0} & \hat{\sigma}^1 \\ -\hat{\sigma}^1 & \hat{0} \end{pmatrix}\begin{pmatrix} \hat{0} & \hat{\sigma}^2 \\ -\hat{\sigma}^2 & \hat{0} \end{pmatrix} = -\begin{pmatrix} \hat{\sigma}^1\hat{\sigma}^2 & \hat{0} \\ \hat{0} & \hat{\sigma}^1\hat{\sigma}^2 \end{pmatrix} = -\mathrm{i}\begin{pmatrix} \hat{\sigma}^3 & \hat{0} \\ \hat{0} & \hat{\sigma}^3 \end{pmatrix}, \tag{6.182}$$

$$\hat{\gamma}^2\hat{\gamma}^3 = \begin{pmatrix} \hat{0} & \hat{\sigma}^2 \\ -\hat{\sigma}^2 & \hat{0} \end{pmatrix}\begin{pmatrix} \hat{0} & \hat{\sigma}^3 \\ -\hat{\sigma}^3 & \hat{0} \end{pmatrix} = -\begin{pmatrix} \hat{\sigma}^2\hat{\sigma}^2 & \hat{0} \\ \hat{0} & \hat{\sigma}^2\hat{\sigma}^3 \end{pmatrix} = -\mathrm{i}\begin{pmatrix} \hat{\sigma}^1 & \hat{0} \\ \hat{0} & \hat{\sigma}^1 \end{pmatrix}, \tag{6.183}$$

$$\hat{\gamma}^3\hat{\gamma}^1 = \begin{pmatrix} \hat{0} & \hat{\sigma}^3 \\ -\hat{\sigma}^3 & \hat{0} \end{pmatrix}\begin{pmatrix} \hat{0} & \hat{\sigma}^1 \\ -\hat{\sigma}^1 & \hat{0} \end{pmatrix} = -\begin{pmatrix} \hat{\sigma}^3\hat{\sigma}^1 & \hat{0} \\ \hat{0} & \hat{\sigma}^3\hat{\sigma}^1 \end{pmatrix} = -\mathrm{i}\begin{pmatrix} \hat{\sigma}^2 & \hat{0} \\ \hat{0} & \hat{\sigma}^2 \end{pmatrix}, \tag{6.184}$$

where the following important properties of the $\hat{\sigma}^j$ matrices were used in the lasts steps:

$$\hat{\sigma}^1\hat{\sigma}^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} = \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix} = \mathrm{i}\hat{\sigma}^3 \tag{6.185}$$

$$\hat{\sigma}^2\hat{\sigma}^3 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & \mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} = \mathrm{i}\hat{\sigma}^1 \tag{6.186}$$

$$\hat{\sigma}^3\hat{\sigma}^1 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \mathrm{i}\hat{\sigma}^2. \tag{6.187}$$

After inserting everything into Eq. 6.180, we get

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - QV\right)^2 \begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi = \left(c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 + c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 + c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2 + m_0^2c^4\right)\begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi$$

$$- c^2\hbar Q\left(B_x\begin{pmatrix} \hat{\sigma}^1 & \hat{0} \\ \hat{0} & \hat{\sigma}^1 \end{pmatrix} + B_y\begin{pmatrix} \hat{\sigma}^2 & \hat{0} \\ \hat{0} & \hat{\sigma}^2 \end{pmatrix} + B_z\begin{pmatrix} \hat{\sigma}^3 & \hat{0} \\ \hat{0} & \hat{\sigma}^3 \end{pmatrix}\right)\Psi. \tag{6.188}$$

Now we have a relativistic equation describing our particle in an electromagnetic field. Let us now separate the mass contribution to the energy from the operator $\mathrm{i}\hbar\partial/\partial t$ and let us call the difference $\hat{H}$ (it becomes clear soon why we choose the same symbol as the symbol used for the Hamiltonian in the Schrödinger equation):

$$\hat{H} = \mathrm{i}\hbar\frac{\partial}{\partial t} - m_0c^2, \tag{6.189}$$

Eq. 6.188 can be rewritten as

$$\left(\hat{H} + m_0c^2 - QV\right)^2\begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi = \left((\hat{H} - QV)^2 + 2m_0c^2(\hat{H} - QV) + m_0^2c^4\right)\begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi =$$

$$\left(c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 + c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 + c^2\left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2 + m_0^2c^4\right)\begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi$$

$$- c^2\hbar Q\left(B_x\begin{pmatrix} \hat{\sigma}^1 & \hat{0} \\ \hat{0} & \hat{\sigma}^1 \end{pmatrix} + B_y\begin{pmatrix} \hat{\sigma}^2 & \hat{0} \\ \hat{0} & \hat{\sigma}^2 \end{pmatrix} + B_z\begin{pmatrix} \hat{\sigma}^3 & \hat{0} \\ \hat{0} & \hat{\sigma}^3 \end{pmatrix}\right)\Psi. \tag{6.190}$$

Dividing both sides of the equation by $2m_0c^2$ gives

$$\left(\frac{(\hat{H} - QV)^2}{2m_0c^2} + \hat{H} - QV\right)\begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi =$$

$$\frac{1}{2m_0}\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x} + QA_x\right)^2 + \left(\mathrm{i}\hbar\frac{\partial}{\partial y} + QA_y\right)^2 + \left(\mathrm{i}\hbar\frac{\partial}{\partial z} + QA_z\right)^2\right)\begin{pmatrix} \hat{1} & \hat{0} \\ \hat{0} & \hat{1} \end{pmatrix}\Psi$$

$$- \frac{\hbar Q}{2m_0}\left(B_x\begin{pmatrix} \hat{\sigma}^1 & \hat{0} \\ \hat{0} & \hat{\sigma}^1 \end{pmatrix} + B_y\begin{pmatrix} \hat{\sigma}^2 & \hat{0} \\ \hat{0} & \hat{\sigma}^2 \end{pmatrix} + B_z\begin{pmatrix} \hat{\sigma}^3 & \hat{0} \\ \hat{0} & \hat{\sigma}^3 \end{pmatrix}\right)\Psi. \tag{6.191}$$

Note that the rest energy of particles m_0c^2 is huge. Unless the eigenvalue of $\hat{H}$ is very large (which is not expected in a standard NMR experiment), the term with m_0c^2 in the denominator of the first term can be safely neglected. For the same reason, the factors $\pm cp_z/(E_t + m_0c^2)$ and $c(p_x \pm \mathrm{i}p_y)/(E_t + m_0c^2)$ in Eq. 6.170 are close to zero for $v \ll c$.

The block-diagonal form of all matrices reveals that the first two equations and the last two equations can be solved separately. Therefore, we can write

$$\hat{H}\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix} \approx$$

$$\left(\frac{1}{2m_0}\left(\left(\mathrm{i}\hbar\frac{\partial}{\partial x}+QA_x\right)^2+\left(\mathrm{i}\hbar\frac{\partial}{\partial y}+QA_y\right)^2+\left(\mathrm{i}\hbar\frac{\partial}{\partial z}+QA_z\right)^2+QV\right)\hat{1}-\frac{\hbar Q}{2m_0}\left(B_x\hat{\sigma}^1+B_y\hat{\sigma}^2+B_z\hat{\sigma}^3\right)\right)\begin{pmatrix} u_1\psi \\ u_2\psi \end{pmatrix}. \tag{6.192}$$

Now it is easy to identify the Hamiltonian of potential electric energy QV and, by comparison with the corresponding equation for an orbital magnetic moment (Eq. 6.104), the Hamiltonian of interactions with the magnetic field

$$-\frac{\hbar Q}{2m_0}\left(B_x\hat{\sigma}^1+B_y\hat{\sigma}^2+B_z\hat{\sigma}^3\right). \tag{6.193}$$

The mentioned comparison also helps us to identify the operator of the components of the *spin magnetic moment*:

$$\hat{\mu}_x = \frac{\hbar Q}{2m_0}\hat{\sigma}^1 = \frac{\hbar Q}{2m_0}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{6.194}$$

$$\hat{\mu}_y = \frac{\hbar Q}{2m_0}\hat{\sigma}^2 = \frac{\hbar Q}{2m_0}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \tag{6.195}$$

$$\hat{\mu}_z = \frac{\hbar Q}{2m_0}\hat{\sigma}^3 = \frac{\hbar Q}{2m_0}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.196}$$

6.9.1 Operators of spin angular momentum

Our final task is to find the operators of the components of the *spin angular momentum*, which also gives us the value of the magnetogyric ratio. Eq. 6.192 itself is not sufficient because it does not say which constants belong to the spin angular momentum and which constitute the magnetogyric ratio. We cannot use the classical definition either because our case does not have a classical counterpart. But we can use the commutation relations Eqs. 6.78–6.81, which define the operators of any angular momentum components. In order to distinguish it from the orbital angular momentum $\vec{L}$, we label the spin angular momentum $\vec{I}$. Operators of I_x, I_y, I_z must fulfill the same commutation relations as the operators of L_x, L_y, L_z:

$$\hat{I}_x\hat{I}_y-\hat{I}_y\hat{I}_x=\mathrm{i}\hbar\hat{I}_z, \qquad \hat{I}_y\hat{I}_z-\hat{I}_z\hat{I}_y=\mathrm{i}\hbar\hat{I}_x, \qquad \hat{I}_z\hat{I}_x-\hat{I}_x\hat{I}_z=\mathrm{i}\hbar\hat{I}_y. \tag{6.197}$$

Comparison with Eqs. 6.185–6.187 shows that the right choice is

$$\boxed{\hat{I}_x=\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{I}_y=\frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad \hat{I}_z=\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \hat{I}^2=\frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.} \tag{6.198}$$

Comparison of Eq. 6.192 with Eq. 6.104 shows that the magnetogyric ratio differs by a factor of 2 from the value for orbital magnetic moment:

$$\gamma = 2\frac{Q}{2m}. \tag{6.199}$$

6.9.2 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 $\hat{I}_z$. 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. These eigenfunctions can be

$$\sqrt{\frac{1}{L^3}}\begin{pmatrix}\psi\\0\end{pmatrix}, \qquad \sqrt{\frac{1}{L^3}}\begin{pmatrix}0\\\psi\end{pmatrix}, \tag{6.200}$$

i.e., the two-dimensional variants of the free-particle wavefunctions from Eq. 6.170 in the low-energy approximation. However, the normalization coefficients and ψ (or ψ^*) can be canceled out in the eigenvalue equations and the eigenfunctions can be replaced by the vectors

$$\begin{pmatrix}1\\0\end{pmatrix}, \qquad \begin{pmatrix}0\\1\end{pmatrix}, \tag{6.201}$$

corresponding to the first and second wavefunctions in Eq. 6.170.

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

$$\hat{I}_z|\alpha\rangle = +\frac{\hbar}{2}|\alpha\rangle \qquad \hat{I}_z|\uparrow\rangle = +\frac{\hbar}{2}|\uparrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = +\frac{\hbar}{2}\begin{pmatrix}1\\0\end{pmatrix}, \tag{6.202}$$

$$\hat{I}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle \qquad \hat{I}_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix}0\\1\end{pmatrix}. \tag{6.203}$$

Note that the vectors used to represent $|\alpha\rangle$ and $|\beta\rangle$ in Eqs. 6.202 and 6.203 are not the only choice. Vectors in Eqs. 6.202 and 6.203 have a phase set to zero (they are made of real numbers). Any other phase ϕ would work as well, e.g.

$$\begin{pmatrix}1\\0\end{pmatrix} \rightarrow \begin{pmatrix}\mathrm{e}^{\mathrm{i}\phi}\\0\end{pmatrix}. \tag{6.204}$$

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

$$\langle I_z\rangle = \langle\alpha|I_z|\alpha\rangle = \begin{pmatrix}1&0\end{pmatrix}\frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = +\frac{\hbar}{2}. \tag{6.205}$$

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

$$\langle I_z\rangle = \langle\beta|I_z|\beta\rangle = \begin{pmatrix}0&1\end{pmatrix}\frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = -\frac{\hbar}{2}. \tag{6.206}$$

- 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

$$\langle I_z\rangle = \langle\alpha|I_z|\beta\rangle = \begin{pmatrix} c_\alpha^* & c_\beta^* \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = (|c_\alpha|^2 - |c_\beta|^2)\frac{\hbar}{2}. \tag{6.207}$$

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 is true in general, but for the sake of simplicity, we just check rotation about the z axis.

We start by writing explicitly the Dirac equation as a set of four equations[8]

$$\mathrm{i}\hbar\frac{\partial(u_1\psi)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(v_1\psi^*)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(v_2\psi^*)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}v_2\psi^*)}{\partial y} + m_0c^2u_1\psi, \tag{6.208}$$

$$\mathrm{i}\hbar\frac{\partial(u_2\psi)}{\partial t} = +\mathrm{i}c\hbar\frac{\partial(v_2\psi^*)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(v_1\psi^*)}{\partial x} + \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}v_1\psi^*)}{\partial y} + m_0c^2u_2\psi, \tag{6.209}$$

$$\mathrm{i}\hbar\frac{\partial(v_1\psi^*)}{\partial t} = -\mathrm{i}c\hbar\frac{\partial(u_1\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u_2\psi)}{\partial x} - \mathrm{i}c\hbar\frac{\partial(\mathrm{i}u_2\psi)}{\partial y} - m_0c^2v_1\psi^*, \tag{6.210}$$

$$\mathrm{i}\hbar\frac{\partial(v_2\psi^*)}{\partial t} = +\mathrm{i}c\hbar\frac{\partial(u_2\psi)}{\partial z} - \mathrm{i}c\hbar\frac{\partial(u_1\psi)}{\partial x} + \mathrm{i}c\hbar\frac{\partial(\mathrm{i}u_1\psi)}{\partial y} - m_0c^2v_2\psi^*. \tag{6.211}$$

Let us assume that we have an original coordinate frame t, x, y, z and a rotated frame t', x', y', z'. If we rotate about z by an angle φ,

$$t' = t \tag{6.212}$$

$$z' = z \tag{6.213}$$

$$x' = \cos\varphi x - \sin\varphi y \tag{6.214}$$

$$y' = \sin\varphi x + \cos\varphi y \tag{6.215}$$

and

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial t'} \tag{6.216}$$

$$\frac{\partial f}{\partial z} = \frac{\partial f}{\partial z'} \tag{6.217}$$

$$\frac{\partial f}{\partial x} = \frac{\partial x'}{\partial x}\frac{\partial f}{\partial x'} + \frac{\partial y'}{\partial x}\frac{\partial f}{\partial y'} = \cos\varphi\frac{\partial f}{\partial x'} + \sin\varphi\frac{\partial f}{\partial y'} \tag{6.218}$$

$$\frac{\partial f}{\partial y} = \frac{\partial x'}{\partial y}\frac{\partial f}{\partial x'} + \frac{\partial y'}{\partial y}\frac{\partial f}{\partial y'} = -\sin\varphi\frac{\partial f}{\partial x'} + \cos\varphi\frac{\partial f}{\partial y'} \tag{6.219}$$

and consequently

$$\frac{\partial f}{\partial x} + \mathrm{i}\frac{\partial f}{\partial y} = \mathrm{e}^{-\mathrm{i}\varphi}\left(\frac{\partial f}{\partial x'} + \mathrm{i}\frac{\partial f}{\partial y'}\right), \tag{6.220}$$

$$\frac{\partial f}{\partial x} - \mathrm{i}\frac{\partial f}{\partial y} = \mathrm{e}^{\mathrm{i}\varphi}\left(\frac{\partial f}{\partial x'} - \mathrm{i}\frac{\partial f}{\partial y'}\right). \tag{6.221}$$

---

[8] Note that we use the form of the Dirac equation which directly defines the relativistic Hamiltonian (Eq. 6.139).

We also need to transform the wavefunction Ψ to the rotated frame. We already know that rotation of a complex function f by an angle ϕ can be written as $f' = f\mathrm{e}^{\mathrm{i}\phi}$. Let us assume that each of component of Ψ rotates by some angle $(\varphi_1, \varphi_2, \varphi_3, \varphi_4,)$ – the key step of our analysis will be to relate values of these angles the actual angle of rotating the coordinate frames φ.

Now we have everything that we need to write the set of Eqs. 6.208–6.211 in the rotated coordinate frame:

$$\mathrm{i}\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_1}u_1\psi')}{\partial t'} = -\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_3}v_1\psi'^*)}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_4+\varphi)}v_2\psi'^*)}{\partial x'} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_4+\varphi)}v_2\psi'^*)}{\partial y'} + m_0c^2\mathrm{e}^{\mathrm{i}\varphi_1}u_1\psi', \tag{6.222}$$

$$\mathrm{i}\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_2}u_2\psi')}{\partial t'} = +\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_4}v_2\psi'^*)}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_3-\varphi)}v_1\psi'^*)}{\partial x'} + \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_3-\varphi)}v_1\psi'^*)}{\partial y'} + m_0c^2\mathrm{e}^{\mathrm{i}\varphi_2}u_2\psi', \tag{6.223}$$

$$\mathrm{i}\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_3}v_1\psi'^*)}{\partial t'} = -\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_1}u_1\psi')}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_2+\varphi)}u_2\psi')}{\partial x'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_2+\varphi)}u_2\psi')}{\partial y'} - m_0c^2\mathrm{e}^{\mathrm{i}\varphi_3}v_1\psi'^*, \tag{6.224}$$

$$\mathrm{i}\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_4}v_2\psi'^*)}{\partial t'} = +\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}\varphi_2}u_2\psi')}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_1-\varphi)}u_1\psi')}{\partial x'} + \mathrm{i}c\hbar\frac{\partial(\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_1-\varphi)}u_1\psi')}{\partial y'} - m_0c^2\mathrm{e}^{\mathrm{i}\varphi_4}v_2\psi'^*. \tag{6.225}$$

According to the first postulate of the special theory of relativity, Eqs. 6.222–6.225 must have the same form as Eqs. 6.208–6.211. In other words, we must eliminate the complex exponential expressions from Eqs. 6.222–6.225. Let us first multiply both sides of the first equation by $\mathrm{e}^{-\mathrm{i}\varphi_1}$, both sides of the second equation by $\mathrm{e}^{-\mathrm{i}\varphi_2}$, both sides of the third equation by $\mathrm{e}^{-\mathrm{i}\varphi_3}$, and both sides of the last equation by $\mathrm{e}^{-\mathrm{i}\varphi_4}$:

$$\mathrm{i}\hbar\frac{\partial(u_1\psi')}{\partial t'} = -\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_3-\varphi_1)}v_1\psi'^*)}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_4-\varphi_1+\varphi)}v_2\psi'^*)}{\partial x'} - \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_4-\varphi_1+\varphi)}v_2\psi'^*)}{\partial y'} + m_0c^2u_1\psi', \tag{6.226}$$

$$\mathrm{i}\hbar\frac{\partial(u_2\psi')}{\partial t'} = +\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_4-\varphi_2)}v_2\psi'^*)}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_3-\varphi_2-\varphi)}v_1\psi'^*)}{\partial x'} + \mathrm{i}c\hbar\frac{\partial(-\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_3-\varphi_2-\varphi)}v_1\psi'^*)}{\partial y'} + m_0c^2u_2\psi', \tag{6.227}$$

$$\mathrm{i}\hbar\frac{\partial(v_1\psi'^*)}{\partial t'} = -\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_1-\varphi_3)}u_1\psi')}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_2-\varphi_3+\varphi)}u_2\psi')}{\partial x'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_2-\varphi_3+\varphi)}u_2\psi')}{\partial y'} - m_0c^2v_1\psi'^*, \tag{6.228}$$

$$\mathrm{i}\hbar\frac{\partial(v_2\psi'^*)}{\partial t'} = +\mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_2-\varphi_4)}u_2\psi')}{\partial z'} - \mathrm{i}c\hbar\frac{\partial(\mathrm{e}^{\mathrm{i}(\varphi_1-\varphi_4-\varphi)}u_1\psi')}{\partial x'} + \mathrm{i}c\hbar\frac{\partial(\mathrm{i}\mathrm{e}^{\mathrm{i}(\varphi_1-\varphi_4-\varphi)}u_1\psi')}{\partial y'} - m_0c^2v_2\psi'^*. \tag{6.229}$$

This cleared the t' and m_0 terms. The exponential expressions disappear from the z' term if $\varphi_1 = \varphi_3$ and $\varphi_2 = \varphi_4$ (i.e., if the rotation of $u_1\psi$ and $v_1\psi^*$ is identical and the same applies to $u_2\psi$ and $v_2\psi^*$). In order to fix the x' and y' terms, we assume that $\varphi_1 = -\varphi_2$ and $\varphi_3 = -\varphi_4$, i.e., that the rotation of $u_1\psi$ and $u_2\psi$ is opposite and the same applies to $v_1\psi^*$ and $v_2\psi^*$. This implies that $u_1\psi$ and $u_2\psi$ describe states with opposite spins (and $v_1\psi^*$ and $v_2\psi^*$ too). Then, $u_1\psi'$ and $v_1\psi'^*$ in the x' and y' terms are multiplied by $\mathrm{e}^{\mathrm{i}(2\varphi_1-\varphi)}$, and $u_2\psi'$ and $v_2\psi'^*$ in the x' and y' terms are multiplied by $\mathrm{e}^{-\mathrm{i}(2\varphi_1-\varphi)}$. In both cases, the exponential expersions disappear (are equal to one) if $\varphi_1 = \varphi/2$. What does it mean? If we rotate the coordinate system by a certain angle, the components of the wavefunction rotate only by half of this angle! The function describing rotation of the wavefunction about z has the form

$$R_j = \mathrm{e}^{\mathrm{i}\frac{I_{z,j}}{\hbar}\frac{\varphi}{2}}. \tag{6.230}$$

This looks very similar to Eq. 6.86, but with one important difference: rotation by 2π (360 °) does not give the same eigenfunction R_j as no rotation ($\varphi = 0$), but changes its sign. Only rotation by 4π (720 °) reverts the system to the initial state!

Eq. 6.86 tells us that the eigenvalues of the operator of the spin angular momentum are half-integer multiples of $\hbar$:

$$I_{z,1} = \frac{\hbar}{2} \qquad I_{z,2} = -\frac{\hbar}{2}. \tag{6.231}$$

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

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

$$\frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \equiv |\rightarrow\rangle, \tag{6.232}$$

$$-\frac{\mathrm{i}}{\sqrt{2}}|\alpha\rangle + \frac{\mathrm{i}}{\sqrt{2}}|\beta\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\\mathrm{i}\end{pmatrix} \equiv |\leftarrow\rangle, \tag{6.233}$$

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

$$\mathrm{e}^{\mathrm{i}\pi/2}\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\ \mathrm{i}\end{pmatrix} = \mathrm{i}\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\ \mathrm{i}\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -1\end{pmatrix}. \tag{6.234}$$

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

$$\hat{I}_x|\rightarrow\rangle = +\frac{\hbar}{2}|\rightarrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = +\frac{\hbar}{2}\cdot\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}, \tag{6.235}$$

$$\hat{I}_x|\leftarrow\rangle = +\frac{\hbar}{2}|\leftarrow\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\ \mathrm{i}\end{pmatrix} = -\frac{\hbar}{2}\cdot\frac{1}{\sqrt{2}}\begin{pmatrix}-\mathrm{i}\\ \mathrm{i}\end{pmatrix}. \tag{6.236}$$

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

$$\frac{1-\mathrm{i}}{2}|\alpha\rangle + \frac{1+\mathrm{i}}{2}|\beta\rangle \quad = \quad \frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\ 1+\mathrm{i}\end{pmatrix} \equiv |\otimes\rangle, \tag{6.237}$$

$$-\frac{1+\mathrm{i}}{2}|\alpha\rangle + \frac{1-\mathrm{i}}{2}|\beta\rangle \quad = \quad \frac{1}{2}\begin{pmatrix}1+\mathrm{i}\\ 1-\mathrm{i}\end{pmatrix}, \equiv |\odot\rangle \tag{6.238}$$

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

$$\mathrm{e}^{\mathrm{i}\pi/4}\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\ 1+\mathrm{i}\end{pmatrix} = \frac{1+\mathrm{i}}{\sqrt{2}}\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\ 1+\mathrm{i}\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \mathrm{i}\end{pmatrix}. \tag{6.239}$$

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

$$\hat{I}_y|\otimes\rangle = +\frac{\hbar}{2}|\otimes\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&-\mathrm{i}\\ \mathrm{i}&0\end{pmatrix}\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\ 1+\mathrm{i}\end{pmatrix} = +\frac{\hbar}{2}\cdot\frac{1}{2}\begin{pmatrix}1-\mathrm{i}\\ 1+\mathrm{i}\end{pmatrix}, \tag{6.240}$$

$$\hat{I}_y|\odot\rangle = -\frac{\hbar}{2}|\odot\rangle \qquad \frac{\hbar}{2}\begin{pmatrix}0&-\mathrm{i}\\ \mathrm{i}&0\end{pmatrix}\frac{1}{2}\begin{pmatrix}1+\mathrm{i}\\ 1-\mathrm{i}\end{pmatrix} = -\frac{\hbar}{2}\cdot\frac{1}{2}\begin{pmatrix}1+\mathrm{i}\\ 1-\mathrm{i}\end{pmatrix}. \tag{6.241}$$

6.10 Real particles

Eq. 6.192, used to derive the value of γ, describes interaction of a particle with an external electromagnetic field. However, charged particles are themselves sources of electromagnetic fields. Therefore, γ is not exactly twice $Q/2m$. In general, the value of γ is

$$\gamma = g\frac{Q}{2m}, \tag{6.242}$$

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 is $g = 2.0023318361(10)$, 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,

Table 6.1: Values of the magnetogyric ratios of selected nuclei

Nucleus	magnetogyric ratio
$^{1}_{1}$H	267.513×10^6 rad.s^{-1}.T^{-1}
$^{13}_{6}$C	67.262×10^6 rad.s^{-1}.T^{-1}
$^{15}_{7}$N	-27.116×10^6 rad.s^{-1}.T^{-1}
$^{19}_{9}$F	251.662×10^6 rad.s^{-1}.T^{-1}
$^{31}_{15}$P	108.291×10^6 rad.s^{-1}.T^{-1}

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.[9] Magnetogyric ratios of the nuclei observed most frequently are listed in Table 6.1

6.11 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

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = -\gamma B_0 \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}, \tag{6.243}$$

which is a set of two equations with separated variables

$$\frac{\mathrm{d}c_\alpha}{\mathrm{d}t} = +\mathrm{i}\frac{\gamma B_0}{2} c_\alpha, \tag{6.244}$$

$$\frac{\mathrm{d}c_\beta}{\mathrm{d}t} = -\mathrm{i}\frac{\gamma B_0}{2} c_\beta, \tag{6.245}$$

with the solution

$$c_\alpha = c_\alpha(t=0)\mathrm{e}^{+\mathrm{i}\frac{\gamma B_0}{2}t} = c_\alpha(t=0)\mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t}, \tag{6.246}$$

$$c_\beta = c_\beta(t=0)\mathrm{e}^{-\mathrm{i}\frac{\gamma B_0}{2}t} = c_\beta(t=0)\mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t}. \tag{6.247}$$

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

$$c_\alpha = \mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t}, \tag{6.248}$$

$$c_\beta = 0. \tag{6.249}$$

Note that the evolution changes only the phase factor, but the system stays in state $|\alpha\rangle$ (all vectors described by Eq. 6.204 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.

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[9] 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.

$$P_\alpha = c_\alpha^* c_\alpha = \mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t}\mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t} = 1, \tag{6.250}$$

$$P_\beta = c_\beta^* c_\beta = 0. \tag{6.251}$$

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

$$c_\alpha = 0, \tag{6.252}$$

$$c_\beta = \mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t}. \tag{6.253}$$

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

$$P_\alpha = c_\alpha^* c_\alpha = 0, \tag{6.254}$$

$$P_\beta = c_\beta^* c_\beta = \mathrm{e}^{-\mathrm{i}\frac{\omega_0}{2}t}\mathrm{e}^{+\mathrm{i}\frac{\omega_0}{2}t} = 1. \tag{6.255}$$

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.

6.12 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

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = -\gamma B_1 \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}, \tag{6.256}$$

which is a set of two equations

$$\frac{\mathrm{d}c_\alpha}{\mathrm{d}t} = \mathrm{i}\frac{\gamma B_1}{2}c_\beta, \tag{6.257}$$

$$\frac{\mathrm{d}c_\beta}{\mathrm{d}t} = \mathrm{i}\frac{\gamma B_1}{2}c_\alpha. \tag{6.258}$$

These equations have similar structure as Eqs. 6.91 and 6.92. Adding and subtracting them leads to the solution

$$c_\alpha + c_\beta = C_+\mathrm{e}^{+\mathrm{i}\frac{\gamma B_1}{2}t} = C_+\mathrm{e}^{-\mathrm{i}\frac{\omega_1}{2}t}, \tag{6.259}$$

$$c_\alpha - c_\beta = C_-\mathrm{e}^{-\mathrm{i}\frac{\gamma B_1}{2}t} = C_-\mathrm{e}^{+\mathrm{i}\frac{\omega_1}{2}t}. \tag{6.260}$$

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

$$c_\alpha = \cos\left(\frac{\omega_1}{2}t\right), \tag{6.261}$$

$$c_\beta = -\mathrm{i}\sin\left(\frac{\omega_1}{2}t\right). \tag{6.262}$$

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

$$P_\alpha = c_\alpha^* c_\alpha = \cos^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} + \frac{1}{2}\cos(\omega_1 t), \tag{6.263}$$

$$P_\beta = c_\beta^* c_\beta = \sin^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} - \frac{1}{2}\cos(\omega_1 t). \tag{6.264}$$

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

$$c_\alpha = -\mathrm{i}\sin\left(\frac{\omega_1}{2}t\right), \tag{6.265}$$

$$c_\beta = \cos\left(\frac{\omega_1}{2}t\right). \tag{6.266}$$

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

$$P_\alpha = c_\alpha^* c_\alpha = \sin^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} - \frac{1}{2}\cos(\omega_1 t), \tag{6.267}$$

$$P_\beta = c_\beta^* c_\beta = \cos^2\left(\frac{\omega_1}{2}t\right) = \frac{1}{2} + \frac{1}{2}\cos(\omega_1 t). \tag{6.268}$$

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 7

Mixed state of non-interacting spins

Literature: A nice short introduction is given in K3.1. The topic is clearly described in K6, L11, C2.2. The mixed state is introduced nicely in B17.2, K6.8, L11.1, and C2.2.2. More specific references are given in the individual sections below.

7.1 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 state vectors and their properties are 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 that motions of the whole molecule, of its atoms, and of electrons and nuclei in the atoms, do not depend on the spin,[1] we can divide the complete wave function into spin wave functions and wave function describing all the other degrees of freedom. In general, the 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. Also, the magnetic fields may depend on the position of the molecule in the sample. 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

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[1] This is a very reasonable assumption in most cases. However, note that it is not true completely: if motions of the magnetic moments and of the molecules were independent, it could not be explained how the magnetic moments reach their equilibrium distribution.

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 allows us to use two-dimensional operator matrices (for spin-1/2 nuclei) instead of multidimensional operator matrices.

Expected value $\langle A\rangle$ of a quantity A for a single nucleus can be calculated using Eq. 6.17 as a trace of the following product of matrices:

$$\langle A\rangle = \mathrm{Tr}\left\{\begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix}\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\right\}. \tag{7.1}$$

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

$$\begin{aligned}\langle A\rangle &= \mathrm{Tr}\left\{\begin{pmatrix} c_{\alpha,1}c_{\alpha,1}^* & c_{\alpha,1}c_{\beta,1}^* \\ c_{\beta,1}c_{\alpha,1}^* & c_{\beta,1}c_{\beta,1}^* \end{pmatrix}\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} + \begin{pmatrix} c_{\alpha,2}c_{\alpha,2}^* & c_{\alpha,2}c_{\beta,2}^* \\ c_{\beta,2}c_{\alpha,2}^* & c_{\beta,2}c_{\beta,2}^* \end{pmatrix}\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} + \cdots\right\} \\ &= \mathrm{Tr}\left\{\left(\begin{pmatrix} c_{\alpha,1}c_{\alpha,1}^* & c_{\alpha,1}c_{\beta,1}^* \\ c_{\beta,1}c_{\alpha,1}^* & c_{\beta,1}c_{\beta,1}^* \end{pmatrix} + \begin{pmatrix} c_{\alpha,2}c_{\alpha,2}^* & c_{\alpha,2}c_{\beta,2}^* \\ c_{\beta,2}c_{\alpha,2}^* & c_{\beta,2}c_{\beta,2}^* \end{pmatrix} + \cdots\right)\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\right\} \\ &= \mathcal{N}\mathrm{Tr}\left\{\underbrace{\begin{pmatrix} \overline{c_\alpha c_\alpha^*} & \overline{c_\alpha c_\beta^*} \\ \overline{c_\beta c_\alpha^*} & \overline{c_\beta c_\beta^*} \end{pmatrix}}_{\hat\rho}\underbrace{\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}}_{\hat A}\right\} = \mathcal{N}\mathrm{Tr}\left\{\hat\rho\hat A\right\}.\end{aligned} \tag{7.2}$$

The matrix $\hat\rho$ is the *(probability) density matrix*, the horizontal bar indicates average over the whole ensemble of nuclei in the sample, and $\mathcal{N}$ is the number of non-interacting nuclei described in the same operator basis.

Why probability density? Because the probability $P = \langle\Psi|\Psi\rangle$, the operator of probability can be written as 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. 6.17 as $\mathrm{Tr}\{\hat\rho\hat 1\} = \mathrm{Tr}\{\hat\rho\}$.

The most important features of the mixed-state approach are listed below:

- 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.[2]

- *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.

7.2 Coherence

Coherence is a very important issue in NMR spectroscopy. It is discussed in K6.9, L11.2, C2.6.

- 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 *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.

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[2] Orthonormality for a set of four matrices $\hat{A}_1, \hat{A}_2, \hat{A}_3, \hat{A}_4$ can be defined as $\mathrm{Tr}\{\hat{A}_j^\dagger \hat{A}_k\} = \delta_{j,k}$, 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 $\hat{A}_j^\dagger$ 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.

7.3 Basis sets

Usual choices of basis matrices are (C2.7.2):

- *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):

$$\sqrt{2}\mathcal{I}_t = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \qquad \sqrt{2}\mathcal{I}_z = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$
$$\sqrt{2}\mathcal{I}_x = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sqrt{2}\mathcal{I}_y = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}. \tag{7.3}$$

- Single-element *population*

$$\mathcal{I}_\alpha = \mathcal{I}_t + \mathcal{I}_z = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix} \qquad \mathcal{I}_\beta = \mathcal{I}_t - \mathcal{I}_z = \begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix} \tag{7.4}$$

  and *transition* operators

$$\mathcal{I}_+ = \mathcal{I}_x + \mathrm{i}\mathcal{I}_y = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \qquad \mathcal{I}_- = \mathcal{I}_x - \mathrm{i}\mathcal{I}_y = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}. \tag{7.5}$$

- A mixed basis

$$\sqrt{2}\mathcal{I}_t = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \qquad \sqrt{2}\mathcal{I}_z = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \qquad \mathcal{I}_+ = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \qquad \mathcal{I}_- = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}. \tag{7.6}$$

7.4 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. Derivation of such equation is nicely described in C2.2.3.

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

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}c_\alpha\\ c_\beta\end{pmatrix} = \begin{pmatrix}H_{\alpha,\alpha} & H_{\alpha,\beta}\\ H_{\beta,\alpha} & H_{\beta,\beta}\end{pmatrix}\begin{pmatrix}c_\alpha\\ c_\beta\end{pmatrix} = \begin{pmatrix}H_{\alpha,\alpha}c_\alpha + H_{\alpha,\beta}c_\beta\\ H_{\beta,\alpha}c_\alpha + H_{\beta,\beta}c_\beta\end{pmatrix}. \tag{7.7}$$

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., $H_{j,k} = H^*_{k,j}$:

$$H_{\alpha,\beta} = H^*_{\beta,\alpha} \qquad H_{\beta,\alpha} = H^*_{\alpha,\beta}. \tag{7.8}$$

If we multiply Eq. 7.7 by the basis functions from left, we obtained the differential equations for c_α and c_β (because the basis functions are orthonormal):

$$(\,1\;\;0\,)\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}c_\alpha\\ c_\beta\end{pmatrix}=\mathrm{i}\hbar\frac{\mathrm{d}c_\alpha}{\mathrm{d}t}=H_{\alpha,\alpha}c_\alpha+H_{\alpha,\beta}c_\beta \tag{7.9}$$

$$(\,0\;\;1\,)\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}c_\alpha\\ c_\beta\end{pmatrix}=\mathrm{i}\hbar\frac{\mathrm{d}c_\beta}{\mathrm{d}t}=H_{\beta,\alpha}c_\alpha+H_{\beta,\beta}c_\beta. \tag{7.10}$$

In general,

$$\frac{\mathrm{d}c_k}{\mathrm{d}t}=-\frac{\mathrm{i}}{\hbar}\sum_l H_{k,l}c_l \tag{7.11}$$

and its complex conjugate (using Eq. 7.8) is

$$\frac{\mathrm{d}c_k^*}{\mathrm{d}t}=+\frac{\mathrm{i}}{\hbar}\sum_l H_{k,l}^*c_l^*=+\frac{\mathrm{i}}{\hbar}\sum_l H_{l,k}c_l^*. \tag{7.12}$$

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

$$\frac{\mathrm{d}(c_jc_k^*)}{\mathrm{d}t}=c_j\frac{\mathrm{d}c_k^*}{\mathrm{d}t}+c_k^*\frac{\mathrm{d}c_j}{\mathrm{d}t}=\frac{\mathrm{i}}{\hbar}\sum_l H_{l,k}c_jc_l^*-\frac{\mathrm{i}}{\hbar}\sum_l H_{j,l}c_lc_k^*. \tag{7.13}$$

For multiple nuclei with the same basis,

$$\frac{\mathrm{d}(c_{j,1}c_{k,1}^*+c_{j,2}c_{k,2}^*+\cdots)}{\mathrm{d}t}=c_{j,1}\frac{\mathrm{d}c_{k,1}^*}{\mathrm{d}t}+c_{k,1}^*\frac{\mathrm{d}c_{j,1}}{\mathrm{d}t}+c_{j,2}\frac{\mathrm{d}c_{k,2}^*}{\mathrm{d}t}+c_{k,2}^*\frac{\mathrm{d}c_{j,2}}{\mathrm{d}t}+\cdots \tag{7.14}$$

$$=\frac{\mathrm{i}}{\hbar}\sum_l H_{l,k}(c_{j,1}c_{l,1}^*+c_{j,2}c_{l,2}^*+\cdots)-\frac{\mathrm{i}}{\hbar}\sum_l H_{j,l}(c_{l,1}c_{k,1}^*+c_{l,2}c_{k,2}^*+\cdots). \tag{7.15}$$

Note that

$$\sum_l(c_{j,1}c_{l,1}^*+c_{j,2}c_{l,2}^*+\cdots)H_{l,k}=\mathcal{N}\sum_l\rho_{j,l}H_{l,k} \tag{7.16}$$

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

$$\sum_l H_{j,l}(c_{l,1}c_{k,1}^*+c_{l,2}c_{k,2}^*+\cdots)=\mathcal{N}\sum_l H_{j,l}\rho_{l,k} \tag{7.17}$$

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

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t}=\frac{\mathrm{i}}{\hbar}(\hat{\rho}\hat{H}-\hat{H}\hat{\rho})=\frac{\mathrm{i}}{\hbar}[\hat{\rho},\hat{H}]=-\frac{\mathrm{i}}{\hbar}[\hat{H},\hat{\rho}] \tag{7.18}$$

or in the units of (angular) frequency

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t}=\mathrm{i}(\hat{\rho}\mathcal{H}-\mathcal{H}\hat{\rho})=\mathrm{i}[\hat{\rho},\mathcal{H}]=-\mathrm{i}[\mathcal{H},\hat{\rho}]. \tag{7.19}$$

Eqs. 7.18 and 7.19 are known as the *Liouville - von Neumann equation.*

7.5 Rotation in operator space

The Liouville - von Neumann equation can be solved using techniques of linear algebra. However, a very simple geometric solution is possible (K7.3, C2.7.3, L11.8) 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 $\mathcal{I}_z$).

Let us look at an example for $\mathcal{H} = \varepsilon_t\mathcal{I}_t + \omega_0\mathcal{I}_z$ and $\hat{\rho} = c_x\mathcal{I}_x + c_y\mathcal{I}_y + c_z\mathcal{I}_z + c_t\mathcal{I}_t$.
Let us 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:

$$[\mathcal{I}_t, \mathcal{I}_j] = 0 \qquad (j = x, y, z, t). \tag{7.20}$$

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

$$[\mathcal{I}_z, \mathcal{I}_z] = [\mathcal{I}_z, \mathcal{I}_t] = 0 \qquad [\mathcal{I}_z, \mathcal{I}_x] = \mathrm{i}\mathcal{I}_y \qquad [\mathcal{I}_z, \mathcal{I}_y] = -\mathrm{i}\mathcal{I}_x. \tag{7.21}$$

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

$$\frac{\mathrm{d}c_x}{\mathrm{d}t}\mathcal{I}_x + \frac{\mathrm{d}c_y}{\mathrm{d}t}\mathcal{I}_y + \frac{\mathrm{d}c_z}{\mathrm{d}t}\mathcal{I}_z + \frac{\mathrm{d}c_t}{\mathrm{d}t}\mathcal{I}_t = \mathrm{i}\left(-\mathrm{i}\omega_0 c_x\mathcal{I}_y + \mathrm{i}\omega_0 c_y\mathcal{I}_x\right). \tag{7.22}$$

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),

$$\frac{1}{2}\begin{pmatrix} 0 & \frac{\mathrm{d}c_x}{\mathrm{d}t} \\ \frac{\mathrm{d}c_x}{\mathrm{d}t} & 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i}\frac{\mathrm{d}c_y}{\mathrm{d}t} \\ \mathrm{i}\frac{\mathrm{d}c_y}{\mathrm{d}t} & 0 \end{pmatrix} + 0 + 0 = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & -\omega_0 c_x \\ \omega_0 c_x & 0 \end{pmatrix} + \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & \mathrm{i}\omega_0 c_y \\ \mathrm{i}\omega_0 c_y & 0 \end{pmatrix}, \tag{7.23}$$

$$\begin{pmatrix} 0 & \frac{\mathrm{d}(c_x - \mathrm{i}c_y)}{\mathrm{d}t} \\ \frac{\mathrm{d}(c_x + \mathrm{i}c_y)}{\mathrm{d}t} & 0 \end{pmatrix} = \mathrm{i}\omega_0\begin{pmatrix} 0 & -(c_x - \mathrm{i}c_y) \\ c_x + \mathrm{i}c_y & 0 \end{pmatrix}. \tag{7.24}$$

This corresponds to a set of two differential equations

$$\frac{\mathrm{d}(c_x - \mathrm{i}c_y)}{\mathrm{d}t} = -\mathrm{i}\omega_0(c_x - \mathrm{i}c_y) \tag{7.25}$$

$$\frac{\mathrm{d}(c_x + \mathrm{i}c_y)}{\mathrm{d}t} = +\mathrm{i}\omega_0(c_x + \mathrm{i}c_y) \tag{7.26}$$

with the same structure as Eqs. 6.94 and 6.95. The solution is

$$c_x - \mathrm{i}c_y = (c_x(0) - \mathrm{i}c_y(0))\mathrm{e}^{-\mathrm{i}\omega_0 t} = c_0\mathrm{e}^{-\mathrm{i}(\omega_0 t + \phi_0)} \tag{7.27}$$

$$c_x + \mathrm{i}c_y = (c_x(0) + \mathrm{i}c_y(0))\mathrm{e}^{+\mathrm{i}\omega_0 t} = c_0\mathrm{e}^{+\mathrm{i}(\omega_0 t + \phi_0)} \tag{7.28}$$

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

$$c_x = c_0\cos(\omega_0 t + \phi_0) \tag{7.29}$$

$$c_y = c_0\sin(\omega_0 t + \phi_0). \tag{7.30}$$

We see that coefficients c_x, c_y, c_z play the same roles as coordinates r_x, r_y, r_z in Eqs. 6.91–6.93, 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.

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 $\mathcal{I}_z$.

7.6 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. 6.17

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

In the next chapter, 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.

Chapter 8

Chemical shift, NMR experiment

Literature: The general strategy is clearly outlined in C2.4, Hamiltonians discussed in L8, thermal equilibrium in L11.3, C2.4.1, K6.8.6, relaxation due to the chemical shift in C5.4.4, K9.10 (very briefly, the quantum approach to relaxation is usually introduced using dipole-dipole interactions as an example). The one-pulse experiment is analyzed in K7.2.1, L11.11 and L11.12.

8.1 Operator of the observed quantity

The quantity observed in the NMR experiment is the *bulk magnetization* $\vec{M}$, i.e., the sum of magnetic moments of all nuclei divided by volume of the sample, assuming isotropic distribution of the nuclei in the sample. 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, as described by Eq. 1.50. 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).

$$\hat{M}_+ = \mathcal{N}\gamma(\hat{I}_x + \mathrm{i}\hat{I}_y) = \mathcal{N}\gamma\hat{I}_+, \tag{8.1}$$

where $\mathcal{N}$ is the number of nuclei in the sample (per unit volume).

8.2 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 (Eq. 1.50). Since $\vec{B}_0$ defines direction of the z axis,

$$\hat{H}_{0,\mathrm{lab}} = -\gamma B_0\hat{I}_z. \tag{8.2}$$

8.3 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, as described in Section 3.1.3). 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[1] 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 $\vec{B}_0$:

$$\hat{H}_{0,\mathrm{rot}} = (-\gamma B_0 - \omega_{\mathrm{rot}})\hat{I}_z = \Omega\hat{I}_z. \tag{8.3}$$

During irradiation by waves with the phase defining x

$$\hat{H}_{1,\mathrm{rot}} = (-\gamma B_0 - \omega_{\mathrm{rot}})\hat{I}_z - \gamma B_1\hat{I}_x = \Omega\hat{I}_z + \omega_1\hat{I}_x. \tag{8.4}$$

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

$$\hat{H}_{1,\mathrm{rot}} = (-\gamma B_0 - \omega_{\mathrm{rot}})\hat{I}_z - \gamma B_1\hat{I}_y = \Omega\hat{I}_z + \omega_1\hat{I}_y. \tag{8.5}$$

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.

8.4 Hamiltonian of chemical shift

Using the description of the magnetic fields of moving electrons discussed in Section 3.2, definition of the chemical shift Hamiltonian is straightforward:

$$\hat{H}_\delta = -\gamma(\hat{I}_x B_{\mathrm{e},x} + \hat{I}_y B_{\mathrm{e},y} + \hat{I}_z B_{\mathrm{e},z}) = -\gamma\begin{pmatrix}\hat{I}_x & \hat{I}_y & \hat{I}_z\end{pmatrix}\begin{pmatrix}B_{\mathrm{e},x}\\ B_{\mathrm{e},y}\\ B_{\mathrm{e},z}\end{pmatrix} =$$

$$= -\gamma\begin{pmatrix}\hat{I}_x & \hat{I}_y & \hat{I}_z\end{pmatrix}\begin{pmatrix}\delta_{xx} & \delta_{xy} & \delta_{xz}\\ \delta_{yx} & \delta_{yy} & \delta_{yz}\\ \delta_{zx} & \delta_{zy} & \delta_{zz}\end{pmatrix}\begin{pmatrix}B_{0,x}\\ B_{0,y}\\ B_{0,z}\end{pmatrix} = -\gamma\hat{\vec{I}}\cdot\underline{\delta}\cdot\vec{B}_0. \tag{8.6}$$

The Hamiltonian of a homogeneous magnetic field aligned with the z-axis of the coordinate frame can be decomposed into

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[1] Formally opposite to ω_{radio}.

- isotropic contribution, independent of rotation in space:

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma B_0 \delta_\mathrm{i}(\hat{I}_z) \tag{8.7}$$

- axial component, dependent on φ and ϑ:

$$\begin{aligned}\hat{H}_{\delta,\mathrm{a}} &= -\gamma B_0 \delta_\mathrm{a}(3\sin\vartheta\cos\vartheta\cos\varphi\hat{I}_x + 3\sin\vartheta\cos\vartheta\sin\varphi\hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z) \\ &= -\gamma B_0 \delta_\mathrm{a}(3a_x a_z\hat{I}_x + 3a_y a_z\hat{I}_y + (3a_z^2 - 1)\hat{I}_z)\end{aligned} \tag{8.8}$$

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

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma B_0 \delta_\mathrm{r}(\; & (-(2\cos^2\chi - 1)\sin\vartheta\cos\vartheta\cos\varphi + 2\sin\chi\cos\chi\sin\vartheta\cos\vartheta\sin\varphi)\hat{I}_x + \\ & (-(2\cos^2\chi - 1)\sin\vartheta\cos\vartheta\sin\varphi - 2\sin\chi\cos\chi\sin\vartheta\cos\vartheta\cos\varphi)\hat{I}_y + \\ & ((2\cos^2\chi - 1)\sin^2\vartheta)\hat{I}_z)\end{aligned}$$

$$= \gamma B_0 \delta_\mathrm{r}((\cos(2\chi)a_x - \sin(2\chi)a_y)a_z\hat{I}_x + (\cos(2\chi)a_y + \sin(2\chi)a_x)a_z\hat{I}_y + \cos(2\chi)(a_z^2 - 1)\hat{I}_z)$$

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

$$\hat{H} = \hat{H}_{0,\mathrm{lab}} + \hat{H}_{\delta,\mathrm{i}} + \hat{H}_{\delta,\mathrm{a}} + \hat{H}_{\delta,\mathrm{r}}. \tag{8.9}$$

8.5 Secular approximation and averaging

The Hamiltonian including the chemical shift 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 χ. 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 $\vec{B}_\mathrm{e}$ 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.*[2] The secular approximation simplifies the Hamiltonian to

$$H = -\gamma B_0(1 + \delta_\mathrm{i} + (3\cos^2\vartheta - 1)\delta_\mathrm{a} + \cos(2\chi)\sin^2\vartheta\delta_\mathrm{r})\hat{I}_z \tag{8.10}$$

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[2] 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 $\hat{H}_{0,\mathrm{lab}}$ (because the field $\vec{B}_\mathrm{e}$ is much smaller than $\vec{B}_0$). *Secular approximation* represents neglecting such small off-diagonal elements in the matrix representation of the total Hamiltonian and keeping only the diagonal secular terms.

- 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 χ are equally probable and independent of ϑ. Therefore, the last term in Eq. 8.10 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:

$$\overline{a_x^2} = \overline{a_y^2} = \overline{a_z^2}. \tag{8.11}$$

The consequence has been already discussed when we described relaxation classically (Eq. 8.12):

$$a_x^2 + a_y^2 + a_z^2 = 1 \Rightarrow \overline{a_x^2 + a_y^2 + a_z^2} = \overline{3a_z^2} \Rightarrow \overline{3a_z^2 - 1} = \overline{(3\cos^2\vartheta - 1)} = 0, \tag{8.12}$$

and the anisotropic and rhombic contributions can be neglected.

The Hamiltonian describing the effects of the static external magnetic field and coherent effects of the electrons in isotropic liquids reduces to

$$H = -\gamma B_0(1+\delta_\mathrm{i})\hat{I}_z. \tag{8.13}$$

Note that the described simplifications can be used only if they are applicable. Eq. 8.13 is valid only in isotropic liquids, not in liquid crystals, stretched gels, polycrystalline powders, monocrystals, etc.!

8.6 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.

We use the mixed state approach to define the state of the sample in thermal equilibrium. Populations of the states can be evaluated using statistical arguments similar to the Boltzmann law in the classical molecular statistics:

$$P_\alpha^{\mathrm{eq}} = \frac{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T}}{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T} + \mathrm{e}^{-E_\beta/k_\mathrm{B}T}}, \tag{8.14}$$

$$P_\beta^{\mathrm{eq}} = \frac{\mathrm{e}^{-E_\beta/k_\mathrm{B}T}}{\mathrm{e}^{-E_\alpha/k_\mathrm{B}T} + \mathrm{e}^{-E_\beta/k_\mathrm{B}T}}, \tag{8.15}$$

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 $\hat{H}$:

$$\hat{H} = -\gamma B_0(1+\delta_\mathrm{i})\hat{I}_z = -\gamma B_0(1+\delta_\mathrm{i})\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} -\gamma B_0(1+\delta_\mathrm{i})\frac{\hbar}{2} & 0 \\ 0 & +\gamma B_0(1+\delta_\mathrm{i})\frac{\hbar}{2} \end{pmatrix}. \tag{8.16}$$

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

$$\mathrm{e}^{\pm\frac{\gamma B_0(1+\delta_\mathrm{i})\hbar}{k_\mathrm{B}T}} \approx 1 \pm \frac{\gamma B_0\hbar}{2k_\mathrm{B}T} \tag{8.17}$$

and calculate the populations as

$$P_{\alpha}^{\mathrm{eq}} = \frac{\mathrm{e}^{-E_{\alpha}/k_{\mathrm{B}}T}}{\mathrm{e}^{-E_{\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta}/k_{\mathrm{B}}T}} = \frac{1+\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}}{1+\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}+1-\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}} = \frac{1+\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}}{2}, \tag{8.18}$$

$$P_{\beta}^{\mathrm{eq}} = \frac{\mathrm{e}^{-E_{\beta}/k_{\mathrm{B}}T}}{\mathrm{e}^{-E_{\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta}/k_{\mathrm{B}}T}} = \frac{1-\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}}{1+\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}+1-\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}} = \frac{1-\frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}}{2}. \tag{8.19}$$

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

$$\hat{\rho}^{\mathrm{eq}} = \begin{pmatrix} \frac{1}{2}+\frac{\gamma B_0\hbar}{4k_{\mathrm{B}}T} & 0 \\ 0 & \frac{1}{2}-\frac{\gamma B_0\hbar}{4k_{\mathrm{B}}T} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\gamma B_0\hbar}{4k_{\mathrm{B}}T}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \mathcal{I}_t + \kappa\mathcal{I}_z, \tag{8.20}$$

where

$$\kappa = \frac{\gamma B_0\hbar}{2k_{\mathrm{B}}T}. \tag{8.21}$$

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.

8.7 Relaxation due to chemical shift anisotropy

The simplified Eq. 8.13 does not describe the effects of fast fluctuations, resulting in relaxation. In order to derive quantum description of relaxation caused by the chemical shift, the Liouville - von Neumann equation must be solved for the complete Hamiltonian including the axial and rhombic contributions.

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

$$\frac{\mathrm{d}\Delta\hat{\rho}}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}_{\delta,\mathrm{a}}+\hat{H}_{\delta,\mathrm{r}},\Delta\hat{\rho}], \tag{8.22}$$

where $\hat{H}_{\delta,\mathrm{a}}$ and $\hat{H}_{\delta,\mathrm{r}}$ are defined by Eqs. 8.8 and 8.9, 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,

$$\Delta\hat{\rho} = d_t\hat{I}_t + d_z\hat{I}_z + d_+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + d_-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t}. \tag{8.23}$$

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

$$\frac{\mathrm{d}(d_z\hat{I}_z + d_+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + d_-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t})}{\mathrm{d}t} = -\frac{\mathrm{i}b}{\hbar}\left[c^z\hat{I}_z + \sqrt{\frac{3}{8}}c^+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + \sqrt{\frac{3}{8}}c^-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t}, d_z\hat{I}_z + d_+\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} + d_-\hat{I}_-\mathrm{e}^{-\mathrm{i}\omega_0 t}\right], \tag{8.24}$$

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

$$c^z = \frac{1}{2}(3\cos^2\vartheta - 1) = \Theta^{\parallel} \tag{8.25}$$

$$c^+ = \sqrt{\frac{3}{2}}\sin\vartheta\cos\vartheta\mathrm{e}^{-\mathrm{i}\varphi} = \sqrt{\frac{2}{3}}\Theta^{\perp}\mathrm{e}^{-\mathrm{i}\varphi} \tag{8.26}$$

$$c^- = \sqrt{\frac{3}{2}}\sin\vartheta\cos\vartheta\mathrm{e}^{+\mathrm{i}\varphi} = \sqrt{\frac{2}{3}}\Theta^{\perp}\mathrm{e}^{+\mathrm{i}\varphi} \tag{8.27}$$

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

$$\frac{\mathrm{d}\Delta\hat{\rho}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int\limits_0^\infty \overline{[\hat{H}_{\delta,\mathrm{a}}(0),[\hat{H}_{\delta,\mathrm{a}}(t),\Delta\hat{\rho}]]}\mathrm{d}t. \tag{8.28}$$

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 $t_j = 0$).[3] 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

$$[\hat{I}_z,\hat{I}_{\pm}] = [\hat{I}_z,\hat{I}_x] \pm \mathrm{i}[\hat{I}_z,\hat{I}_y] = \pm\hbar(\hat{I}_x \pm \mathrm{i}\hat{I}_y) = \pm\hbar\hat{I}_{\pm} \tag{8.29}$$

and

$$[\hat{I}_+,\hat{I}_-] = [\hat{I}_x,\hat{I}_x] - \mathrm{i}[\hat{I}_x,\hat{I}_y] + \mathrm{i}[\hat{I}_y,\hat{I}_x] + [\hat{I}_y,\hat{I}_y] = 2\hbar\hat{I}_z. \tag{8.30}$$

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

Let us start with M_z. According to Eq. 6.17,

$$\langle\Delta M_z\rangle = \mathrm{Tr}\{\hat{M}_z\Delta\hat{\rho}\} \tag{8.31}$$

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. 9.32)

$$\hat{M}_z = \mathcal{N}\gamma\hat{I}_z, \tag{8.32}$$

where $\mathcal{N}$ is the number of molecules per volume element 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. 8.28 reduces to

$$\frac{\mathrm{d}d_z}{\mathrm{d}t}\hat{I}_z \tag{8.33}$$

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

$$[\hat{I}_z,[\hat{I}_z,\hat{I}_z]] = 0 \qquad [\hat{I}_+,[\hat{I}_-,\hat{I}_z]] = 2\hbar^2\hat{I}_z \qquad [\hat{I}_-,[\hat{I}_+,\hat{I}_z]] = 2\hbar^2\hat{I}_z \tag{8.34}$$

After substituting into Eq. 8.28,

$$\frac{\mathrm{d}d_z}{\mathrm{d}t}\mathrm{Tr}\{\hat{I}_z\hat{I}_z\} = -\left(\frac{3}{4}b^2\int\limits_0^\infty\overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \frac{3}{4}b^2\int\limits_0^\infty\overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right)d_z\mathrm{Tr}\{\hat{I}_z\hat{I}_z\} \tag{8.35}$$

$$\frac{\mathrm{d}\Delta\langle M_z\rangle}{\mathrm{d}t} = -\left(\frac{3}{4}b^2\int\limits_0^\infty\overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \frac{3}{4}b^2\int\limits_0^\infty\overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right)\Delta\langle M_z\rangle \tag{8.36}$$

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

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

$$R_1 = \frac{3}{4}b^2\Re\left\{\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right\} \tag{8.37}$$

As already discussed in the classical description of relaxation, 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. Therefore,

$$\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t + \int_{-\infty}^0 \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right) = \frac{1}{2}\int_{-\infty}^\infty \overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t. \tag{8.38}$$

$$\int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t = \frac{1}{2}\left(\int_0^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t + \int_{-\infty}^0 \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t\right) = \frac{1}{2}\int_{-\infty}^\infty \overline{c^-(0)c^+(t)}\mathrm{e}^{-\mathrm{i}\omega_0 t}\mathrm{d}t, \tag{8.39}$$

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

The relaxation rate R_1 can be therefore written in the same form as derived classically.

$$R_1 = \frac{3}{4}b^2\left(\frac{1}{2}J(\omega_0) + \frac{1}{2}J(-\omega_0)\right) \approx \frac{3}{4}b^2 J(\omega_0) \tag{8.40}$$

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 molecular motions are assumed to be completely random and independent of the distribution of magnetic moments, M_z is expected to decay to zero, which doe not happen in reality. If the coupling between molecular motions and magnetic moment distribution is described correctly by the quantum theory, the transition $|\beta\rangle \rightarrow |\alpha\rangle$ is slightly more probable.[4] This drives the system back to the equilibrium distribution of magnetic moments.

Let us continue with M_+. According to Eq. 6.17,

$$\Delta\langle M_+\rangle \equiv \langle M_+\rangle = \mathrm{Tr}\{\hat{M}_+\Delta\hat{\rho}\} \tag{8.41}$$

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

$$\hat{M}_+ = \mathcal{N}\gamma\hat{I}_+ = \mathcal{N}\gamma(\hat{I}_x + \mathrm{i}\hat{I}_y). \tag{8.42}$$

Due to the orthogonality of basis matrices, the left-hand side of Eq. 8.28 reduces to

$$\frac{\mathrm{d}d_+}{\mathrm{d}t}\hat{I}_+\mathrm{e}^{\mathrm{i}\omega_0 t} \tag{8.43}$$

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:

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[4] It can be described as $J(\omega_0) = \mathrm{e}^{-\hbar\omega_0/k_\mathrm{B}T}J(-\omega_0)$ and taken into account by working with $\Delta\hat{\rho}$ and $\langle\Delta M_z\rangle$ instead of $\hat{\rho}$ and $\langle M_z\rangle$.

$$[\hat{I}_z,[\hat{I}_z,\hat{I}_+]]=\hbar^2\hat{I}_+ \qquad [\hat{I}_+,[\hat{I}_-,\hat{I}_+]]=2\hbar^2\hat{I}_+ \qquad [\hat{I}_-,[\hat{I}_+,\hat{I}_+]]=0. \tag{8.44}$$

After substituting into Eq. 8.28,

$$\frac{\mathrm{d}d_+}{\mathrm{d}t}\mathrm{Tr}\{\hat{I}_+\hat{I}_+\}=-\left(b^2\int\limits_0^\infty\overline{c^z(0)c^z(t)}\mathrm{d}t+\frac{3}{4}b^2\int\limits_0^\infty\overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right)d_+\mathrm{Tr}\{\hat{I}_+\hat{I}_+\} \tag{8.45}$$

$$\frac{\mathrm{d}\langle M_+\rangle}{\mathrm{d}t}=-\left(b^2\int\limits_0^\infty\overline{c^z(0)c^z(t)}\mathrm{d}t+\frac{3}{4}b^2\int\limits_0^\infty\overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right)\langle M_+\rangle \tag{8.46}$$

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.

$$R_2=b^2\int\limits_0^\infty\overline{c^z(0)c^z(t)}\mathrm{d}t+\Re\left\{\frac{3}{4}b^2\int\limits_0^\infty\overline{c^+(0)c^-(t)}\mathrm{e}^{\mathrm{i}\omega_0 t}\mathrm{d}t\right\}. \tag{8.47}$$

Note that the first integral in 8.47 is a real number, equal to R_0 derived by the classical analysis.
Using the same arguments as for M_z,

$$R_2=b^2\left(\frac{1}{2}J(0)+\frac{3}{8}J(\omega_0)\right)\approx R_0+\frac{1}{2}R_1. \tag{8.48}$$

What is the physical interpretation of the obtained equation? Two terms in Eq. 8.48 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 in Section4.2 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 $\overline{c^-(0)c^+(t)}$ contribute 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[5]:

$$R_2=b^2\left(\frac{1}{2}J(0)+\frac{3}{4}\frac{1}{2}J(-\omega_0)\right)\approx R_0+\frac{1}{2}R_1. \tag{8.49}$$

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[5] 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.

8.8 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.

8.8.1 Excitation by radio wave pulses

At the beginning of the experiment, the density matrix describes thermal equilibrium (Eq. 8.20):

$$\hat{\rho}(0) = \mathcal{I}_t + \kappa\mathcal{I}_z. \tag{8.50}$$

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

$$\mathcal{H} = \varepsilon_t\cdot\mathcal{I}_t - \gamma B_0(1+\delta_\mathrm{i})\mathcal{I}_z - \gamma B_1(1+\delta_\mathrm{i})\cos(\omega_\mathrm{rot}t)\mathcal{I}_x - \gamma B_1(1+\delta_\mathrm{i})\sin(\omega_\mathrm{rot}t)\mathcal{I}_y, \tag{8.51}$$

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 $\cos(\omega_\mathrm{rot}t)$ and $\sin(\omega_\mathrm{rot}t)$ terms.

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

$$\mathcal{H} = \varepsilon_t\cdot\mathcal{I}_t + \underbrace{(-\gamma B_0(1+\delta_\mathrm{i}) - \omega_\mathrm{rot})}_{\Omega}\mathcal{I}_z + \underbrace{(-\gamma B_1(1+\delta_\mathrm{i}))}_{\omega_1}\mathcal{I}_x, \tag{8.52}$$

but it still contains non-commuting terms ($\mathcal{I}_x$ *vs.* $\mathcal{I}_z$). Let us 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 μs corresponds to 40 μs for a full circle, $1/40\,\mu\text{s} = 25\,\text{kHz}$).

- Typical values of R_1 are $10^{-1}\,\text{s}^{-1}$ to $10^{0}\,\text{s}^{-1}$ and typical values of R_2 are $10^{-1}\,\text{s}^{-1}$ to $10^{2}\,\text{s}^{-1}$ 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.[6] The carrier frequency ω_radio is often set to the precession frequency of 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":

$$\hat{\rho}(0) = \mathcal{I}_t + \kappa\mathcal{I}_z \longrightarrow \hat{\rho}(\tau_\text{p}) = \mathcal{I}_t + \kappa(\mathcal{I}_z\cos(\omega_1\tau_\text{p}) - \mathcal{I}_y\sin(\omega_1\tau_\text{p})). \tag{8.53}$$

For a 90° pulse,

$$\hat{\rho}(\tau_\text{p}) = \mathcal{I}_t - \kappa\mathcal{I}_y. \tag{8.54}$$

8.8.2 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

$$\hat{\rho}(t) = \mathcal{I}_t + \kappa(-\mathcal{I}_y\cos(\Omega t) + \mathcal{I}_x\sin(\Omega t)). \tag{8.55}$$

The measured quantity M_+ can be expressed as (Eq. 6.17)

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[6] 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.

$$\langle M_+\rangle = \mathrm{Tr}\{\hat{M}_+\hat{\rho}(t)\} = \mathcal{N}\gamma\hbar\mathrm{Tr}\{\mathcal{I}_+(\mathcal{I}_t + \kappa(-\mathcal{I}_y\cos(\Omega t) + \mathcal{I}_x\sin(\Omega t))\}. \tag{8.56}$$

The relevant traces are

$$\mathrm{Tr}\{\mathcal{I}_+\mathcal{I}_t\} = \mathrm{Tr}\left\{\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}\frac{1}{2}&0\\0&\frac{1}{2}\end{pmatrix}\right\} = \mathrm{Tr}\left\{\begin{pmatrix}0&\frac{1}{2}\\0&0\end{pmatrix}\right\} = 0 \tag{8.57}$$

$$\mathrm{Tr}\{\mathcal{I}_+\mathcal{I}_x\} = \mathrm{Tr}\left\{\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}0&\frac{1}{2}\\\frac{1}{2}&0\end{pmatrix}\right\} = \mathrm{Tr}\left\{\begin{pmatrix}\frac{1}{2}&0\\0&0\end{pmatrix}\right\} = \frac{1}{2} \tag{8.58}$$

$$\mathrm{Tr}\{\mathcal{I}_+\mathcal{I}_y\} = \mathrm{Tr}\left\{\begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}0&-\frac{\mathrm{i}}{2}\\\frac{\mathrm{i}}{2}&0\end{pmatrix}\right\} = \mathrm{Tr}\left\{\begin{pmatrix}\frac{\mathrm{i}}{2}&0\\0&0\end{pmatrix}\right\} = \frac{\mathrm{i}}{2} \tag{8.59}$$

Including relaxation and expressing κ

$$\langle M_+\rangle = \frac{\mathcal{N}\gamma^2\hbar^2B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2t}(\sin(\Omega t) - \mathrm{i}\cos(\Omega t)). \tag{8.60}$$

which can be rewritten as

$$\langle M_+\rangle = \frac{\mathcal{N}\gamma^2\hbar^2B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2t}\left(\cos\left(\Omega t - \frac{\pi}{2}\right) + \mathrm{i}\sin\left(\Omega t - \frac{\pi}{2}\right)\right)) = \frac{\mathcal{N}\gamma^2\hbar^2B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2t}\mathrm{e}^{\mathrm{i}\Omega t}\mathrm{e}^{-\mathrm{i}\frac{\pi}{2}}. \tag{8.61}$$

We know that in order to obtain purely Lorentzian (absorption) real component of the spectrum by Fourier transformation, the signal should evolve as $\mathrm{e}^{-R_2t}\mathrm{e}^{\mathrm{i}\Omega t}$. We see that magnetization described by Eq. 8.61 is shifted from the ideal signal by a phase of $-\pi/2$. However, this is true only if 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 (corresponding to multiplying Eq. 8.61 by $\mathrm{e}^{\mathrm{i}\pi/2}$). It tells us that we can ignore the phase shift and write the phase-corrected signal as

$$\langle M_+\rangle = \frac{\mathcal{N}\gamma^2\hbar^2B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2t}(\cos(\Omega t) + \mathrm{i}\sin(\Omega t)) = \frac{\mathcal{N}\gamma^2\hbar^2B_0}{4k_\mathrm{B}T}\mathrm{e}^{-R_2t}\mathrm{e}^{\mathrm{i}\Omega t}. \tag{8.62}$$

8.8.3 Spectrum and signal-to-noise ratio

Knowing the expected magnetization, we can try to describe the one-dimensional NMR spectrum quantitatively. To do it, we need to know

1. how is the detected signal related to the magnetization. Here, Eq. 1.50 helps us: μ in Eq. 1.50 is simply magnetization multiplied by the volume sensed by the detector coil.

2. how is the time-dependent signal converted to a frequency spectrum. Here, the answer is described in Chapter 5, the most important step is the Fourier transform.[7]

3. how is the noise defined. Here, we use the result of statistical mechanics showing that the square of the thermal noise of electrons is $\langle n^2 \rangle = 4Rk_\mathrm{B}T\Delta f$, where R is resistance, T is temperature, and Δf is the frequency bandwidth of the detector.

If we do not include relaxation, neglect effect of the preamplifier, resistance of the sample, and assume that the receiver coil and sample have the same temperature, the result of the analysis is

$$\text{Signal/noise} = K\frac{\mathcal{N}\gamma^{5/2}\hbar^2 B_0^{3/2}}{k_\mathrm{B}^{3/2}T_\mathrm{sample}^{3/2}(\Delta f)^{1/2}}, \tag{8.63}$$

where K includes geometry and construction factors, and Δf is the receiver bandwidth.

In the most sensitive NMR probes, the motions of the electrons are suppressed by cooling the receiver coil to a very low temperature, approximately 20 K. Therefore, we have to include the sample and coil temperature separately. If the effect of preamplifier is included, we get a bit more complex relation

$$\text{Signal/noise} = K\frac{\mathcal{N}\gamma^{5/2}\hbar^2 B_0^{3/2}}{k_\mathrm{B}^{3/2}T_\mathrm{sample}\sqrt{(T_\mathrm{coil} + T_\mathrm{sample}R'/R + (1+R'/R)\,T')\Delta f}}, \tag{8.64}$$

where R is the resistance of the coil, R' is the resistance induced by the sample in the coil (proportional to the conductivity and therefore to the ionic strength of the sample), and T' is so called noise temperature of the amplifier.[8] The actual sensitivity also depends on relaxation,[9] apodization (or other tricks of processing), and is also proportional to square root of the ratio of the time of signal acquisition to the overall time of the experiment.[10]

The numerical values given by Eqs. 8.63–8.64 are of little practical use. However, it is useful to notice how sensitivity depends on individual factors (temperature, field, magnetogyric ratio of the observed nucleus).

8.8.4 Conclusions

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

- The analysis of a one-pulse NMR experiment shows that the density matrix evolves as

  $$\hat{\rho}(t) \propto (\mathcal{I}_x\cos(\Omega t + \phi) + \mathcal{I}_y\sin(\Omega t) + \phi) + \text{terms orthogonal to } \mathcal{I}_+, \tag{8.65}$$

  the magnetization rotates during signal acquisition as

  $$\langle M_+ \rangle = |M_+|\mathrm{e}^{-R_2 t}\mathrm{e}^{\mathrm{i}\Omega t} \tag{8.66}$$

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

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[7] We already assumed that the phase correction was applied. Another factor determining the shape of the spectrum in practice is apodization, but we can ignore it now for the sake of simplicity.

[8] The input noise is amplified by the factor $(1 + T'/T)G$, where G is the gain of the preamplifier.

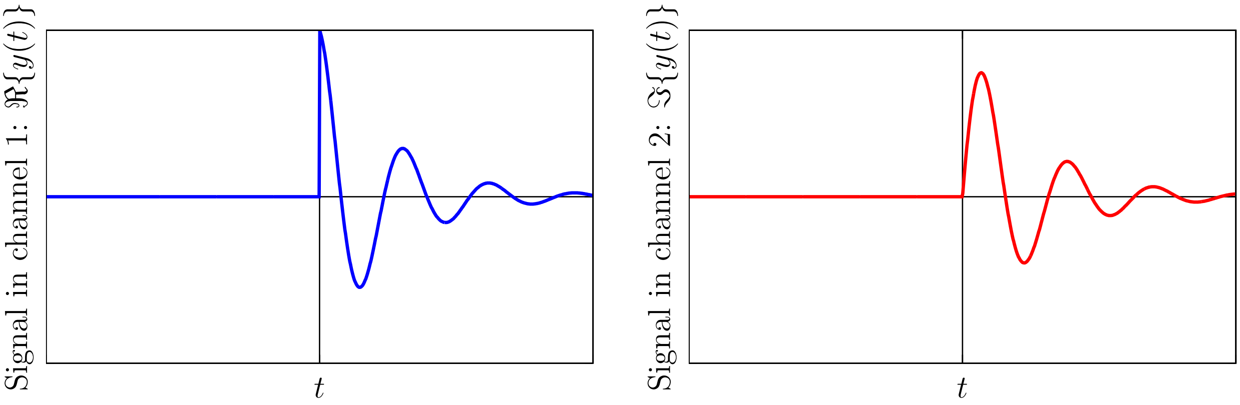
[9] At low temperatures, Boltzmann distribution is more favorable but line broadening more severe (mostly due to higher viscosity of the solvent at low temperature). Therefore, the temperature dependence of sensitivity on the temperature has a maximum (interestingly close to room temperature for medium-size proteins in aqueous solutions).

[10] In many experiments (but not necessarily in the one-dimensional experiment), recycle delay (waiting for the sample to return close to the equilibrium before the next measurement) is much longer than the actual signal acquisition.

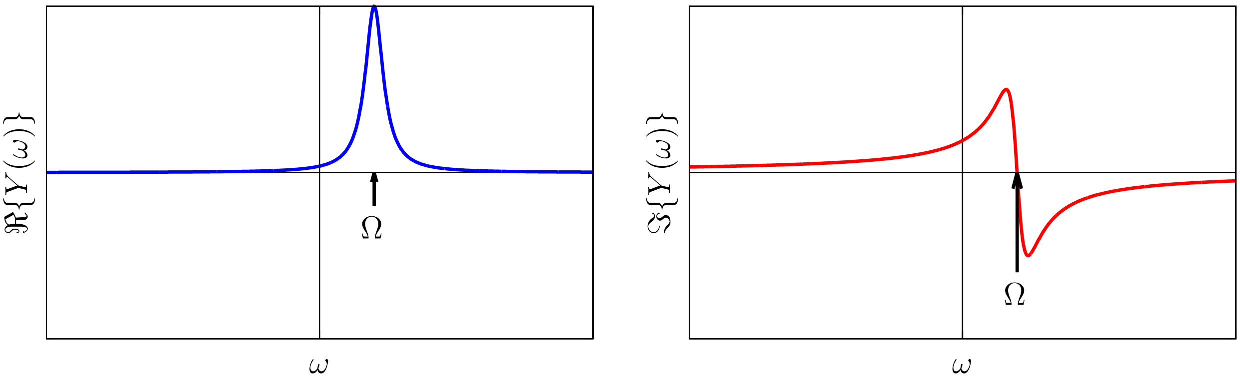
- Fourier transform gives a complex signal proportional to

$$\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_{\mathrm{B}}T}\left(\frac{R_2}{R_2^2+(\omega-\Omega)^2}-\mathrm{i}\frac{\omega-\Omega}{R_2^2+(\omega-\Omega)^2}\right). \tag{8.67}$$

- 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:



After Fourier transformation:



- The signal-to-noise ratio (without relaxation) is proportional to $\gamma^{5/2}B_0^{3/2}$, with the optimal temperature given by relaxation properties (close to room temperatures for proteins in aqueous solutions).

Chapter 9

Product operators, dipolar coupling

Literature: The product operator formalism for multi-spin systems is described in B17.4, B18, C2.5.1, C2.7, L15. The dipole-dipole Hamiltonian is discussed in L9.3. Relaxtion is described K9, L19–L20, C5 in different manners. All texts are excellent. It is very helpful to read them all if you really want to get an insight. However, the topic is difficult and absorbing the information requires a lot of time.

9.1 Dipolar coupling

So far, we analyzed effects of various fields on nuclei, but we assumed that all nuclei are independent and their properties can be described by operators composed of two-dimensional matrices. Now we take into account also mutual interactions – interactions with fields generated by other nuclei.

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

$$\vec{B}_2 = \vec{\nabla} \times \vec{A}_2, \tag{9.1}$$

where

$$\vec{\nabla} \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right). \tag{9.2}$$

Let us assume (classically) that the source of the magnetic moment of nucleus 2 is a current loop. It can be derived from Maxwell equations that the vector potential A_2 in a distance much larger than radius of the loop is

$$\vec{A}_2 = \frac{\mu_0}{4\pi} \frac{\vec{\mu}_2 \times r}{r^3}, \tag{9.3}$$

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

$$\vec{B}_2 = \frac{\mu_0}{4\pi} \vec{\nabla} \times \frac{\vec{\mu}_2 \times \vec{r}}{r^3}. \tag{9.4}$$

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

$$\begin{aligned}
B_{2,x} &= \frac{\mu_0}{4\pi r^5}((3r_x^2 - r^2)\mu_{2,x} + 3r_x r_y \mu_{2,y} + 3r_x r_z \mu_{2,z}) && (9.5)\\
B_{2,y} &= \frac{\mu_0}{4\pi r^5}(3r_x r_y \mu_{2,x} + (3r_y^2 - r^2)\mu_{2,y} + 3r_y r_z \mu_{2,z}) && (9.6)\\
B_{2,z} &= \frac{\mu_0}{4\pi r^5}(3r_x r_z \mu_{2,x} + 3r_y r_z \mu_{2,y} + (3r_z^2 - r^2)\mu_{2,z}), && (9.7)
\end{aligned}$$

which can by described by a matrix equation

$$\begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} = \frac{\mu_0}{4\pi r^5} \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}. \tag{9.8}$$

The matrix in Eq. 9.8 represents a tensor describing the geometric relations of the dipolar coupling and has the same form as the matrix in Eq. 3.41, 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. 9.8. Like the anisotropic part of the chemical shift tensor, the matrix in Eq. 9.8 simplifies to

$$\frac{\mu_0}{4\pi r^3} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{9.9}$$

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

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \longrightarrow \frac{1}{r^2} \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix}, \tag{9.10}$$

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

Classical electrodynamics tells us that the energy of the interaction with the field of the second dipolar magnetic moments ($E = -\vec{\mu}_1 \cdot \vec{B}_2$) is

$$\begin{aligned}
E = -\frac{\mu_0 \gamma_1 \gamma_2}{4\pi r^3} \quad & \big((3\sin^2\vartheta\cos^2\varphi - 1)\mu_{1x}\mu_{2x} + (3\sin^2\vartheta\sin^2\varphi - 1)\mu_{1y}\mu_{2y} + (3\cos^2\vartheta - 1)\mu_{1z}\mu_{2z} + \\
& + \; 3\sin^2\vartheta\sin\varphi\cos\varphi\mu_{1x}\mu_{2y} + 3\sin\vartheta\cos\vartheta\cos\varphi\mu_{1x}\mu_{2z} + 3\sin\vartheta\cos\vartheta\sin\varphi\mu_{1y}\mu_{2z} \\
& + \; 3\sin^2\vartheta\sin\varphi\cos\varphi\mu_{1y}\mu_{2x} + 3\sin\vartheta\cos\vartheta\cos\varphi\mu_{1z}\mu_{2x} + 3\sin\vartheta\cos\vartheta\sin\varphi\mu_{1z}\mu_{2y}\big) \,.
\end{aligned} \tag{9.11}$$

Having the classical description of the interaction of two magnetic dipolar moments, we can ask how the quantum description should be modified if the magnetic moments interact. 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, there are $2 \times 2 = 4$ states. Therefore, the probability density matrix should describe the pair of magnetic moments and its four states as one entity. Furthermore, the classical expression of the interaction energy (Eq. 9.11) suggests that the Hamiltonian should be built from operators representing *products* of individual components of the interacting magnetic moments. Let us know look for a basis that fulfils these requirements.

9.2 Product operators

The density matrix for four states is a 4×4 matrix. Basis used for such density matrices must consist of $4^2 = 16$ matrices. The density matrix for N states is 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*[1] of basis matrices of spins without mutual interactions. For example, Cartesian single-spin operators can be used to create a basis for two spins (see Table 9.1) using the following direct products:

$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_t(12) \tag{9.12}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_{1x}(12) \tag{9.13}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_{1y}(12) \tag{9.14}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_t(2) = \mathcal{I}_{1z}(12) \tag{9.15}$$
$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_x(2) = \mathcal{I}_{2x}(12) \tag{9.16}$$
$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_y(2) = \mathcal{I}_{2y}(12) \tag{9.17}$$
$$2 \cdot \mathcal{I}_t(1) \otimes \mathcal{I}_z(2) = \mathcal{I}_{2z}(12) \tag{9.18}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_x(2) = 2\mathcal{I}_{1x}\mathcal{I}_{2x}(12) \tag{9.19}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_y(2) = 2\mathcal{I}_{1x}\mathcal{I}_{2y}(12) \tag{9.20}$$
$$2 \cdot \mathcal{I}_x(1) \otimes \mathcal{I}_z(2) = 2\mathcal{I}_{1x}\mathcal{I}_{2z}(12) \tag{9.21}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_x(2) = 2\mathcal{I}_{1y}\mathcal{I}_{2x}(12) \tag{9.22}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_y(2) = 2\mathcal{I}_{1y}\mathcal{I}_{2y}(12) \tag{9.23}$$
$$2 \cdot \mathcal{I}_y(1) \otimes \mathcal{I}_z(2) = 2\mathcal{I}_{1y}\mathcal{I}_{2z}(12) \tag{9.24}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_x(2) = 2\mathcal{I}_{1z}\mathcal{I}_{2x}(12) \tag{9.25}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_y(2) = 2\mathcal{I}_{1z}\mathcal{I}_{2y}(12) \tag{9.26}$$
$$2 \cdot \mathcal{I}_z(1) \otimes \mathcal{I}_z(2) = 2\mathcal{I}_{1z}\mathcal{I}_{2z}(12), \tag{9.27}$$

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[2] $\frac{1}{2}\hat{1}$, 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 2×2 matrices, but $\mathcal{I}_{1x}(12)$ and $\mathcal{I}_{2x}(12)$ are different 4×4 matrices. Basis matrices for more nuclei are derived in the same manner, e.g. $2\mathcal{I}_{1z}\mathcal{I}_{2x}(12) \otimes \mathcal{I}_y(3) = 4\mathcal{I}_{1z}\mathcal{I}_{2x}\mathcal{I}_{3y}(123)$.

The basis presented in Table 9.1 represents one of many possible choices. Another

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[1] Direct product $\hat{A} \otimes \hat{B}$ is a mathematical operation when each element of the matrix $\hat{A}$ is multiplied by the whole matrix $\hat{B}$.

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

Table 9.1: Cartesian basis of product operators for a pair of spin-$\frac{1}{2}$ nuclei

$\mathcal{I}_t = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +1 \end{pmatrix}$	$\mathcal{I}_{1z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$	$\mathcal{I}_{2z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$	$2\mathcal{I}_{1z}\mathcal{I}_{2z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & +1 \end{pmatrix}$
$\mathcal{I}_{1x} = \frac{1}{2}\begin{pmatrix} 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +1 \\ +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \end{pmatrix}$	$2\mathcal{I}_{1x}\mathcal{I}_{2z} = \frac{1}{2}\begin{pmatrix} 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \\ +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$	$\mathcal{I}_{1y} = \frac{1}{2}\begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & +\mathrm{i} & 0 & 0 \end{pmatrix}$	$2\mathcal{I}_{1y}\mathcal{I}_{2z} = \frac{1}{2}\begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & +\mathrm{i} \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & -\mathrm{i} & 0 & 0 \end{pmatrix}$
$\mathcal{I}_{2x} = \frac{1}{2}\begin{pmatrix} 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 \\ 0 & 0 & +1 & 0 \end{pmatrix}$	$2\mathcal{I}_{1z}\mathcal{I}_{2x} = \frac{1}{2}\begin{pmatrix} 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	$\mathcal{I}_{2y} = \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & +\mathrm{i} & 0 \end{pmatrix}$	$2\mathcal{I}_{1z}\mathcal{I}_{2y} = \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & +\mathrm{i} \\ 0 & 0 & -\mathrm{i} & 0 \end{pmatrix}$
$2\mathcal{I}_{1x}\mathcal{I}_{1x} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & +1 \\ 0 & 0 & +1 & 0 \\ 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \end{pmatrix}$	$2\mathcal{I}_{1y}\mathcal{I}_{1y} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & +1 & 0 \\ 0 & +1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$	$2\mathcal{I}_{1x}\mathcal{I}_{1y} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & +\mathrm{i} & 0 \\ 0 & -\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \end{pmatrix}$	$2\mathcal{I}_{1y}\mathcal{I}_{1x} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & -\mathrm{i} & 0 \\ 0 & +\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \end{pmatrix}$

possible basis is shown in Table 9.2. Eqs. 7.4 and 7.5 can be used to convert product operators of the basis sets in Tables 9.1 and 9.2.

9.3 Liouville - von Neumann equation

The Liouville - von Neumann equation can be written in the same form as for spins without mutual interactions (Eq. 7.19):

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = \mathrm{i}(\hat{\rho}\mathcal{H} - \mathcal{H}\hat{\rho}) = \mathrm{i}[\hat{\rho}, \mathcal{H}] = -\mathrm{i}[\mathcal{H}, \hat{\rho}], \tag{9.28}$$

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.

$$[\mathcal{I}_{n,x}, \mathcal{I}_{n,y}] = \mathrm{i}\mathcal{I}_{n,z} \qquad [\mathcal{I}_{n,y}, \mathcal{I}_{n,z}] = \mathrm{i}\mathcal{I}_{n,x} \qquad [\mathcal{I}_{n,z}, \mathcal{I}_{n,x}] = \mathrm{i}\mathcal{I}_{n,y} \tag{9.29}$$

$$[\mathcal{I}_{n,j}, 2\mathcal{I}_{n,k}\mathcal{I}_{n',l}] = 2[\mathcal{I}_{n,j}, \mathcal{I}_{n,k}]\mathcal{I}_{n',l} \tag{9.30}$$

$$[2\mathcal{I}_{n,j}\mathcal{I}_{n',l}, 2\mathcal{I}_{n,k}\mathcal{I}_{n',m}] = [\mathcal{I}_{n,j}, \mathcal{I}_{n,k}]\delta_{lm}, \tag{9.31}$$

Table 9.2: Single-element basis of product operators for a pair of spin-$\frac{1}{2}$ nuclei

$\mathcal{I}_{1\alpha}\mathcal{I}_{2\alpha}=\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1\alpha}\mathcal{I}_{2\beta}=\begin{pmatrix}0&0&0&0\\0&1&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1\beta}\mathcal{I}_{2\alpha}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&1&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1\beta}\mathcal{I}_{2\beta}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&1\end{pmatrix}$
$\mathcal{I}_{1\alpha}\mathcal{I}_{2+}=\begin{pmatrix}0&1&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1\alpha}\mathcal{I}_{2-}=\begin{pmatrix}0&0&0&0\\1&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1\beta}\mathcal{I}_{2+}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1\beta}\mathcal{I}_{2-}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}$
$\mathcal{I}_{1+}\mathcal{I}_{2\alpha}=\begin{pmatrix}0&0&1&0\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1-}\mathcal{I}_{2\alpha}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1+}\mathcal{I}_{2\beta}=\begin{pmatrix}0&0&0&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1-}\mathcal{I}_{2\beta}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\0&1&0&0\end{pmatrix}$
$\mathcal{I}_{1+}\mathcal{I}_{2+}=\begin{pmatrix}0&0&0&1\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1+}\mathcal{I}_{2-}=-\begin{pmatrix}0&0&0&0\\0&0&1&0\\0&0&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1-}\mathcal{I}_{2+}=-\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&1&0&0\\0&0&0&0\end{pmatrix}$	$\mathcal{I}_{1-}\mathcal{I}_{2-}=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\1&0&0&0\end{pmatrix}$

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 $l\neq m$.

9.4 Operator of the observed quantity

In order to describe the observed signal for a system of different nuclei, Eq. 9.32, defining the operator of complex magnetization, must be slightly modified

$$\hat{M}_{+}=\sum_{n}\mathcal{N}_n\gamma_n(\hat{I}_{n,x}+\mathrm{i}\hat{I}_{n,y})=\sum_{n}\mathcal{N}_n\gamma_n\hat{I}_{n,+},\tag{9.32}$$

where the index n distinguishes different types of nuclei and $\mathcal{N}_n$ is the number of nuclei of each type in the sample (per unit volume).

9.5 Hamiltonian of dipolar coupling

As usually, Hamiltonian of the dipolar coupling can be obtained using the classical description of the energy (Eq. 9.11). 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

$$\begin{aligned}\hat{H}_D&=-\gamma_1(\hat{I}_{1,x}B_{2,x}+\hat{I}_{1,y}B_{2,y}+\hat{I}_{1,z}B_{2,z})=-\gamma_1\left(\,\hat{I}_{1,x}\;\hat{I}_{1,y}\;\hat{I}_{1,z}\,\right)\begin{pmatrix}B_{2,x}\\B_{2,y}\\B_{2,z}\end{pmatrix}=\\&=-\frac{\mu_0\gamma_1\gamma_2}{4\pi r^5}\left(\,\hat{I}_{1,x}\;\hat{I}_{1,y}\;\hat{I}_{1,z}\,\right)\begin{pmatrix}3r_x^2-r^2&3r_xr_y&3r_xr_z\\3r_xr_y&3r_y^2-r^2&3r_yr_z\\3r_xr_z&3r_yr_z&3r_z^2-r^2\end{pmatrix}\begin{pmatrix}\hat{I}_{2,x}\\\hat{I}_{2,y}\\\hat{I}_{2,z}\end{pmatrix}=\vec{I}_1\cdot\underline{D}\cdot\vec{I}_2\end{aligned}\tag{9.33}$$

where $\underline{D}$ is the tensor of direct dipole-dipole interactions (dipolar coupling).

The Hamiltonian can be written in spherical coordinates as

$$\begin{aligned}\hat{H}_D = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3} & \Big((3\sin^2\vartheta\cos^2\varphi-1)\hat{I}_{1x}\hat{I}_{2x} + (3\sin^2\vartheta\sin^2\varphi-1)\hat{I}_{1y}\hat{I}_{2y} + (3\cos^2\vartheta-1)\hat{I}_{1z}\hat{I}_{2z} + \\ & + \ 3\sin^2\vartheta\sin\varphi\cos\varphi\hat{I}_{1x}\hat{I}_{2y} + 3\sin\vartheta\cos\vartheta\cos\varphi\hat{I}_{1x}\hat{I}_{2z} + 3\sin\vartheta\cos\vartheta\sin\varphi\hat{I}_{1y}\hat{I}_{2z} \\ & + \ 3\sin^2\vartheta\sin\varphi\cos\varphi\hat{I}_{1y}\hat{I}_{2x} + 3\sin\vartheta\cos\vartheta\cos\varphi\hat{I}_{1z}\hat{I}_{2x} + 3\sin\vartheta\cos\vartheta\sin\varphi\hat{I}_{1z}\hat{I}_{2y}\Big). \qquad (9.34)\end{aligned}$$

9.6 Secular approximation and averaging

Similarly to the chemical-shift Hamiltonian, 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[3] $(r^2 - \langle r_z^2\rangle)/2$ 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

$$\hat{H}_D = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^5}\left(3\langle r_z^2\rangle - r^2\right)\left(\hat{I}_{1,z}\hat{I}_{2,z} - \frac{1}{2}\hat{I}_{1,x}\hat{I}_{2,x} - \frac{1}{2}\hat{I}_{1,y}\hat{I}_{2,y}\right) \qquad (9.35)$$

$$= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\frac{3\langle\cos^2\vartheta\rangle - 1}{2}\left(2\hat{I}_{1,z}\hat{I}_{2,z} - \hat{I}_{1,x}\hat{I}_{2,x} - \hat{I}_{1,y}\hat{I}_{2,y}\right). \qquad (9.36)$$

- 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

$$\hat{H}_D = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^5}\left(3\langle r_z^2\rangle - r^2\right)\hat{I}_{1,z}\hat{I}_{2,z} = -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\frac{3\langle\cos^2\vartheta\rangle - 1}{2}2\hat{I}_{1,z}\hat{I}_{2,z}. \qquad (9.37)$$

- 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:

$$\overline{r_x^2} = \overline{r_y^2} = \overline{r_z^2}. \qquad (9.38)$$

  Finally,

$$r_x^2 + r_y^2 + r_z^2 = r^2 \Rightarrow \overline{r_x^2 + r_y^2 + r_z^2} = \overline{3r_z^2} = r^2 \Rightarrow \overline{3r_z^2 - r^2} = r\overline{(3\cos^2\vartheta - 1)} = 0. \qquad (9.39)$$

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. Last but not least, the dipole-dipole interactions represent a very important source of relaxation.

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

9.7 Dipole-dipole relaxation

Rotation of the molecule (and internal motions) change the orientation of the internuclear 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 3.41 and 9.8. 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 $\hat{I}_\pm = \hat{I}_x \pm \mathrm{i}\hat{I}_y$):

$$\begin{aligned}
\hat{I}_{1x}\hat{I}_{2z} &= \frac{1}{2}(+\hat{I}_{1+}\hat{I}_{2z} + \hat{I}_{1-}\hat{I}_{2z}), && (9.40)\\
\hat{I}_{1y}\hat{I}_{2z} &= \frac{\mathrm{i}}{2}(-\hat{I}_{1+}\hat{I}_{2z} + \hat{I}_{1-}\hat{I}_{2z}), && (9.41)\\
\hat{I}_{1z}\hat{I}_{2x} &= \frac{1}{2}(+\hat{I}_{1z}\hat{I}_{2+} + \hat{I}_{1z}\hat{I}_{2-}), && (9.42)\\
\hat{I}_{1z}\hat{I}_{2y} &= \frac{\mathrm{i}}{2}(-\hat{I}_{1z}\hat{I}_{2+} + \hat{I}_{1z}\hat{I}_{2-}). && (9.43)
\end{aligned}$$

Since

$$\begin{aligned}
\cos\varphi + \mathrm{i}\sin\varphi &= \mathrm{e}^{\mathrm{i}\varphi}, && (9.44)\\
\cos\varphi - \mathrm{i}\sin\varphi &= \mathrm{e}^{-\mathrm{i}\varphi}, && (9.45)
\end{aligned}$$

$$\begin{aligned}
&3\sin\vartheta\cos\vartheta(\hat{I}_{1x}\hat{I}_{2z}\cos\varphi + \hat{I}_{1y}\hat{I}_{2z}\sin\varphi + \hat{I}_{1z}\hat{I}_{2x}\cos\varphi + \hat{I}_{1z}\hat{I}_{2y}\sin\varphi).\\
&= \frac{3}{2}\sin\vartheta\cos\vartheta(\hat{I}_{1+}\hat{I}_{2z}\mathrm{e}^{-\mathrm{i}\varphi} + \hat{I}_{1-}\hat{I}_{2z}\mathrm{e}^{\mathrm{i}\varphi} + \hat{I}_{1z}\hat{I}_{2+}\mathrm{e}^{-\mathrm{i}\varphi} + \hat{I}_{1z}\hat{I}_{2-}\mathrm{e}^{\mathrm{i}\varphi}) \qquad (9.46)
\end{aligned}$$

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

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

$$
\begin{aligned}
&= \frac{3}{4}\sin^2\vartheta\,(\ \hat{I}_{1+}\hat{I}_{2-}(\cos^2\varphi + \sin^2\varphi\, +\, \mathrm{i}\sin\varphi\cos\varphi - \mathrm{i}\sin\varphi\cos\varphi)\\
&\qquad +\hat{I}_{1-}\hat{I}_{2+}(\cos^2\varphi + \sin^2\varphi\, -\, \mathrm{i}\sin\varphi\cos\varphi + \mathrm{i}\sin\varphi\cos\varphi)\\
&\qquad +\hat{I}_{1+}\hat{I}_{2+}(\cos^2\varphi - \sin^2\varphi\, -\, \mathrm{i}\sin\varphi\cos\varphi - \mathrm{i}\sin\varphi\cos\varphi)\\
&\qquad +\hat{I}_{1-}\hat{I}_{2-}(\cos^2\varphi - \sin^2\varphi\, +\, \mathrm{i}\sin\varphi\cos\varphi + \mathrm{i}\sin\varphi\cos\varphi)\ )\\
&\qquad -\frac{1}{4}(2\hat{I}_{1+}\hat{I}_{2-} + 2\hat{I}_{1-}\hat{I}_{2+})\\
&\qquad = \frac{1}{4}\hat{I}_{1+}\hat{I}_{2-}(3\sin^2\vartheta - 2)\, +\, \frac{1}{4}\hat{I}_{1-}\hat{I}_{2+}(3\sin^2\vartheta - 2)\\
&\qquad\quad +\frac{3}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\vartheta\mathrm{e}^{-\mathrm{i}2\varphi}\, +\, \frac{3}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\vartheta\mathrm{e}^{\mathrm{i}2\varphi}\\
&\qquad = -\frac{1}{4}\hat{I}_{1+}\hat{I}_{2-}(3\cos^2\vartheta - 1)\, -\, \frac{1}{4}\hat{I}_{1-}\hat{I}_{2+}(3\cos^2\vartheta - 1)\\
&\qquad\quad +\frac{3}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\vartheta\mathrm{e}^{-\mathrm{i}2\varphi}\, +\, \frac{3}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\vartheta\mathrm{e}^{\mathrm{i}2\varphi}.
\end{aligned}
\tag{9.47}
$$

Using Eqs. 9.46 and 9.47 and moving to the interaction frame ($\hat{I}_{n\pm} \to \hat{I}_{n\pm}\mathrm{e}^{\pm\mathrm{i}\omega_{0,n}t}$), Eq. 9.34 is converted to

$$
\begin{aligned}
\hat{H}_D^I &= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\Big(\hat{I}_{1z}\hat{I}_{2z}(3\cos^2\vartheta - 1)\\
&\quad -\frac{1}{4}\hat{I}_{1+}\hat{I}_{2-}(3\cos^2\vartheta - 1)\mathrm{e}^{\mathrm{i}(\omega_{0,1}-\omega_{0,2})t} - \frac{1}{4}\hat{I}_{1-}\hat{I}_{2+}(3\cos^2\vartheta - 1)\mathrm{e}^{-\mathrm{i}(\omega_{0,1}-\omega_{0,2})t}\\
&\quad +\frac{3}{2}\hat{I}_{1+}\hat{I}_{2z}\sin\vartheta\cos\vartheta\mathrm{e}^{-\mathrm{i}\varphi}\mathrm{e}^{\mathrm{i}(\omega_{0,1})t} + \frac{3}{2}\hat{I}_{1-}\hat{I}_{2z}\sin\vartheta\cos\vartheta\mathrm{e}^{\mathrm{i}\varphi}\mathrm{e}^{-\mathrm{i}(\omega_{0,1})t}\\
&\quad +\frac{3}{2}\hat{I}_{1z}\hat{I}_{2+}\sin\vartheta\cos\vartheta\mathrm{e}^{-\mathrm{i}\varphi}\mathrm{e}^{\mathrm{i}(\omega_{0,2})t} + \frac{3}{2}\hat{I}_{1z}\hat{I}_{2-}\sin\vartheta\cos\vartheta\mathrm{e}^{\mathrm{i}\varphi}\mathrm{e}^{-\mathrm{i}(\omega_{0,2})t}\\
&\quad +\frac{3}{4}\hat{I}_{1+}\hat{I}_{2+}\sin^2\vartheta\mathrm{e}^{-\mathrm{i}2\varphi}\mathrm{e}^{\mathrm{i}(\omega_{0,1}+\omega_{0,2})t} + \frac{3}{4}\hat{I}_{1-}\hat{I}_{2-}\sin^2\vartheta\mathrm{e}^{\mathrm{i}2\varphi}\mathrm{e}^{-\mathrm{i}(\omega_{0,1}+\omega_{0,2})t}\ \Big)\\
&= -\frac{\mu_0\gamma_1\gamma_2}{4\pi r^3}\Big(2\hat{I}_{1z}\hat{I}_{2z}c^{zz} - \frac{1}{2}c^{+-}\hat{I}_{1+}\hat{I}_{2-} - \frac{1}{2}c^{-+}\hat{I}_{1-}\hat{I}_{2+}\\
&+\sqrt{\frac{3}{2}}\Big(c^{+z}\hat{I}_{1+}\hat{I}_{2z} + c^{-z}\hat{I}_{1-}\hat{I}_{2z} + c^{z+}\hat{I}_{1z}\hat{I}_{2+} + c^{z-}\hat{I}_{1z}\hat{I}_{2-} + c^{++}\hat{I}_{1+}\hat{I}_{2+} + c^{--}\hat{I}_{1-}\hat{I}_{2-}\Big)\ \Big).
\end{aligned}
\tag{9.48}
$$

Similarly to Eq. 8.28, the dipole-dipole relaxation is described by

$$
\frac{\mathrm{d}\Delta\hat{\rho}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^\infty \overline{[\hat{H}_D(0),[\hat{H}_D(t),\Delta\hat{\rho}]]}\mathrm{d}t. \tag{9.49}
$$

The right-hand side can be simplified dramatically by the *secular approximation* as in Eq. 8.28: all terms with $\mathrm{e}^{\pm\mathrm{i}\omega_{0,n}t}$ 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 $t_j = 0$).[4] 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,

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

$$\left[\hat{I}_{1z}\hat{I}_{2z},[\hat{I}_{1z}\hat{I}_{2z},\hat{I}_{1z}]\right] = 0, \tag{9.50}$$

$$\left[\hat{I}_{1-}\hat{I}_{2+},[\hat{I}_{1+}\hat{I}_{2-},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}-\hat{I}_{2z}), \tag{9.51}$$

$$\left[\hat{I}_{1+}\hat{I}_{2-},[\hat{I}_{1-}\hat{I}_{2+},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}-\hat{I}_{2z}), \tag{9.52}$$

$$\left[\hat{I}_{1+}\hat{I}_{2z},[\hat{I}_{1-}\hat{I}_{2z},\hat{I}_{1z}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1z}, \tag{9.53}$$

$$\left[\hat{I}_{1-}\hat{I}_{2z},[\hat{I}_{1+}\hat{I}_{2z},\hat{I}_{1z}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1z}, \tag{9.54}$$

$$\left[\hat{I}_{1z}\hat{I}_{2+},[\hat{I}_{1z}\hat{I}_{2-},\hat{I}_{1z}]\right] = 0, \tag{9.55}$$

$$\left[\hat{I}_{1z}\hat{I}_{2-},[\hat{I}_{1z}\hat{I}_{2+},\hat{I}_{1z}]\right] = 0, \tag{9.56}$$

$$\left[\hat{I}_{1+}\hat{I}_{2+},[\hat{I}_{1-}\hat{I}_{2-},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}+\hat{I}_{2z}), \tag{9.57}$$

$$\left[\hat{I}_{1-}\hat{I}_{2-},[\hat{I}_{1+}\hat{I}_{2+},\hat{I}_{1z}]\right] = \hbar^2(\hat{I}_{1z}+\hat{I}_{2z}), \tag{9.58}$$

$$\left[\hat{I}_{1z}\hat{I}_{2z},[\hat{I}_{1z}\hat{I}_{2z},\hat{I}_{1+}]\right] = \frac{1}{4}\hbar^2\hat{I}_{1+}, \tag{9.59}$$

$$\left[\hat{I}_{1+}\hat{I}_{2-},[\hat{I}_{1-}\hat{I}_{2+},\hat{I}_{1+}]\right] = \hbar^2\hat{I}_{1+}, \tag{9.60}$$

$$\left[\hat{I}_{1-}\hat{I}_{2+},[\hat{I}_{1+}\hat{I}_{2-},\hat{I}_{1+}]\right] = 0, \tag{9.61}$$

$$\left[\hat{I}_{1+}\hat{I}_{2z},[\hat{I}_{1-}\hat{I}_{2z},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+}, \tag{9.62}$$

$$\left[\hat{I}_{1-}\hat{I}_{2z},[\hat{I}_{1+}\hat{I}_{2z},\hat{I}_{1+}]\right] = 0, \tag{9.63}$$

$$\left[\hat{I}_{1z}\hat{I}_{2+},[\hat{I}_{1z}\hat{I}_{2-},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+}, \tag{9.64}$$

$$\left[\hat{I}_{1z}\hat{I}_{2-},[\hat{I}_{1z}\hat{I}_{2+},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+}, \tag{9.65}$$

$$\left[\hat{I}_{1+}\hat{I}_{2+},[\hat{I}_{1-}\hat{I}_{2-},\hat{I}_{1+}]\right] = 0, \tag{9.66}$$

$$\left[\hat{I}_{1-}\hat{I}_{2-},[\hat{I}_{1+}\hat{I}_{2+},\hat{I}_{1+}]\right] = \frac{1}{2}\hbar^2\hat{I}_{1+}. \tag{9.67}$$

The relaxation rates can be then derived as described for the relaxation due to the chemical shift.

The following equations describe relaxation due to the dipole-dipole interactions in a pair of nuclei in a rigid spherical molecule:

$$\begin{aligned}\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} &= -\frac{1}{8}b^2(2J(\omega_{0,1}-\omega_{0,2})+6J(\omega_{0,1})+12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{1z}\rangle \\ &+\frac{1}{8}b^2(2J(\omega_{0,1}-\omega_{0,2})-12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{2z}\rangle \\ &= -R_{\mathrm{a}1}\Delta\langle M_{1z}\rangle - R_{\mathrm{x}}\Delta\langle M_{2z}\rangle, \qquad (9.68)\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} &= -\frac{1}{8}b^2(2J(\omega_{0,1}-\omega_{0,2})+6J(\omega_{0,2})+12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{2z}\rangle \\ &+\frac{1}{8}b^2(2J(\omega_{0,1}-\omega_{0,2})-12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{1z}\rangle \\ &= -R_{\mathrm{a}2}\Delta\langle M_{2z}\rangle - R_{\mathrm{x}}\Delta\langle M_{1z}\rangle, \qquad (9.69)\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}\langle M_{1+}\rangle}{\mathrm{d}t} &= -\frac{1}{8}b^2(4J(0)+6J(\omega_{0,2})+J(\omega_{0,1}-\omega_{0,2})+3J(\omega_{0,1})+6J(\omega_{0,1}+\omega_{0,2}))\langle M_{1+}\rangle \\ &= -R_{2,1}\langle M_{1+}\rangle = -\left(R_{0,1}+\frac{1}{2}R_{\mathrm{a}1}\right)\langle M_{1+}\rangle, \qquad (9.70)\end{aligned}$$

where

$$b = -\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r^3}. \qquad (9.71)$$

The relaxation rate R_1 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. 9.68 and 9.69. The solution is simple if $J(\omega_{0,1}) = J(\omega_{0,2}) = J(\omega_0) \Rightarrow R_{\mathrm{a}1} = R_{\mathrm{a}2} = R_{\mathrm{a}}$ (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).[5]

$$\frac{\mathrm{d}\Delta\langle M_z\rangle}{\mathrm{d}t} = -\frac{1}{8}b^2(6J(\omega)+24J(2\omega))\Delta\langle M_z\rangle = -\underbrace{(R_{\mathrm{a}}+R_{\mathrm{x}})}_{R_1}\Delta\langle M_z\rangle. \qquad (9.72)$$

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 $3b^2J(\omega_{0,1})/4$ term, describing the $|\alpha\rangle \leftrightarrow |\beta\rangle$ transition[6] of nucleus 1, the *auto-relaxation rate* $R_{\mathrm{a}1}$ contains terms depending on the sum and difference of the

---

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

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

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*, $3b^2J(\omega_{0,2})/4$. 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 $3b^2J(\omega_{0,2})/4$ (single quantum contribution to R_1, analogous to R_1 due to the chemical schift anisotropy). Such changes have the similar effect as the *chemical or conformational exchange*, modifying the size of the chemical shift tensor. Therefore, $3b^2J(\omega_{0,2})/4$ adds to R_0 like the exchange contribution.

Chapter 10

2D spectroscopy, NOESY

Literature: A very nice explanation of the principles of two-dimensional spectroscopy can be found in K8.1–K8.2. The idea of 2D spectroscopy, but for a different type of experiment (COSY) is also presented in C4.1, L5.6 and L5.9.

10.1 Two-dimensional spectroscopy

In order to describe principles of 2D spectroscopy, we first analyze an experiment consisting of three 90° pulses and two delays before data acquisition:

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

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

10.1.1 Thermal equilibrium

Before we analyze evolution of the density matrix in a 2D experiment, we must define its initial form.

Again, we start from the thermal equilibrium and use the Hamiltonian. The difference from the case of isolated nuclei is that we need to define a 4 × 4 density matrix in order to describe a pair of mutually interacting nuclei. As explained above, the off-diagonal elements of the equilibrium density matrix (proportional to $\mathcal{I}_x$ and $\mathcal{I}_y$) are equal to zero. The four diagonal elements describe average populations of four stationary states of a system composed of (isolated) nuclear pairs: $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. These populations are:

$$P^{\mathrm{eq}}_{\alpha\alpha} = \frac{\mathrm{e}^{-E_{\alpha\alpha}/k_\mathrm{B}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\alpha\beta}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\beta}/k_\mathrm{B}T}} \approx \frac{1-\frac{E_{\alpha\alpha}}{k_\mathrm{B}T}}{4}, \tag{10.1}$$

$$P^{\mathrm{eq}}_{\alpha\beta} = \frac{\mathrm{e}^{-E_{\alpha\beta}/k_\mathrm{B}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\alpha\beta}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\beta}/k_\mathrm{B}T}} \approx \frac{1-\frac{E_{\alpha\beta}}{k_\mathrm{B}T}}{4}, \tag{10.2}$$

$$P^{\mathrm{eq}}_{\beta\alpha} = \frac{\mathrm{e}^{-E_{\beta\alpha}/k_\mathrm{B}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\alpha\beta}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\beta}/k_\mathrm{B}T}} \approx \frac{1-\frac{E_{\beta\alpha}}{k_\mathrm{B}T}}{4}, \tag{10.3}$$

$$P^{\mathrm{eq}}_{\beta\beta} = \frac{\mathrm{e}^{-E_{\beta\beta}/k_\mathrm{B}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\alpha\beta}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\alpha}/k_\mathrm{B}T}+\mathrm{e}^{-E_{\beta\beta}/k_\mathrm{B}T}} \approx \frac{1-\frac{E_{\beta\beta}}{k_\mathrm{B}T}}{4}. \tag{10.4}$$

The energies $E_{\alpha\alpha}$, $E_{\alpha\beta}$, $E_{\beta\alpha}$, and $E_{\beta\beta}$ are the eigenvalues of the total Hamiltonian, which should include effects of the external field $\vec{B}_0$, of chemical shifts of both nuclei, and of their dipolar coupling. However, the dipolar coupling in isotropic liquids is averaged to zero. It is therefore sufficient to write the total Hamiltonian as

$$\hat{H} = -\gamma_1 B_0(1+\delta_{1,\mathrm{i}})\hat{I}_{1,z} - \gamma_2 B_0(1+\delta_{2,\mathrm{i}})\hat{I}_{2,z} = -\gamma_1 B_0(1+\delta_{1,\mathrm{i}})\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} - \gamma_2 B_0(1+\delta_{2,\mathrm{i}})\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} =$$
$$\frac{B_0\hbar}{2}\begin{pmatrix} -\gamma_1(1+\delta_{1,\mathrm{i}})-\gamma_2(1+\delta_{2,\mathrm{i}}) & 0 & 0 & 0 \\ 0 & -\gamma_1(1+\delta_{1,\mathrm{i}})+\gamma_2(1+\delta_{2,\mathrm{i}}) & 0 & 0 \\ 0 & 0 & +\gamma_1(1+\delta_{1,\mathrm{i}})-\gamma_2(1+\delta_{2,\mathrm{i}}) & 0 \\ 0 & 0 & 0 & +\gamma_1(1+\delta_{1,\mathrm{i}})+\gamma_2(1+\delta_{2,\mathrm{i}}) \end{pmatrix}, \tag{10.5}$$

where the diagonal elements (eigenavalues) are the energies of the individual states. Therefore,

$$P^{\mathrm{eq}}_{\alpha\alpha} \approx \frac{1-\frac{E_{\alpha\alpha}}{k_\mathrm{B}T}}{4} = \frac{1}{4} + \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T} + \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T}, \tag{10.6}$$

$$P^{\mathrm{eq}}_{\alpha\beta} \approx \frac{1-\frac{E_{\alpha\beta}}{k_\mathrm{B}T}}{4} = \frac{1}{4} + \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T} - \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T}, \tag{10.7}$$

$$P^{\mathrm{eq}}_{\beta\alpha} \approx \frac{1-\frac{E_{\beta\alpha}}{k_\mathrm{B}T}}{4} = \frac{1}{4} - \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T} + \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T}, \tag{10.8}$$

$$P^{\mathrm{eq}}_{\beta\beta} \approx \frac{1-\frac{E_{\beta\beta}}{k_\mathrm{B}T}}{4} = \frac{1}{4} - \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T} - \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_\mathrm{B}T}. \tag{10.9}$$

$$\tag{10.10}$$

Neglecting the chemical shifts ($\delta_{1,\mathrm{i}} \ll 1, \delta_{2,\mathrm{i}} \ll 1$)

$$\hat{\rho}^{\mathrm{eq}} = \begin{pmatrix} \frac{1}{4}+\frac{\gamma_1 B_0\hbar}{8k_\mathrm{B}T}+\frac{\gamma_2 B_0\hbar}{8k_\mathrm{B}T} & 0 & 0 & 0 \\ 0 & \frac{1}{4}+\frac{\gamma_1 B_0\hbar}{8k_\mathrm{B}T}-\frac{\gamma_2 B_0\hbar}{8k_\mathrm{B}T} & 0 & 0 \\ 0 & 0 & \frac{1}{4}-\frac{\gamma_1 B_0\hbar}{8k_\mathrm{B}T}+\frac{\gamma_2 B_0\hbar}{8k_\mathrm{B}T} & 0 \\ 0 & 0 & 0 & \frac{1}{4}-\frac{\gamma_1 B_0\hbar}{8k_\mathrm{B}T}-\frac{\gamma_2 B_0\hbar}{8k_\mathrm{B}T} \end{pmatrix} \tag{10.11}$$

$$= \frac{1}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + \frac{\gamma_1 B_0\hbar}{8k_\mathrm{B}T}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{\gamma_2 B_0\hbar}{8k_\mathrm{B}T}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{10.12}$$

$$= \frac{1}{2}\left(\mathcal{I}_t + \kappa_1 \mathcal{I}_{1,z} + \kappa_2 \mathcal{I}_{2,z}\right), \tag{10.13}$$

where

$$\kappa_j = \frac{\gamma_j B_0 \hbar}{4 k_\mathrm{B} T}. \tag{10.14}$$

10.1.2 Evolution in the absence of dipolar coupling

We start with an analysis for two non-interacting magnetic moments, e.g. of two protons with different chemical shift δ_i too far from each other. The pair of protons is an example of a homonuclear system, where all nuclei have the same γ. Since we have neglected the very small effect of different chemical shifts in Eq. 10.13, the values of κ are also the same for both protons. As in the one-pulse experiment, we follow the coherent evolution of $\hat{\rho}$ step-by-step, and add the effect of relaxation *ad hoc*.

- $\hat{\rho}(\mathrm{a}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa(\mathcal{I}_{1z} + \mathcal{I}_{2z})$
  We start from the thermal equilibrium described by Eq. 10.13. Note that the matrices are different than for the single-spin mixed state, but the constant is the same.

- $\hat{\rho}(\mathrm{b}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa(-\mathcal{I}_{1y} - \mathcal{I}_{2y})$
  Here we describe the effect of the 90° pulse. For detailed analysis, see the one-pulse experiment.

- $\hat{\rho}(\mathrm{c}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa\left(-\cos(\Omega_1 t_1)\mathcal{I}_{1y} + \sin(\Omega_1 t_1)\mathcal{I}_{1x} - \cos(\Omega_2 t_1)\mathcal{I}_{2x} + \sin(\Omega_2 t_1)\mathcal{I}_{2y}\right)$
  Here we describe evolution during t_1 exactly as in the one-pulse experiment.To keep the equations short, we replace the goniometric terms describing the evolution by (time-dependent) coefficients c_{11}, c_{21}, s_{11}, and s_{21}:
  $\hat{\rho}(\mathrm{c}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa\left(-c_{11}\mathcal{I}_{1y} + s_{11}\mathcal{I}_{1x} - c_{21}\mathcal{I}_{2y} + s_{21}\mathcal{I}_{2x}\right)$
  The coefficients c_{11}, c_{21}, s_{11}, and s_{21} deserve some attention. First, note that the first subscript specifies the nucleus and the second subscript specifies the time period (so-far, it is always 1 because we have analyzed only evolution during t_1). Second, we include the effect of relaxation into the coefficients:
  $c_{11} \to \mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1) \qquad s_{11} \to \mathrm{e}^{-R_{2,1}t_1}\sin(\Omega_1 t_1)$
  $c_{21} \to \mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1) \qquad s_{21} \to \mathrm{e}^{-R_{2,2}t_1}\sin(\Omega_2 t_1)$

- $\hat{\rho}(\mathrm{d}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa\left(-c_{11}\mathcal{I}_{1z} + s_{11}\mathcal{I}_{1x} - c_{21}\mathcal{I}_{2z} + s_{21}\mathcal{I}_{2x}\right)$
  Here we analyze the effect of the second 90° pulse, similarly to the step a → b. The x-pulse does not affect x magnetization, rotates $-y$ magnetization further to $-z$. The final magnetization is parallel with $\vec{B}_0$, but the equilibrium polarization is inverted.

- $\hat{\rho}(\mathrm{e}) = ?$
  This is a new case, it should be analyzed carefully. Here perform the analysis 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 $R_1 \approx 1\,\mathrm{s}^{-1}$. The delay τ_m is usually longer than 0.1 s. Let us 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. Therefore, 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 $\mathcal{H} = \Omega_1\mathcal{I}_{1z} + \Omega_2\mathcal{I}_{2z}$. Consequently,
  $\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa\left(-\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{11}\mathcal{I}_{1z} - \mathrm{e}^{-R_1\tau_\mathrm{m}}c_{21}\mathcal{I}_{2z}\right) = \frac{1}{2}\mathcal{I}_t - \mathcal{A}_1\mathcal{I}_{1z} - \mathcal{A}_2\mathcal{I}_{2z}$
  We further simplified the notation by introducing the factors $\mathcal{A}_1$ and $\mathcal{A}_2$. Again, we include the relaxation effects into $\mathcal{A}_1$ and $\mathcal{A}_2$ when we express the measurable signal:
  $\mathcal{A}_1 \to \frac{\kappa}{2}\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}c_{11} = \frac{\kappa}{2}\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)$
  $\mathcal{A}_2 \to \frac{\kappa}{2}\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}c_{21} = \frac{\kappa}{2}\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)$

- $\hat{\rho}(\mathrm{f}) = \frac{1}{2}\mathcal{I}_t + \mathcal{A}_1\mathcal{I}_{1y} + \mathcal{A}_2\mathcal{I}_{2y}$
  Here we analyze the effect of the third pulse, in the same manner as we analyzed the first pulse.

- $\hat{\rho}(t_2) = \frac{1}{2}\mathcal{I}_t + \mathcal{A}_1(\cos(\Omega_1 t_2)\mathcal{I}_{1y} - \sin(\Omega_1 t_2)\mathcal{I}_{1x}) + \mathcal{A}_2(\cos(\Omega_2 t_2)\mathcal{I}_{2y} - \sin(\Omega_2 t_2)\mathcal{I}_{2x})$
  In the last step, we analyze evolution during data acquisition.

Having $\hat{\rho}(t_2)$, we can calculate $\langle M_+\rangle$. As the size of the matrices increased, it is more convenient to use the orthonormality of the basis than to calculate all matrix products. It follows from the definition of orthonormal matrices that for the two-spin matrices

$$\mathrm{Tr}\left\{(\mathcal{I}_{n,x} + \mathrm{i}\mathcal{I}_{n,y})\mathcal{I}_{n,x}\right\} = 1, \tag{10.15}$$
$$\mathrm{Tr}\left\{(\mathcal{I}_{n,x} + \mathrm{i}\mathcal{I}_{n,y})\mathcal{I}_{n,y}\right\} = \mathrm{i}, \tag{10.16}$$

and traces of products with other matrices are zero. Applying the orthonormality relations to the obtained $\hat{\rho}(t_2)$ and introducing relaxation, we get

$$\begin{aligned}\langle M_+\rangle = \mathcal{N}\gamma\hbar\big(&\mathcal{A}_1(\mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_2)\mathcal{I}_{1y} - \mathrm{e}^{-R_{2,1}t_2}\sin(\Omega_1 t_2)\mathcal{I}_{1x}) \\ &+\mathcal{A}_2(\mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_2)\mathcal{I}_{2y} - \mathrm{e}^{-R_{2,2}t_2}\sin(\Omega_2 t_2)\mathcal{I}_{2x})\big)\,.\end{aligned} \tag{10.17}$$

Note that the resulting phase is shifted by $\pi/2$ similarly to Eq. 8.65, but in the opposite direction. After applying the phase correction, Fourier transform of the signal provides spectrum in the form (cf. Eq. 8.67)

$$\mathcal{N}\gamma\hbar\left(\left(\frac{\mathcal{A}_1 R_{2,1}}{R_{2,1}^2+(\omega-\Omega_1)^2}+\frac{\mathcal{A}_2 R_{2,2}}{R_{2,2}^2+(\omega-\Omega_2)^2}\right)-\mathrm{i}\left(\frac{\mathcal{A}_1(\omega-\Omega_1)}{R_{2,1}^2+(\omega-\Omega_1)^2}+\frac{\mathcal{A}_2(\omega-\Omega_2)}{R_{2,2}^2+(\omega-\Omega_2)^2}\right)\right). \tag{10.18}$$

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 $c_{11} = \mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_1)$ and $c_{21} = \mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_1)$. 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.

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.

10.2 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. Such approach is known as Nuclear Overhauser effect spectroscopy (NOESY) and is used frequently to measure distances between protons in molecules.

As described by Eq. 9.68, relaxation of nucleus 1 is influenced by the state of nucleus 2 (and vice versa):

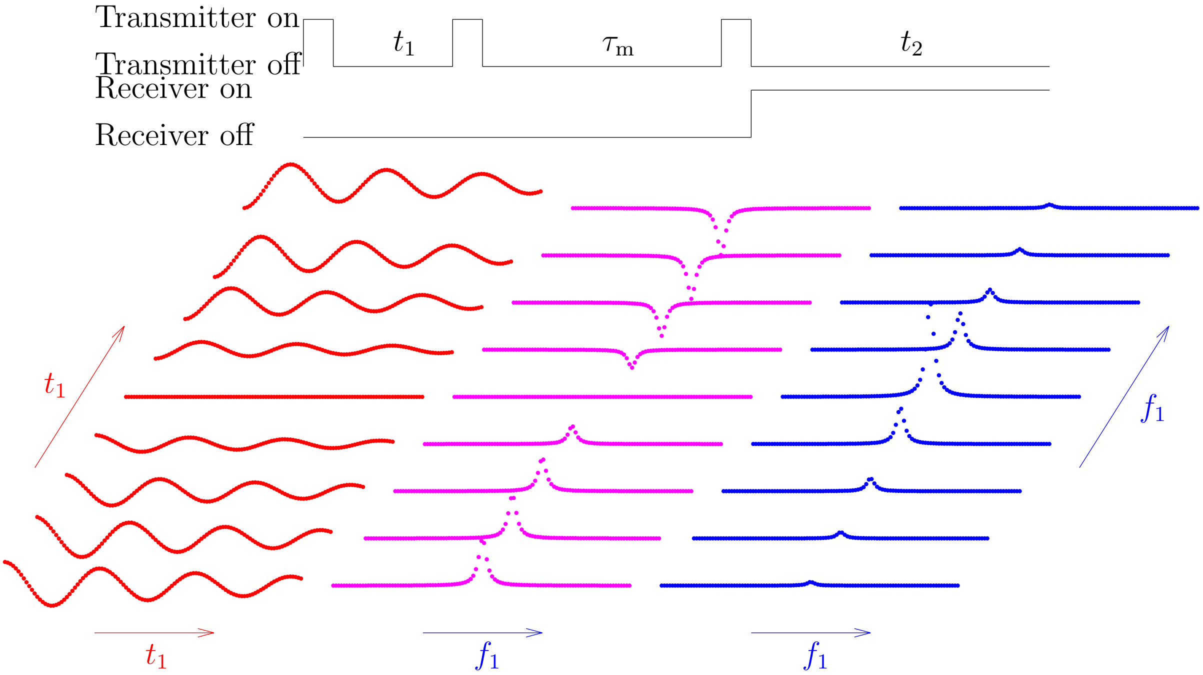

Figure 10.1: Principle of two-dimensional spectroscopy (experiment NOESY). The acquired signal is shown in red, the signal after Fourier transform in the direct dimension is shown in magenta, and the signal after Fourier transform in both dimensions is shown in blue.

$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}1}\Delta\langle M_{1z}\rangle + R_{\mathrm{x}}\Delta\langle M_{2z}\rangle \tag{10.19}$$

$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}2}\Delta\langle M_{2z}\rangle + R_{\mathrm{x}}\Delta\langle M_{1z}\rangle. \tag{10.20}$$

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

$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}}\Delta\langle M_{1z}\rangle + R_{\mathrm{x}}\Delta\langle M_{2z}\rangle, \tag{10.21}$$

$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}}\Delta\langle M_{2z}\rangle + R_{\mathrm{x}}\Delta\langle M_{1z}\rangle. \tag{10.22}$$

Such set of differential equations can be solved easily e.g. by the substitutions $\Delta_+ = \Delta\langle M_{1z}\rangle + \Delta\langle M_{2z}\rangle$ and $\Delta_- = \Delta\langle M_{2z}\rangle - \Delta\langle M_{1z}\rangle$.

The result is

$$\Delta_+ = \Delta_+(0)\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})t}, \tag{10.23}$$

$$\Delta_- = \Delta_-(0)\mathrm{e}^{-(R_{\mathrm{a}}-R_{\mathrm{x}})t}. \tag{10.24}$$

Returning back to $\Delta\langle M_{1z}\rangle$ and $\Delta\langle M_{2z}\rangle$,

$$\Delta\langle M_{1z}\rangle = \left((1-\zeta)\Delta\langle M_{1z}\rangle(0) + \zeta\Delta\langle M_{2z}\rangle(0)\right)\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})t}, \tag{10.25}$$

$$\Delta\langle M_{2z}\rangle = \left((1-\zeta)\Delta\langle M_{2z}\rangle(0) + \zeta\Delta\langle M_{1z}\rangle(0)\right)\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})t}, \tag{10.26}$$

where $\zeta = (1-\mathrm{e}^{2R_{\mathrm{x}}t})/2$. Therefore, the amplitudes $\mathcal{A}_1$ and $\mathcal{A}_2$ in our two-dimensional experiment are

$$\mathcal{A}_1 = \frac{\kappa}{2}((1-\zeta)c_{11} + \zeta c_{21})\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})\tau_{\mathrm{m}}}, \tag{10.27}$$

$$\mathcal{A}_2 = \frac{\kappa}{2}((1-\zeta)c_{21} + \zeta c_{11})\mathrm{e}^{-(R_{\mathrm{a}}+R_{\mathrm{x}})\tau_{\mathrm{m}}}. \tag{10.28}$$

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

$$\zeta \mathrm{e}^{-(R_\mathrm{a}+R_\mathrm{x})\tau_\mathrm{m}} = -\frac{1}{2}\left(\mathrm{e}^{R_\mathrm{x}\tau_\mathrm{m}} - \mathrm{e}^{-R_\mathrm{x}\tau_\mathrm{m}}\right)\mathrm{e}^{-R_\mathrm{a}\tau_\mathrm{m}}. \tag{10.29}$$

For short τ_m, $\mathrm{e}^{R_\mathrm{x}\tau_\mathrm{m}} - \mathrm{e}^{-R_\mathrm{x}\tau_\mathrm{m}} \approx 1 + R_\mathrm{x}\tau_\mathrm{m} - 1 + R_\mathrm{x}\tau_\mathrm{m}$ and $\mathrm{e}^{-R_\mathrm{a}\tau_\mathrm{m}}$ is close to one. Therefore, the cross-peak intensities are approximately proportional to

$$-\frac{1}{2}\left(\mathrm{e}^{R_\mathrm{x}\tau_\mathrm{m}} - \mathrm{e}^{-R_\mathrm{x}\tau_\mathrm{m}}\right)\mathrm{e}^{-R_\mathrm{a}\tau_\mathrm{m}} \approx -R_\mathrm{x}\tau_\mathrm{m} = \left(\frac{\mu_0}{8\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}(J(0) - 6J(2\omega_0))\tau_\mathrm{m}, \tag{10.30}$$

where the difference of the precession frequencies due to different chemical shifts was neglected ($\omega_{0,1} = \omega_{0,2}$ because $\gamma_1 = \gamma_2$). Hence, the cross-peak intensity is proportional to r^{-6} in the linear approximation. If the molecular motions are slow, $2\omega_0\tau_\mathrm{C} \gg 1 \Rightarrow J(0) > 6J(2\omega_0)$, and cross-peaks have the same sign as diagonal peaks. However, if the molecular motions are fast (e.g., if the molecule is small), the sign is opposite.

Chapter 11

J-coupling, spin echoes

Literature: The through-bond coupling (J-coupling) is described in L14 and L15, the Hamiltonian is presented in L9.4 and J-coupled spins are described in L14.2, L14.3, and L14.5. Spin echoes are nicely described in K7.8 and also presented in LA.10.

11.1 Through-bond coupling

Magnetic moments of nuclei connected by covalent bonds interact also indirectly, via interactions with magnetic moments of the electrons of the bonds. This type of interaction is known as *J-coupling*, *through-bond coupling*, *hyperfine coupling*, or *scalar coupling* (see below).

In principle, both orbital and spin magnetic moments of electrons can contribute to the J-coupling, but the contribution of the orbital magnetic moments is usually negligible (coupling between hydrogen nuclei in water is an interesting exception). The contribution of the electron spin can be described in the following manner. Energy of the interaction between the (spin) magnetic moment of nucleus $\vec{\mu}_{\mathrm{n}}$ and the magnetic field generated by the spin magnetic moment of electron $\vec{B}_{\mathrm{e}}$ is given by

$$E = -\vec{\mu}_{\mathrm{n}} \cdot \vec{B}_{\mathrm{e}}. \tag{11.1}$$

Distribution of the electron density in the molecule is described by orbitals. The interaction between the nucleus and electron outside the nucleus is nothing else but the through-space interaction between two dipolar magnetic moments. This interaction is averaged to zero. Contributions of p-, d- and higher orbitals to the density inside the nucleus are negligible because these wave functions are close to zero in the center. Therefore, only s-orbitals are important. The interaction between the nucleus and electron *inside* the nucleus can be simulated by a hypothetical current loop giving the correct magnetic moment when treated classically. If $\vec{B}$ of such a loop is calculated, its integral over the volume inside the nucleus is proportional to the magnetic moment:

$$\vec{B}_{\mathrm{e,in}} = \frac{2}{3}\mu_0\vec{\mu}_{\mathrm{e,in}}. \tag{11.2}$$

The expected value of the electron magnetic moment in the volume of the nucleus V_{n} is given by

$$\langle\vec{\mu}_{\mathrm{e}}\rangle_{\mathrm{inside}} = \int_{V_{\mathrm{n}}} \psi(r)^*\hat{\mu}_{\mathrm{e}}\psi(r)\mathrm{d}V, \tag{11.3}$$

where ψ is the wave function (s orbital in our case) and r is the distance from the center of the atom. Since $\vec{\mu}_{\mathrm{e}}$ is constant in the nucleus,

$$\psi(r)^*\hat{\mu}_{\mathrm{e}}\psi(r) = \hat{\mu}_{\mathrm{e}}\psi(r)^*\psi(r) = \hat{\mu}_{\mathrm{e}}|\psi(r)|^2. \tag{11.4}$$

Combining Eqs. 11.1–11.4 gives the energy

$$E = -\frac{2\mu_0}{3}\langle\vec{\mu}_\mathrm{n}\cdot\vec{\mu}_\mathrm{e}\rangle|\psi(\mathrm{inside})|^2 \tag{11.5}$$

and the corresponding Hamiltonian

$$\hat{H}_\mathrm{F} = -\frac{2\mu_0\gamma_\mathrm{n}\gamma_\mathrm{e}}{3}\left(\vec{\hat{I}}_\mathrm{n}\cdot\vec{\hat{I}}_\mathrm{e}\right)f_\mathrm{inside}, \tag{11.6}$$

where $\vec{\hat{I}}_\mathrm{n}$ and $\vec{\hat{I}}_\mathrm{e}$ are operators of the spin of the nucleus and the electron, respectively, γ_n and γ_e are magnetogyric ratios of the spin of the nucleus and the electron, respectively, and f_inside is equal to one inside the nucleus and to zero outside the nucleus. This type of interaction is known as the *Fermi contact interaction* and does not depend on orientation of the molecule in the magnetic field, as documented by the scalar vecor in Eq. 11.6.

The simplest example of the J-coupling in chemical compounds is J-interaction in 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 $|\beta\alpha\rangle$ allow all interacting particles to be in the opposite[1] state (H$^\uparrow$-e$^\downarrow$-e$^\uparrow$-C$^\downarrow$ and H$^\downarrow$-e$^\uparrow$-e$^\downarrow$-C$^\uparrow$, respectively) and their interactions are are energetically more favorable than those of 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. However, the sign of the coupling constant can be predicted easily if only the Fermi contact interaction is considered: $J < 0$ for a two-bond coupling (H$^\uparrow$-e$^\downarrow$-e$^\uparrow$-C$^\downarrow$-e$^\uparrow$-e$^\downarrow$-H$^\uparrow$ and H$^\downarrow$-e$^\uparrow$-e$^\downarrow$-C$^\uparrow$-e$^\downarrow$-e$^\uparrow$-H$^\downarrow$) and $J > 0$ for a three-bond coupling (H$^\uparrow$-e$^\downarrow$-e$^\uparrow$-C$^\downarrow$-e$^\uparrow$-e$^\downarrow$-C$^\uparrow$-e$^\downarrow$-e$^\uparrow$-H$^\downarrow$ and H$^\downarrow$-e$^\uparrow$-e$^\downarrow$-C$^\uparrow$-e$^\downarrow$-e$^\uparrow$-C$^\downarrow$-e$^\uparrow$-e$^\downarrow$-H$^\uparrow$).

In general, 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), similarly to the chemical shift and through-space dipole-dipole coupling. Therefore, the interaction is described by tensors (like chemical shift or dipolar coupling):

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

$$= 2\pi(\,\hat{I}_x\;\hat{I}_y\;\hat{I}_z\,)\begin{pmatrix}J_{xx} & J_{xy} & J_{xz}\\ J_{yx} & J_{yy} & J_{yz}\\ J_{zx} & J_{zy} & J_{zz}\end{pmatrix}\begin{pmatrix}\hat{I}_{x1}\\ \hat{I}_{y1}\\ \hat{I}_{z1}\end{pmatrix} = 2\pi\,\vec{\hat{I}}_1\cdot\underline{J}\cdot\,\vec{\hat{I}}_2 \tag{11.7}$$

However, the 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[2]) part of the tensor is considered and the interaction is called *scalar coupling*:

---

[1] Note, however, that the magnetogyric constants of electrons are negative. Therefore, the orientations of angular momenta and magnetic moments of electrons are *opposite*. The energetically more favorable orientation of the *magnetic moments* of electrons is *parallel* with the magnetic moments of the nuclei.

[2] Note that the Fermi contact interaction depends on scalar product of magnetic moment vectors, Eq. 11.6 does not include tensors.

$$2\pi\begin{pmatrix} J_{xx} & 0 & 0 \\ 0 & J_{yy} & 0 \\ 0 & 0 & J_{zz} \end{pmatrix} = 2\pi\frac{J_{xx}+J_{yy}+J_{zz}}{3}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 2\pi J\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{11.8}$$

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.

11.2 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*,

$$\hat{H}_J = \pi J\left(2\hat{I}_{1,z}\hat{I}_{2,z} + 2\hat{I}_{1,x}\hat{I}_{2,x} + 2\hat{I}_{1,y}\hat{I}_{2,y}\right). \tag{11.9}$$

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

$$\hat{H}_J = 2\pi J\hat{I}_{1,z}\hat{I}_{2,z} = \pi J\left(2\hat{I}_{1,z}\hat{I}_{2,z}\right). \tag{11.10}$$

11.3 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.

11.4 Spectroscopy in the presence of J-coupling

11.4.1 Thermal equilibrium

Derivation of the initial form of a density matrix for two nuclei interacting through bonds (J-coupling) is very similar to that described for two nuclei interacting through space (dipolar coupling) in Section 10.1.1.

Before we analyze evolution of the density matrix in a 2D experiment, we must define its initial form. Again, we start from the thermal equilibrium and use the Hamiltonian. The difference from the case of isolated nuclei is that we need to define a 4×4 density matrix in order to describe a pair of mutually interacting nuclei. As explained above, the off-diagonal elements of the equilibrium density matrix (proportional to $\mathcal{I}_x$ and $\mathcal{I}_y$) are equal to zero. The four diagonal elements describe average populations of four stationary states of a system composed of (isolated) nuclear pairs: $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. These populations are:

$$P^{\mathrm{eq}}_{\alpha\alpha} = \frac{\mathrm{e}^{-E_{\alpha\alpha}/k_{\mathrm{B}}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\alpha\beta}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\beta}/k_{\mathrm{B}}T}} \approx \frac{1-\frac{E_{\alpha\alpha}}{k_{\mathrm{B}}T}}{4}, \tag{11.11}$$

$$P^{\mathrm{eq}}_{\alpha\beta} = \frac{\mathrm{e}^{-E_{\alpha\beta}/k_{\mathrm{B}}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\alpha\beta}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\beta}/k_{\mathrm{B}}T}} \approx \frac{1-\frac{E_{\alpha\beta}}{k_{\mathrm{B}}T}}{4}, \tag{11.12}$$

$$P^{\mathrm{eq}}_{\beta\alpha} = \frac{\mathrm{e}^{-E_{\beta\alpha}/k_{\mathrm{B}}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\alpha\beta}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\beta}/k_{\mathrm{B}}T}} \approx \frac{1-\frac{E_{\beta\alpha}}{k_{\mathrm{B}}T}}{4}, \tag{11.13}$$

$$P^{\mathrm{eq}}_{\beta\beta} = \frac{\mathrm{e}^{-E_{\beta\beta}/k_{\mathrm{B}}T}}{\mathrm{e}^{-E_{\alpha\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\alpha\beta}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\alpha}/k_{\mathrm{B}}T}+\mathrm{e}^{-E_{\beta\beta}/k_{\mathrm{B}}T}} \approx \frac{1-\frac{E_{\beta\beta}}{k_{\mathrm{B}}T}}{4}. \tag{11.14}$$

In principle, the total Hamiltonian also includes the term $\hat{H}_J$, which describes the J coupling and which is not averaged to zero.

$$\hat{H} = -\gamma_1 B_0(1+\delta_{1,\mathrm{i}})\hat{I}_{1,z} - \gamma_2 B_0(1+\delta_{2,\mathrm{i}})\hat{I}_{2,z} + 2\pi J \hat{I}_{1,z}\hat{I}_{2,z} = \tag{11.15}$$

$$-\gamma_1 B_0(1+\delta_{1,\mathrm{i}})\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} - \gamma_2 B_0(1+\delta_{2,\mathrm{i}})\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{\pi J}{2}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{11.16}$$

where the diagonal elements (eigenavalues) are the energies of the individual states. Therefore, the populations (diagonal elements of the density matrix) should be given by

$$P^{\mathrm{eq}}_{\alpha\alpha} \approx \frac{1-\frac{E_{\alpha\alpha}}{k_{\mathrm{B}}T}}{4} = \frac{1}{4} + \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \frac{\pi J\hbar}{16k_{\mathrm{B}}T}, \tag{11.17}$$

$$P^{\mathrm{eq}}_{\alpha\beta} \approx \frac{1-\frac{E_{\alpha\beta}}{k_{\mathrm{B}}T}}{4} = \frac{1}{4} + \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \frac{\pi J\hbar}{16k_{\mathrm{B}}T}, \tag{11.18}$$

$$P^{\mathrm{eq}}_{\beta\alpha} \approx \frac{1-\frac{E_{\beta\alpha}}{k_{\mathrm{B}}T}}{4} = \frac{1}{4} - \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \frac{\pi J\hbar}{16k_{\mathrm{B}}T}, \tag{11.19}$$

$$P^{\mathrm{eq}}_{\beta\beta} \approx \frac{1-\frac{E_{\beta\beta}}{k_{\mathrm{B}}T}}{4} = \frac{1}{4} - \gamma_1(1+\delta_{1,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \gamma_2(1+\delta_{2,\mathrm{i}})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \frac{\pi J\hbar}{16k_{\mathrm{B}}T}. \tag{11.20}$$

$$\tag{11.21}$$

However, the values of J in typical organic compounds are at least six orders of magnitude lower than the frequencies measured even at low-field magnets ($J \leq 200\,\mathrm{Hz}$ vs. $200\,\mathrm{MHz}$). As a consequence, the contribution of J-coupling can be safely neglected, and the initial density matrix is identical to that derived for a pair of nuclei interacting through space (Eq. 10.13).

Neglecting the chemical shifts ($\delta_{1,\mathrm{i}} \ll 1, \delta_{2,\mathrm{i}} \ll 1$)

$$\hat{\rho}^{\mathrm{eq}} = \begin{pmatrix} \frac{1}{4} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} + \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} & 0 & 0 & 0 \\ 0 & \frac{1}{4} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} - \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} & 0 & 0 \\ 0 & 0 & \frac{1}{4} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} - \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} & 0 \\ 0 & 0 & 0 & \frac{1}{4} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} - \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} \end{pmatrix} \tag{11.22}$$

$$= \frac{1}{4}\begin{pmatrix} 1\,0\,0\,0 \\ 0\,1\,0\,0 \\ 0\,0\,1\,0 \\ 0\,0\,0\,1 \end{pmatrix} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{11.23}$$

$$= \frac{1}{2}\left(\mathcal{I}_t + \kappa_1 \mathcal{I}_{1,z} + \kappa_2 \mathcal{I}_{2,z}\right), \tag{11.24}$$

where

$$\kappa_j = \frac{\gamma_j B_0 \hbar}{4k_\mathrm{B}T}. \tag{11.25}$$

11.4.2 Evolution in the presence of J-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 $\omega_{\mathrm{rot}} = -\omega_{\mathrm{radio}}$

$$\mathcal{H} = \underbrace{-\gamma_1 B_0(1+\delta_{\mathrm{i}1})}_{\Omega_1}\mathcal{I}_{1z} \underbrace{-\gamma_1 B_0(1+\delta_{\mathrm{i}2})}_{\Omega_2}\mathcal{I}_{2z} + \pi J\left(2\mathcal{I}_{1z}\mathcal{I}_{2z} + 2\mathcal{I}_{1x}\mathcal{I}_{2x} + 2\mathcal{I}_{1y}\mathcal{I}_{2y}\right). \tag{11.26}$$

However, if the precession frequencies differ, the Hamiltonian simplifies to a form where all components commute. Therefore, the Liouville - von Neumann equation can be solved 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 $\hat{\rho}(\mathrm{b}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa(-\mathcal{I}_{1y} - \mathcal{I}_{2y})$ 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

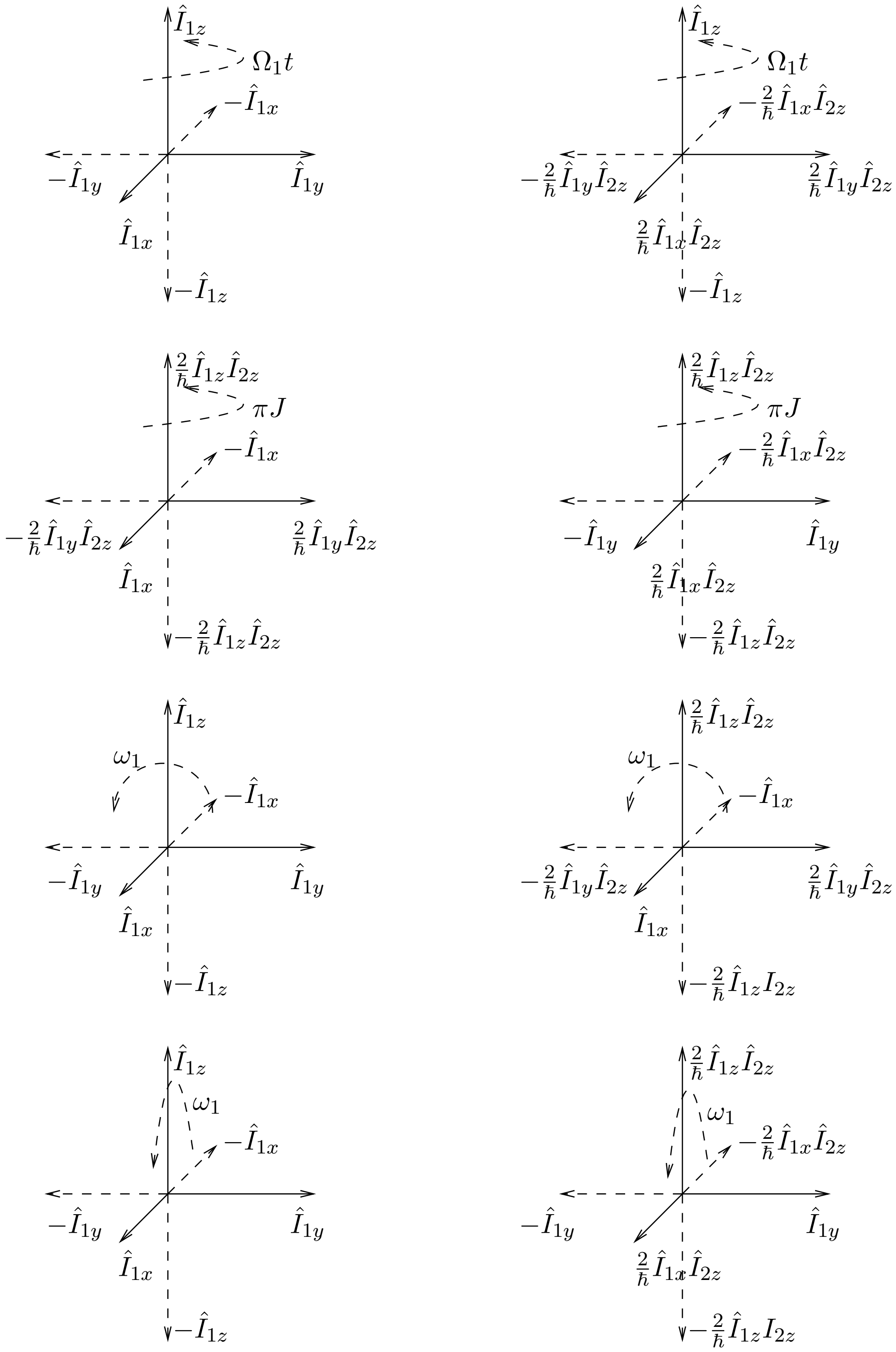

Figure 11.1: Rotations in product operator space

$$\mathcal{I}_{1t} \longrightarrow \mathcal{I}_{1t} \longrightarrow \mathcal{I}_{1t} \tag{11.27}$$

$$-\mathcal{I}_{1y} \longrightarrow \begin{cases} -c_1\mathcal{I}_{1y} \longrightarrow \begin{cases} -c_1c_J\,\mathcal{I}_{1y} \\ +c_1s_J\,2\mathcal{I}_{1x}\mathcal{I}_{2z} \end{cases} \\ +s_1\mathcal{I}_{1x} \longrightarrow \begin{cases} +s_1c_J\,\mathcal{I}_{1x} \\ +s_1s_J\,2\mathcal{I}_{1y}\mathcal{I}_{2z} \end{cases} \end{cases} \tag{11.28}$$

$$-\mathcal{I}_{2y} \longrightarrow \begin{cases} -c_2\mathcal{I}_{2y} \longrightarrow \begin{cases} -c_2c_J\,\mathcal{I}_{2y} \\ +c_2s_J\,2\mathcal{I}_{2x}\mathcal{I}_{1z} \end{cases} \\ +s_2\mathcal{I}_{2x} \longrightarrow \begin{cases} +s_2c_J\,\mathcal{I}_{2x} \\ +s_2s_J\,2\mathcal{I}_{2y}\mathcal{I}_{1z} \end{cases} \end{cases} \tag{11.29}$$

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

$$c_1 = \cos(\Omega_1 t) \qquad s_1 = \sin(\Omega_1 t) \tag{11.30}$$

$$c_2 = \cos(\Omega_2 t) \qquad s_2 = \sin(\Omega_2 t) \tag{11.31}$$

$$c_J = \cos(\pi J t) \qquad s_J = \sin(\pi J t) \tag{11.32}$$

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

$$\frac{\kappa}{4}\left(\mathrm{e}^{-R_{2,1}t}\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t}+\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t}\right)+\mathrm{e}^{-R_{2,2}t}\left(\mathrm{e}^{\mathrm{i}(\Omega_2-\pi J)t}+\mathrm{e}^{\mathrm{i}(\Omega_2+\pi J)t}\right)\right) \tag{11.33}$$

which gives two doublets in the spectrum after Fourier transform:

$$\begin{aligned} &\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16k_{\mathrm{B}}T}\left(\frac{R_{2,1}}{R_{2,1}^2+(\omega-\Omega_1+\pi J)^2}+\frac{R_{2,1}}{R_{2,1}^2+(\omega-\Omega_1-\pi J)^2}\right. \\ &\qquad\left.+\frac{R_{2,2}}{R_{2,2}^2+(\omega-\Omega_2+\pi J)^2}+\frac{R_{2,2}}{R_{2,2}^2+(\omega-\Omega_2-\pi J)^2}\right), \\ -\mathrm{i}&\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16k_{\mathrm{B}}T}\left(\frac{(\omega-\Omega_1+\pi J)}{R_{2,1}^2+(\omega-\Omega_1+\pi J)^2}+\frac{(\omega-\Omega_1-\pi J)}{R_{2,1}^2+(\omega-\Omega_1-\pi J)^2}\right. \\ &\qquad\left.+\frac{(\omega-\Omega_2+\pi J)}{R_{2,2}^2+(\omega-\Omega_2+\pi J)^2}+\frac{(\omega-\Omega_2-\pi J)}{R_{2,2}^2+(\omega-\Omega_2-\pi J)^2}\right). \end{aligned} \tag{11.34}$$

11.5 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, respectively, if $\gamma_1 \neq \gamma_2$. For the sake of simplicity, relaxation is not included.

The *vector analysis* is shown in Figure 11.2, where the solid arrows represent components of $\mu_1 \perp \vec{B}_0$ for spin 2 in $|\alpha\rangle$, dashed arrows represent components of $\mu_1 \perp \vec{B}_0$ for spin 2 in $|\beta\rangle$, and colors indicate different $\delta_{\rm i}$.

11.5.1 Free evolution

Evolution of the system of two nuclei in the presence of scalar coupling was already described in Section 11.4.2. The vector analysis is shown in Figure 11.2A).

- $\hat{\rho}(\mathrm{a}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa_1\mathcal{I}_z + \frac{1}{2}\kappa_2\mathcal{S}_z$
  thermal equilibrium, the constants κ_1 and κ_2 are different because the nuclei have different γ.

- $\hat{\rho}(\mathrm{b}) = \frac{1}{2}\mathcal{I}_t - \frac{1}{2}\kappa_1\mathcal{I}_y + \frac{1}{2}\kappa_2\mathcal{S}_z$
  90° pulse applied to nucleus 1 only

- $\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa_1\left(-c_1c_J\mathcal{I}_y + s_1c_J\mathcal{I}_x + c_1s_J2\mathcal{I}_x\mathcal{S}_z + s_1s_J2\mathcal{I}_y\mathcal{S}_z\right) + \frac{1}{2}\kappa_2\mathcal{S}_z$
  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 larger angle than dashed arrows in Fig. 11.2A.

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).

11.5.2 Refocusing echo

The *refocusing echo* consists of a 90° pulse exciting magnetic moment 1 and a 180° pulse applied to the excited nucleus in the middle of the echo:

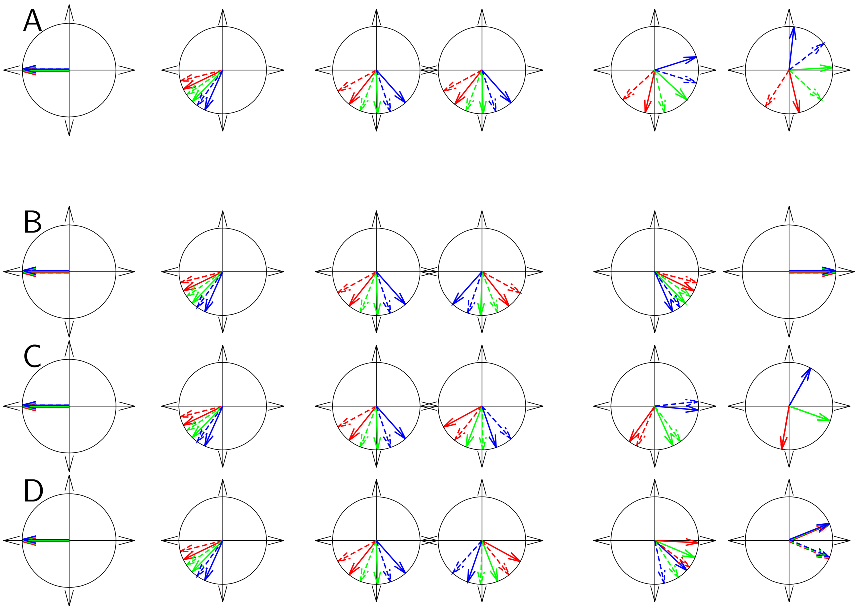

Figure 11.2: Vector analysis of spin echoes for ^{1}H (nucleus 1) and ^{13}C (nucleus 2) in an isolated –CH– group. In individual rows, evolution of magnetization vectors in the plane $\perp \vec{B}_0$ is shown for three protons (distinguished by colors) with slightly different precession frequency due 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.

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

The vector analysis is shown in Figure 11.2B). 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 $+\mathcal{I}_y$:
$\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa_1\mathcal{I}_y + \frac{1}{2}\kappa_2\mathcal{S}_z$

11.5.3 Decoupling echo

The *refocusing echo* consists of a 90° pulse exciting magnetic moment 1 and a 180° pulse applied to 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 vector analysis is shown in Figure 11.2C). 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:
$\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa_1 (c_1\mathcal{I}_y - s_1\mathcal{I}_x) - \frac{1}{2}\kappa_2\mathcal{S}_z$

11.5.4 Coupling echo

The *coupling echo* consists of a 90° pulse exciting magnetic moment 1 and 180° pulses applied to both nuclei in the middle of the echo:

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

The vector analysis is shown in Figure 11.2D). 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. 11.2B 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).

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:

$\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa_1\left(c_J\mathcal{I}_y - s_J 2\mathcal{I}_x\mathcal{S}_z\right) - \frac{1}{2}\kappa_2\mathcal{S}_z$

Chapter 12

INEPT, HSQC, APT

Literature: INEPT, HSQC, and APT experiments are nicely described in K7.10, K8.7, and K12.4.4., respectively. INEPT is discussed in detail in L16.3., HSQC in C7.1.1. Decoupling trains are reviewed in C3.5.

12.1 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 $1/4|J|$
- 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. 12.1).

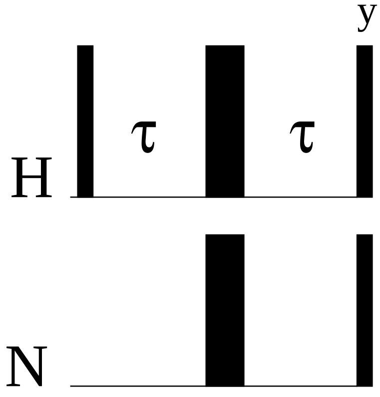

Figure 12.1: INEPT pulse sequence applied to ^{1}H and ^{15}N.

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

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

$$\mathcal{I}_t \longrightarrow \mathcal{I}_t \longrightarrow \mathcal{I}_t \tag{12.1}$$

$$-2\mathcal{I}_z\mathcal{S}_y \longrightarrow \left\{\begin{array}{l} -c_2\;2\mathcal{I}_z\mathcal{S}_y \longrightarrow \left\{\begin{array}{l} -c_2c_J\;2\mathcal{I}_z\mathcal{S}_y \\ +c_2s_J\;\mathcal{S}_x \end{array}\right. \\ +s_2\;2\mathcal{I}_x\mathcal{S}_z \longrightarrow \left\{\begin{array}{l} +s_2c_J\;2\mathcal{I}_z\mathcal{S}_x \\ +s_2s_J\;\mathcal{S}_y \end{array}\right. \end{array}\right. \tag{12.2}$$

$$\mathcal{S}_y \longrightarrow \left\{\begin{array}{l} +c_2\mathcal{S}_y \longrightarrow \left\{\begin{array}{l} +c_2c_J\;\mathcal{S}_y \\ -c_2s_J\;2\mathcal{S}_x\mathcal{I}_z \end{array}\right. \\ -s_2\mathcal{S}_x \longrightarrow \left\{\begin{array}{l} -s_2c_J\;\mathcal{S}_x \\ -s_2s_J\;2\mathcal{S}_y\mathcal{I}_z \end{array}\right. \end{array}\right. \tag{12.3}$$

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

$$\frac{\kappa_2}{4}\mathrm{e}^{-R_2t}\left(\mathrm{e}^{-\mathrm{i}(\Omega_2-\pi J)t} - \mathrm{e}^{-\mathrm{i}(\Omega_2+\pi J)t}\right) + \frac{\kappa_1}{4}\mathrm{e}^{-R_2t}\left(\mathrm{e}^{-\mathrm{i}(\Omega_2-\pi J)t} + \mathrm{e}^{-\mathrm{i}(\Omega_2+\pi J)t}\right) \tag{12.4}$$

The real part of the spectrum obtained by Fourier transform is

$$\begin{aligned} &\frac{\mathcal{N}{\gamma_2}^2\hbar^2B_0}{16k_\mathrm{B}T}\left(\frac{R_2}{R_2^2+(\omega-\Omega_2+\pi J)^2} - \frac{R_2}{R_2^2+(\omega-\Omega_2-\pi J)^2}\right) + \\ &\frac{\mathcal{N}{\gamma_1}^2\hbar^2B_0}{16k_\mathrm{B}T}\left(+\frac{R_2}{R_2^2+(\omega-\Omega_2+\pi J)^2} + \frac{R_2}{R_2^2+(\omega-\Omega_2-\pi J)^2}\right) \end{aligned} \tag{12.5}$$

- 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.

---

[1] The analysis is done for $J > 0$. If $J < 0$ (e.g. for one-bond ^{1}H-^{15}N coupling), all blue terms have the opposite sign.

- 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 (INEPT).*

- 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.

12.2 HSQC

Heteronuclear Single-Quantum Correlation (HSQC) is a 2D pulse sequence using scalar coupling to correlate frequencies of two magnetic moments with different γ (Fig. 12.2).

- 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 $\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathcal{I}_t - \frac{1}{2}\kappa_1\left(2\mathcal{I}_z\mathcal{S}_y\right) + \frac{1}{2}\kappa_2\mathcal{S}_y$

- During an echo with a decoupling 180° pulse at the proton frequency (red pulse in Fig. 12.2), anti-phase single quantum coherences evolve according to the chemical shift
  $\hat{\rho}(\mathrm{e}) \longrightarrow \frac{1}{2}\mathcal{I}_t + \frac{1}{2}\kappa_1\left(c_{21}2\mathcal{I}_z\mathcal{S}_y - s_{21}2\mathcal{I}_z\mathcal{S}_x\right) + \frac{1}{2}\kappa_2\left(c_{11}\mathcal{S}_y - s_{11}\mathcal{S}_x\right).$

- 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 90° pulse applied to S converts $\mathcal{S}_y$ to $\mathcal{S}_z$. Since the pulse sequence does not contain any more 90° pulses, this does not contribute to the signal and we can ignore it. Also, we ignore the red term which never evolves to a measurable coherence because it commutes with all Hamiltonians. The $\mathcal{S}_x$ is not affected by the 90° pulses and we should follow its fate.

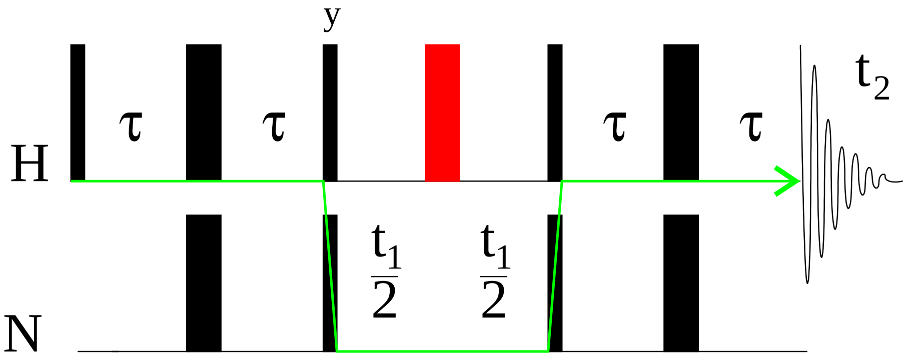

Figure 12.2: ^{1}H,^{15}N HSQC pulse sequence.

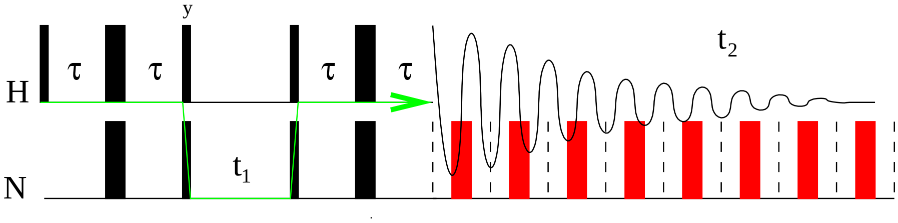

Figure 12.3: Idea of the decoupling in the direct dimension.

- 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 $\frac{1}{2}\kappa_1 \cos(\Omega_2 t_1)\mathcal{I}_x$ (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). The green coherence $\mathcal{S}_x$ evolves to $-2\mathcal{I}_z\mathcal{S}_y$. As no 90° pulse is applied to S after the last echo, this coherence does not contribute to the signal and can be ignored.

- During acquisition, both chemical shift and scalar coupling evolve in the experiment described in Fig. 12.2. 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 splitting by $\pm\pi J$ was removed by the red decoupling pulse in the indirect dimension.

12.2.1 Decoupling trains

Splitting of peaks in the direct dimension in spectra recorded by the pulse sequence in Fig. 12.2 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 $0\,^\circ$ (x), or $180\,^\circ$ ($-x$), 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.

12.2.2 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, cf. Section 8.8.3)
- 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)

12.3 APT

The attached proton test (APT) is useful for analysis of systems with multiple protons, most often CH$_n$ (C, CH, CH$_2$, CH$_3$). The experiment consists of ^{13}C excitation, recoupling echo (discussed in Section 11.5.4), and ^{13}C acquisition with proton decoupling. In the following analysis, the ^{13}C operators are labeled $\mathcal{S}_x$, $\mathcal{S}_y$, $\mathcal{S}_z$, and relaxation is ignored for the sake of simplicity.

- $\hat{\rho}(\mathrm{a}) = \frac{1}{2^n}\mathcal{I}_t + \frac{\kappa_1}{2^n}\sum\limits_{j=1}^{n}(\mathcal{I}_{jz}) + \frac{\kappa_2}{2^n}\mathcal{S}_z$

  The probability density matrix at equilibrium is described in a similar manner as for one or two magnetic moments, the extension to the multinuclear system is reflected by the scaling constant $1/2^n$, where n is the number of protons attached to ^{13}C.

- $\hat{\rho}(\mathrm{b}) = \frac{1}{2^n}\mathcal{I}_t + \frac{\kappa_1}{2^n}\sum\limits_{j=1}^{n}(\mathcal{I}_{jz}) - \frac{\kappa_2}{2^n}\mathcal{S}_y$ Excitation of ^{13}C is an analogy of cases discussed above.

- Understanding of the next step is critical for the analysis. The general conclusions of Section 11.5.4 apply, but the actual form of the density matrix must be derived for each system. The general conclusions are: evolution of Ω_2 (^{13}C frequency offset) due tho the ^{13}C chemical shift 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), therefore only $\mathcal{I}_{jz}$ contributions are present for protons.

- The actual analysis for ^{13}CH$_2$ and ^{13}CH$_3$ groups requires extension of the density matrix to $2^{n+1} \times 2^{n+1}$ dimensions. Construction of the basis matrices for such 4^{n+1}-dimensional operator space involves additional direct products with the matrices $\mathcal{I}_t$, $\mathcal{I}_x$, $\mathcal{I}_y$, $\mathcal{I}_z$. Evolution of the $2^{n+1} \times 2^{n+1}$ matrices is governed by their commutation rules, three-dimensional subspaces where "rotations" of operators take place are define by these commutation rules.

- When the rules are applied, the analysis gives
$$\hat{\rho}(\mathrm{e}) = \frac{1}{2^n}\mathcal{I}_t + \frac{\kappa_1}{2^n}\sum_{j=1}^{n}(\mathcal{I}_{jz}) + \frac{\kappa_2}{2^n}\begin{cases} n=0: & \mathcal{S}_y \\ n=1: & c\mathcal{S}_y - s2\mathcal{I}_{1z}\mathcal{S}_x \\ n=2: & c^2\mathcal{S}_y - sc(2\mathcal{I}_{1z}\mathcal{S}_x + 2\mathcal{I}_{2z}\mathcal{S}_x) - s^2 4\mathcal{I}_{1z}\mathcal{I}_{2z}\mathcal{S}_y \\ n=3: & c^3\mathcal{S}_y - sc^2(2\mathcal{I}_{1z}\mathcal{S}_x + 2\mathcal{I}_{2z}\mathcal{S}_x + 2\mathcal{I}_{3z}\mathcal{S}_x) \\ & -s^2c(4\mathcal{I}_{1z}\mathcal{I}_{2z}\mathcal{S}_y + 4\mathcal{I}_{1z}\mathcal{I}_{3z}\mathcal{S}_y + 4\mathcal{I}_{2z}\mathcal{I}_{3z}\mathcal{S}_y) \\ & +s^3 8\mathcal{I}_{1z}\mathcal{I}_{2z}\mathcal{I}_{3z}\mathcal{S}_x \end{cases}$$
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. Note that the fact that the proton decoupling is used tells us in advance that the terms containing $\mathcal{I}_{jz}$ need not be analyzed. Therefore the knowledge of exact commutation rules is not necessary, the only important conclusion is that the observable contributions to the density matrix are modulated by $\cos^n(2\pi J\tau)$ for CH$_n$. During acquisition, these terms 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 ⇒ useful chemical information.

Chapter 13

COSY

Literature: COSY is described in detail in L16.1, C6.2.1., and K8.3 (with a detailed discussion of DQF-COSY in K8.4).

13.1 Homonucler correlation: 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).

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

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

- $\hat{\rho}(\mathrm{c}) = \frac{1}{2}\mathcal{I}_t$
  $+\frac{1}{2}\kappa(-c_{11}c_{J1}\mathcal{I}_{1y} + s_{11}c_{J1}\mathcal{I}_{1x} + c_{11}s_{J1}2\mathcal{I}_{1x}\mathcal{I}_{2z} + s_{11}s_{J1}2\mathcal{I}_{1y}\mathcal{I}_{2z})$
  $+\frac{1}{2}\kappa(-c_{21}c_{J1}\mathcal{I}_{2y} + s_{21}c_{J1}\mathcal{I}_{2x} + c_{21}s_{J1}2\mathcal{I}_{1z}\mathcal{I}_{2x} + s_{21}s_{J1}2\mathcal{I}_{1z}\mathcal{I}_{2y})$,
  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
  $\hat{\rho}(\mathrm{d}) = \frac{1}{2}\mathcal{I}_t$
  $+\frac{1}{2}\kappa(-c_{11}c_{J1}\mathcal{I}_{1z} + \boxed{s_{11}c_{J1}\mathcal{I}_{1x}} - c_{11}s_{J1}2\mathcal{I}_{1x}\mathcal{I}_{2y} - \boxed{s_{11}s_{J1}2\mathcal{I}_{1z}\mathcal{I}_{2y}})$

$+\frac{1}{2}\kappa(-c_{21}c_{J1}\mathcal{I}_{2z}+\boxed{s_{21}c_{J1}\mathcal{I}_{2x}}-c_{21}s_{J1}2\mathcal{I}_{1y}\mathcal{I}_{2x}-\boxed{s_{21}s_{J1}2\mathcal{I}_{1y}\mathcal{I}_{2z}})$.
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
  $$c_{ik}c_{iJ}=\frac{c_{ik}^{-}+c_{ik}^{+}}{2} \quad s_{ik}s_{iJ}=\frac{c_{ik}^{-}-c_{ik}^{+}}{2} \quad c_{ik}s_{iJ}=\frac{-s_{ik}^{-}+s_{ik}^{+}}{2} \quad s_{ik}c_{iJ}=\frac{s_{ik}^{-}+s_{ik}^{+}}{2}, \tag{13.1}$$
  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
  $$\left(\underbrace{(s_{11}^{-}+s_{11}^{+})(c_{12}^{-}+c_{12}^{+})}_{[\Omega_1,\Omega_1]}+\underbrace{(c_{21}^{-}-c_{21}^{+})(-s_{12}^{-}+s_{12}^{+})}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1x}$$
  $$+\left(\underbrace{(s_{11}^{-}+s_{11}^{+})(s_{12}^{-}+s_{12}^{+})}_{[\Omega_1,\Omega_1]}+\underbrace{(c_{21}^{-}-c_{21}^{+})(c_{12}^{-}-c_{12}^{+})}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1y}$$
  The first and second line show coherences providing the real and imaginary component of the complex signal acquired in the direct dimension (t_2).

- Evaluation of the traces of $\hat{M}+\hat{\rho}(t_2)$ gives the follwong modulation of the signal:
  $$\underbrace{(s_{11}^{-}+s_{11}^{+})\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_2}+\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_2}\right)}_{[\Omega_1,\Omega_1]}+\mathrm{i}\underbrace{(c_{21}^{-}-c_{21}^{+})\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_2}-\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_2}\right)}_{[\Omega_2,\Omega_1]}$$

The imaginary signal in the indirect dimension is obtained by repeating acquisition for each increment of t_1 with a different phase of the second 90 ° pulse (shifted by 90 °, which correspons to the direction y in the rotating coordinate system).

- The second 90° pulse with the y phase creates the following coherences
$$\hat{\rho}(\mathrm{d}) = \frac{1}{2}\mathcal{I}_t$$
$$+\frac{1}{2}\kappa(-\boxed{c_{11}c_{J1}\mathcal{I}_{1y}}-s_{11}c_{J1}\mathcal{I}_{1z}-\boxed{c_{11}s_{J1}2\mathcal{I}_{1z}\mathcal{I}_{2x}}+s_{11}s_{J1}2\mathcal{I}_{1y}I_{2x})$$
$$+\frac{1}{2}\kappa(-\boxed{c_{21}c_{J1}\mathcal{I}_{2y}}-s_{21}c_{J1}\mathcal{I}_{2z}-\boxed{c_{21}s_{J1}2\mathcal{I}_{1x}\mathcal{I}_{2z}}+s_{21}s_{J1}2\mathcal{I}_{1x}I_{2y}).$$

- The terms in black frames evolve with the chemical shift of the first nucleus during acquisition:
$$\boxed{c_{11}c_{J1}\mathcal{I}_{1y} \rightarrow c_{11}c_{J1}s_{12}c_{J2}\mathcal{I}_{1x} - c_{11}c_{J1}c_{12}c_{J2}\mathcal{I}_{1y} + \text{ unmeasurable anti-phase coherences}}$$
$$\boxed{-s_{21}s_{J1}2\mathcal{I}_{1x}\mathcal{I}_{2z} \rightarrow c_{21}s_{J1}s_{12}s_{J2}\mathcal{I}_{1x} - c_{21}s_{J1}c_{12}s_{J2}\mathcal{I}_{1y} + \text{ unmeasurable anti-phase coherences}}.$$
The terms contributing to the signal can be written as
$$\left(\underbrace{(c_{11}^{-}+c_{11}^{+})(s_{12}^{-}+s_{12}^{+})}_{[\Omega_1,\Omega_1]}+\underbrace{(-s_{21}^{-}-s_{21}^{+})(c_{12}^{-}-c_{12}^{+})}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1x}$$
$$-\left(\underbrace{(c_{11}^{-}+c_{11}^{+})(c_{12}^{-}+c_{12}^{+})}_{[\Omega_1,\Omega_1]}+\underbrace{(-s_{21}^{-}+s_{21}^{+})(-s_{12}^{-}+s_{12}^{+})}_{[\Omega_2,\Omega_1]}\right)\mathcal{I}_{1y}.$$

- Evaluation of the traces of $\hat{M}+\hat{\rho}(t_2)$ gives the follwong modulation of the signal:
$$-\mathrm{i}\underbrace{(c_{11}^{-}+c_{11}^{+})\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_2}+\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_2}\right)}_{[\Omega_1,\Omega_1]}+\underbrace{(-s_{21}^{-}+s_{21}^{+})\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_2}-\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_2}\right)}_{[\Omega_2,\Omega_1]}$$

Now we combine signals obtained with the different phases of the second pulse.

- The *hypercomplex* signal is modulated as
$$\mathrm{e}^{-\mathrm{i}\frac{\pi}{2}}\underbrace{\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_1}+\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_1}\right)\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_2}+\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_2}\right)}_{[\Omega_1,\Omega_1]}$$
$$+\underbrace{\left(\mathrm{e}^{\mathrm{i}(\Omega_2-\pi J)t_1}-\mathrm{e}^{\mathrm{i}(\Omega_2+\pi J)t_1}\right)\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_2}-\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_2}\right)}_{[\Omega_2,\Omega_1]},$$
where we replaced $-\mathrm{i}$ by $\mathrm{e}^{-\mathrm{i}\pi/2}$.

- 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. The obtained spectrum contains diagonal peaks and cross-peaks, but (in contrast to the simple two-pulse variant of the COSY experiment) both diagonal peaks and cross-peaks have the same phase.[1] This version of the experiment is known as *double-quantum filtered* 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:

  $$\mathrm{e}^{-\mathrm{i}\frac{\pi}{2}}\underbrace{\left(\mathrm{e}^{\mathrm{i}(\Omega_2-\pi J)t_1}+\mathrm{e}^{\mathrm{i}(\Omega_2+\pi J)t_1}\right)\left(\mathrm{e}^{\mathrm{i}(\Omega_2-\pi J)t_2}+\mathrm{e}^{\mathrm{i}(\Omega_2+\pi J)t_2}\right)}_{[\Omega_2,\Omega_2]}$$

  $$+\underbrace{\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t_1}-\mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t_1}\right)\left(\mathrm{e}^{\mathrm{i}(\Omega_2-\pi J)t_2}-\mathrm{e}^{\mathrm{i}(\Omega_2+\pi J)t_2}\right)}_{[\Omega_1,\Omega_2]}.$$

  This signal represents the other dianonal and off-diagonal peak in the spectrum.

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[1] We cannot use phase cycling to remove the green terms resulting in the unwanted diagonal peaks because phase cycling can distinguish multi-quantum coherences from single-quantum ones, but it cannot distinguish anti-phase single quantum coherences from in-phase single quantum coherences.