A Brief Lecture Note for Solid State NMR

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Preface

To the solid state NMR lovers that are hesitating or intimidated by the physics

I can still recall how intimidated I was as a graduate student when reading the literature papers and textbooks. Facing the complicated formulas and derivations, I found it was often difficult or impossible to follow or even start the derivation and couldn't figure out how one step led to the next. It was especially humiliating when sometimes the authors say "naturally/obviously" etc.

I really love this field. I stayed in this field, despite my poor understanding of many classic experiments in my mind, not sure about how those conclusions came by in classic papers.

Finally I get the opportunity to redeem myself in my sabbatical semester. With tenure in my hand and temporarily forget about the pressure of work, I can really sit down to clear up all those questions for myself, and more importantly, maybe help those beginners just like me.

Well, it is actually not a perfect time in terms of knowledge. I have been away from all the course work for quite some years now. I have to stumble around with some of the statistical thermodynamics, basic electrical circuit analysis, and quantum mechanics.

But I think if I can do it, every graduate with a little bit maths and physics background can do as well.

I also recognize the two factors that matter more than the knowledge or background: patience, and perseverance. Very honestly, I can tell you that I often got stuck in certain derivation steps in writing this material. Aging does take away many of my strengths, but I would not easily get frustrated or upset now than I was 15 years ago. If I can't figure it out right away, I would just take a breath, and do something else for a change. Take my time, and ponder it back and forth while I do something else.

If you can do that, I guarantee you, every time, every single time, you will come back with a nice solution. So, please don't be intimidated by the complicated derivation formulas in papers, all you need to do is to follow logic, follow physics and think. That is actually the beauty of physics, isn't it?

Eventually, I compiled my understanding of many classic papers and parts of textbooks, and produce this short tutorial. The goal is to help some beginners with minimum background and little physics training to catch up with what I think as some core concepts in theory and experiments of solid state NMR, so that they should be able to understand most of current solid state NMR papers in journals.

Why I didn't submit this tutorial for any journal?

Well, first of all, nothing in this material is new scientifically, or at most very little of it. All I did was filling in the missing steps of many classical papers in ssNMR(or NMR).

Secondly, I may not be able to afford the time to make it the quality in terms of presentation for formal publication. It takes time to make nice figures and format, and I am not very good at presentation. In addition, I doubt any journal would accept something with such lengthy and detailed derivation. It just takes too much space. However, I would think these detailed steps are what would be most helpful for beginners. It's just like to teach babies how to walk, by holding their hands, leading them step by step.

Finally, I really want to help as many NMR lovers as possible. The best way would be make it completely public, open source, instead of publishing it and then others have to pay for this knowledge.

May more young people join NMR.

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Chapter 1 Introduction to NMR

We will introduce some fundamental concepts in magnetic resonances, including what is gyromagnetic ratio, angular and spin momentum, categories of magnetic materials, the low sensitivity of NMR. It may require some knowledge of quantum mechanics, classical mechanics, and a bit of thermodynamics. However, you can quickly catch up by reading relative terms on some online lecture note or Wikipedia.

1.1 Nucleus and its gyromagnetic ratio in classical and quantum mechanical picture

Atoms are the basic chemical compositions in chemical and biological activities. Each atom consists of a nucleus with one or more electrons bound to the nucleus. The valence electrons (out shell) participate in chemical reactions to associate with those of other atoms, alter the chemical properties of the molecule, and induce corresponding changes of its biological functions. Such as O in CO_2 molecule behaves differently than the O in CO. This change of valence electrons also induces change of NMR signals, manifested as the shift of NMR resonances, called chemical shifts. This correlation is used to derive the structure of proteins, or electronic/magnetic properties in condensed matter materials.

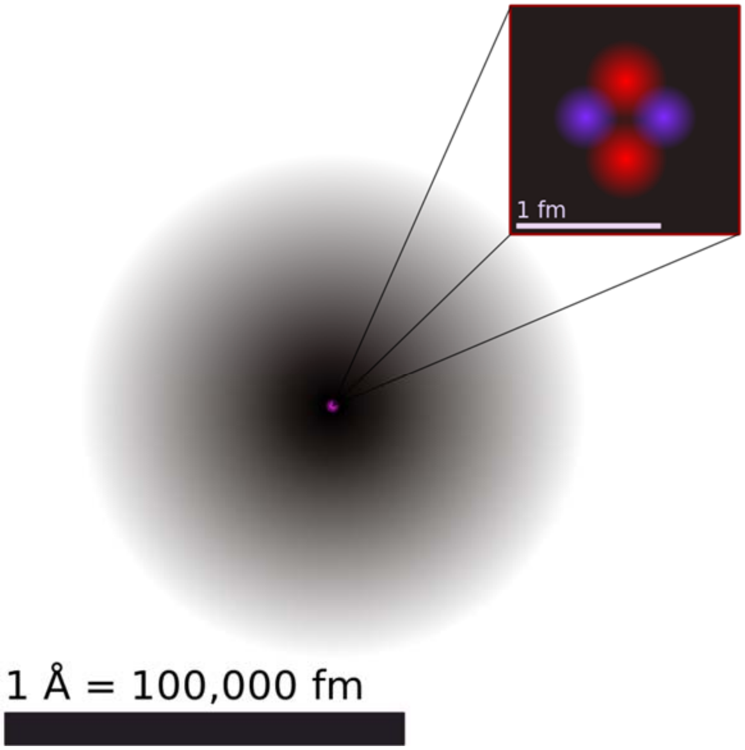


Figure 1.Illustration of the Helium atom, adapted from Wikipedia

The size of atom, for example, a helium atom, is roughly 1 Angstrom (10^{-10}m). The electrons are not static, but moving around outside the atom, which is described as electron cloud. In quantum mechanics we describe the distribution of electrons as wave function $\varphi(r)$. The nucleus at the center of the atom, is around 1 femtometer (10^{-15}m) size.

If we make an analogy, that an atom is a football field, then the nucleus is about the size of a sesame seed. If the atom is the Earth, the nucleus will be about 60 m size. However, more than 99.94% mass of the atom is located at the nucleus. The properties of nucleus will not change during chemical or biological reaction. In addition, nucleus has its underlying structure, composed of protons and neutrons. Protons, neutrons and many nuclei carry a unique quantum mechanic property called "spin". In presence of external magnetic field, these particles precess around the magnetic field, and give rise to the phenomena magnetic resonance. The ratio between the precessing frequency (Larmor frequency) and the magnetic field, is a parameter named gyromagnetic ratio γ, in the unit of rad/(Ts). Or $\gamma/2\pi$ in unit of Hz/T. For example, γ is 42.5774 MHz/T for proton, 10.7084 MHz/T for ${}^{13}C$, and -4.316 MHz/T for ${}^{15}N$. The sign here indicates the sense of precessing (+clockwise or -counterclockwise.)

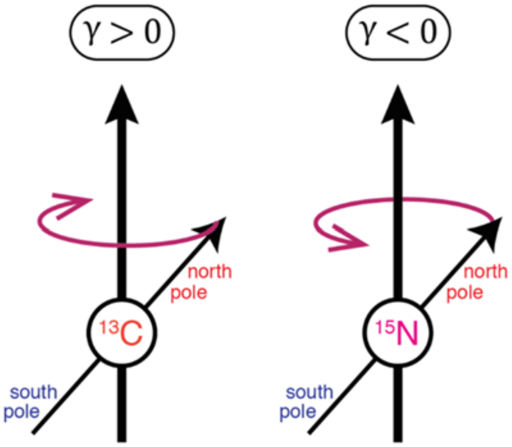


Figure 2.Gyromagnetic ratio of 13C and 15N, wikipedia.

So what consequence does this precessing motion of nucleus cause?

Classical picture of precessing motion of nucleus:

From classical picture of view, if you have a charged particle q moving around in a circle r in time T (assume it is periodic, basically we use here a loop current to model the electron clouds or the precessing of nucleus), it should induce a current:

$$I = \frac{q}{T} = \frac{q\vec{v}}{2\pi r} \tag{1.1}$$

Such a loop current produces a magnetic moment $\vec{\mu}$:

$$\vec{\mu} = I\vec{S} = \frac{q\pi r^2}{T} = \frac{q\pi r^2 \vec{v}}{2\pi r} = \frac{qr\vec{v}}{2} \tag{1.2}$$

At the same time, such a gyration motion (rotation motion) also creates an angular momentum $\vec{J}$:

$$\vec{J} = \vec{r} \times m\vec{v} = rmv \tag{1.3}$$

The ratio between $\vec{J}$ and $\vec{\mu}$ is the gyromagnetic ratio γ:

$$\gamma = \frac{\vec{\mu}}{\vec{J}} = \frac{qr\vec{v}}{2} \times \frac{1}{rm\vec{v}} = \frac{q}{2m} \tag{1.4}$$

So this classic picture allows you to see that gyromagnetic ratio is related to the charge and mass of the particle. (Think about γ for electron, proton, ^{13}C and ^{15}N, what estimation can you get?)

Quantum mechanical picture of precessing motion of nucleus:

Of course, nucleus or nucleons are much smaller particles beyond the scope of classical mechanics. We need quantum mechanics. For an isolated (non-interacting) electron, the Hamiltonian H is:

$$H = \frac{1}{2m}(\vec{p} - \frac{q}{c}\vec{A})^2 + q\phi \tag{1.5}$$

Where $\vec{p}$ is momentum operator $\vec{p} = -i\hbar\vec{\nabla} = -i\hbar(\vec{e}_x\frac{\partial}{\partial x} + \vec{e}_y\frac{\partial}{\partial y} + \vec{e}_z\frac{\partial}{\partial z})$, $\vec{A}$ is the vector potential associated with magnetic $\vec{H} = \vec{B} = \vec{\nabla} \times \vec{A}$, (here we assume it is vacuum, or the magnetization of the material is 0, so magnetic induction or magnetic field density $\vec{B}$ is the same as the magnetic field strength $\vec{H}$.

In general $\vec{B} \neq \vec{H}$, $\vec{B} = \mu_0(\vec{H} + \vec{M}) = (1 + \chi_m)\mu_0\vec{H} = \frac{\mu}{\mu_0}\mu_0\vec{H} = \mu_r\mu_0\vec{H}$, where μ_0 is the magnetic permeability of space ($4\pi \times 10^{-7}$ N·A^{-2}), μ_r is the relative permeability, and χ_m (dimensionless) is magnetic susceptibility.

In Eq. 1.5, ϕ is the scalar field associated with electric field E: $\vec{E} = -\nabla\phi - \frac{\partial\vec{A}}{\partial t}$.

What does magnetic permeability mean? Conceptually, it means how will a medium support the formation of a magnetic field within itself. How will they impact our NMR experiment?

What are diamagnetism, paramagnetism, antiferromagnetism and ferromagnetism?

Diamagnetic materials exhibit no magnetic moment by itself. But external magnetic field will induce an internal magnetic field from the material opposing the direction of the external magnetic field. It has a negative χ_m or μ_r less than 1. The effect is very small in general, created by the preferential precessing of the orbital electrons around the external magnetic field and producing a very small magnetic field opposing the external magnetic field (as shall be seen in chemical shift/shielding calculation in Sect. 5.4). Most protein/life materials are diamagnetic. Superconductor can be viewed as a perfect diamagnetic material that can expel completely the external magnetic field.

Paramagnetic materials also do not exhibit any permanent magnetic moment. However, in the presence of an external magnetic field, an internal field produced by the orbital motions of electrons will be aligned with the direction of the external magnetic field. It has a positive χ_m or μ_r greater than 1. The induced field is linear in strength to the external magnetic field. Its magnitude is normally larger than that of diamagnetic shift, but also very weak.

Ferromagnetism is created by the alignment of magnetic dipole moment (and also orbital angular momentum) of unpaired electrons. These unpaired electrons tend to align their spins in parallel due to the exchange interactions, because of the Pauli exclusion principle (if they have same spin orientation, they can't physically located in the same orbital state, which in return decreases the electrostatic energy of the electrons compared to the anti-parallel alignment that can assume the same orbital) This exchange interaction is normally much stronger (1000 folds) than the magnetic dipole-dipole interactions, which would have spins anti-parallel aligned. At temperatures higher than the so called Curie temperature (what is the Curie temperature?), thermal motion will randomize the orientation and kill the alignment.

Using the vector potential and assume there is no time varying fields,

$$\vec{A} = \frac{1}{2} H_0 \vec{e}_z \times \vec{r} \tag{1.6}$$

This expression is the equivalent to say that you have an external magnetic field H_0 along e_z direction. $\vec{H} = H_0 \vec{e}_z$. Please prove it.

The corresponding x, y, z components of the vector potential are:

$A_x = -\frac{1}{2} H_0 y$; $A_y = \frac{1}{2} H_0 x$; and $A_z=0$;

Hence, the Hamiltonian can be rewritten as:

$$H = \frac{1}{2m} \sum_i (\vec{p}_i - \frac{q}{c} A_i)^2 + q\phi \tag{1.7}$$

Where the subscript i means x, y, and z components.

Rearrange the equation:

$$H = \frac{1}{2m} [(p_x^2 + p_y^2 + p_z^2) - \frac{qH_0}{C} (xp_y - yp_x) + \frac{q^2 H_0^2}{4c^2} (x^2 + y^2)] + q\phi$$

$$H = \frac{1}{2m} \left[\vec{p}^2 - \frac{qH_0}{c} J_z + \frac{q^2 H_0^2}{4c^2} (x^2 + y^2) \right] + q\phi$$

$$H = H_a + H_b + H_c$$

Here we have:

$$H_a = \frac{\vec{p}^2}{2m}$$

$$H_b = -\frac{q}{2mc} J_z H_0 = -\frac{q}{2mc} L_z H_0$$

$$H_c = \frac{q^2 H_0^2}{8mc^2}(x^2 + y^2)$$

The second term is nothing but the interaction of angular momentum with external magnetic field:

$$H_{zeeman} = -\vec{\mu} \cdot \vec{H} = -\mu H_0 = -\gamma I_z H_0 = -\omega_0 I_z \tag{1.8}$$

Where ω_0 is the Larmor frequency.

By comparing to H_b, the gyromagnetic ratio γ is:

$$\gamma = \frac{q}{2mc}$$

Here we note there is an extra c in the denominator, this is because we used the formula in cgs unit in the above quantum mechanics derivation. To convert to SI unit, all charges has to multiply a factor of c, then you can see the quantum mechanical derivation of gyromagnetic ratio is the same as the above classical derivation.

In more rigorous derivation,

$$\gamma = \frac{q}{2m} g_e \tag{1.9}$$

Where g_e for electron is about 2, which can be measured by one-electron cyclotron.

1.2 Magnetic susceptibility in typical diamagnetic materials.

Therefore, back to the second term, if we assume $\omega_0 = \frac{qH_0}{2mc}$, then the third term can be rewritten as:

$$H_c = \frac{q^2 H_0^2}{8mc^2}(x^2 + y^2) = \frac{1}{2} m\omega_0^2 (x^2 + y^2)$$

We can compare the magnitude of H_b and H_c. We can treate $x^2 + y^2$ as r^2, where r is the orbital radius, which can be simplified as the Bohr radius. Bohr radius is the most probable distance between the electron and nucleus in a hydrogen atom at its ground state. We will replace the angular momentum operator J_z in H_b by $\hbar$. Can you show that the third term is less than 10^{-4} compared to the second term?

So the above quantum mechanical derivation shows that the motion of charged particle produces a coupling with external magnetic field similar to that predicted in the classical picture, the Zeeman interaction, manifested as the coupling between the angular momentum and the external magnetic field. The coefficient resembles the gyromagnetic ratio (except missing the correct g factor in more rigorous derivations).

In 1905, Paul Langevin presented an explanation for the diamagnetism due to orbital electrons just like the second term:

$$H_b = -\frac{q}{2m} J_z H_0 = -\frac{q}{2m} L_z H_0$$

$$\omega_0 = \frac{eH_0}{2m} = 8.7935 \times 10^{10} T^{-1} s^{-1} \times H_0$$

Here we used the relation 1 Tesla = 1 kg/(C·s). Compared to the true value of electron gyromagnetic ratio, it is smaller by a factor of 2 due to the missing g-factor. Let's pretend that we still don't know the g factor, in a 14 Tesla magnetic field (600MHz proton resonance frequency), this will give us

$$\omega_0 = \frac{eH_0}{2m} = 8.7935 \times 10^{10}\, T^{-1} s^{-1} \times 14\, T = 1.231\ \times 10^{12}\, rad/s$$

To lower the energy, the angular momentum associated with orbital motion need to assume parallel alignment to H_0, magnetic moment associated with the current loop of the electron should then be antiparallel to H_0, and is diamagnetic. We can easily calculate the current from the circulating frequency:

$$I = \frac{e\omega_0}{2\pi} = \frac{e^2 H_0}{4m\pi} = 1.602 \times 10^{-19} C \times 1.959 \times 10^{11} Hz = 3.138 \times 10^{-8} A$$

The magnetic moment associated with the current then can be calculated as:

$$\vec{\mu} = I \cdot S = \frac{e^2 H_0}{4m\pi} \times \pi(x^2 + y^2)$$

Let's use the electron in proton's parameter r=a$_0$=5.29x10^{-11} m, so $x^2 + y^2 = \frac{2}{3} r^2$

$$\mu = I \cdot S = \frac{e^2 H_0}{4m\pi} \times \frac{2\pi r^2}{3} = 3.138 \times 10^{-8} A \times \frac{2\pi(5.29 \times 10^{-11})^2}{3} m^2$$

$$= 1.83917 \times 10^{-28} A \cdot m^2$$

The total magnetic field strength for proton in per volume water is

$$M = n\mu_0\mu$$

Where n is the density of proton per volume water. The free space magnetic permeability is

$$\mu_0 = 1.257 \times 10^{-6}\ T \cdot m/A$$

$$M = n\mu_0\mu$$

$$= 6.022 \times \frac{10^{23}}{Mol} \times 10^{6} \frac{g}{m^3} \div \frac{18g}{Mol} \times 1.257 \times 10^{-6}\, T \cdot \frac{m}{A} \times 1.83917 \times 10^{-28} A \cdot m^2$$

$$= 7.73438 \times 10^{-7}\mathrm{T}$$

Remember the direction of the field is opposing the external field, so there should be a negative sign: $M = -7.73438 \times 10^{-7}\mathrm{T}$

Of course, we have oxygen in water as well, which has six electrons outside the nuclei, therefore, the current will be six times (but its radius will be larger than that of proton as well)

According to the definition of magnetic susceptibility, we can estimate the per volume magnetic susceptibility of proton in water is $\chi = -\frac{M}{H} = -\frac{7.73438\times10^{-7}\mathrm{T}}{14T} = -5.52456 \times 10^{-8}$

This rough estimation is about 20 fold larger than the true value of water's susceptibility is -9.051x10^{-9} (m^3/kg). But you get the idea how to use simple known constants to estimate the physical parameters of interest.

1.3 Spin polarization and Curie's law

In addition to the angular momentum associated with orbital motions, elementary particles also can possess another angular momentum called spin angular momentum (normally represented by I or S in quantum mechanics). They are also quantized, as proved experimentally by Stern-Gerlach experiment in 1922. Just like the orbital angular momentum, any elementary particles with nonzero spins, will exhibit a dipolar magnetic moment μ associated with the spin: $\mu = \gamma I$, where γ is the gyromagnetic ratio. The only difference is, the particle can be charge neutral, and no actual physical orbital motion is needed to produce the magnetic moment. But similar to angular momentum, you can imagine these spins are vectors, with a specific direction. Without external magnetic field, these spins and the magnetic moments exhibit no preferred alignment.

When an external magnetic field is present, the spins and the magnetic moment will assume a preferred direction, along the magnetic field. The projection of the spin operator is then quantized along this direction. The projection of spin and orbital angular momentum I_z to the magnetic field direction also assume discrete values between –I, -I+1, -I+2,…I-2, I-1, I, where I is the major angular momentum value. For electron, ^{1}H, ^{13}C, and ^{15}N, as the major spin quantum number is ½, so the quantized I_z can only be either -1/2 or 1/2.

In NMR experiments, we normally work with macroscopic amount of samples (~ 1 μM sample is needed to produce a reasonable NMR signal in solid state NMR, for example). Why is that? This is because not all magnetic moments will align. Let's do a simple estimation, assume we have N identical nuclei with spin I and they only interact with the external magnetic field H_0, without interactions between each other. The Hamiltonian of the system is just the Zeeman term:

$$H = -\mu \cdot H_0 = -\gamma H_0 I_z \hbar$$

These particles can assume energy from $-\gamma H_0 I\hbar$ to $\gamma H_0 I\hbar$. The total magnetization is the sum of the magnetic moment of all particles. However, the distribution of their spin orientation is neither entirely random nor completely aligned, but following the Boltzmann distribution. This evaluation has to be done by thermodynamic statistics. For a single spin:

$$P_m = \frac{e^{-\frac{E_m}{kT}}}{Z} \tag{1.10}$$

Where the partition function $Z = \sum_{m=-I}^{I} e^{-\frac{E_m}{kT}}$, $E_m = -m\gamma H_0\hbar$.

For a system of N non-interacting spins, the total energy should be: $E = \sum_{i=1}^{N}(-m_i\gamma H_0\hbar)$, and the total system magnetic moment is: $\mu = \sum_{i=1}^{N} \mu_i$.

We can write a specific state function of the system as $|a\rangle = |m_1, m_2, \dots m_i, \dots m_N\rangle$, where m_i represents the spin alignment state of particle i with m_i assuming quantized value between –I to I.

A particle would like to align along the magnetic field (assume γ is positive) for lower energy.

The observed magnetization M is the trace evaluation:

$$M = \frac{\sum_a \sum_{i=-I}^{N} \mu_i \exp\left(-\frac{E_a}{kT}\right)}{Z}$$

$$= \frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| \sum_{i=-I}^{N} \mu_i \exp\left(-\frac{E_a}{kT}\right) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp(-\frac{E_a}{kT})} \tag{1.11}$$

Since all particles are identical, we can evaluate the contribution from jth particle, and the system total M would be N fold of this value, as shown below:

$$M = N\frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| \mu_i \exp(-\frac{E_a}{kT}) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp(-\frac{E_a}{kT})}$$

$$= N\frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| \gamma I_{jz}\hbar \exp(-\frac{E_a}{kT}) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp(-\frac{E_a}{kT})}$$

$$= N\gamma\hbar\frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| I_{jz} \exp\left(-\frac{E_a}{kT}\right) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp(-\frac{E_a}{kT})}$$

$$= N\gamma\hbar \frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| I_{jz} \exp\left(\frac{I_{jz}\gamma H_0 \hbar}{kT}\right) \exp\left(\frac{\sum_{i\neq j} I_{iz}\gamma H_0 \hbar}{kT}\right) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp\left(\frac{I_{jz}\gamma H_0 \hbar}{kT}\right) \exp\left(\frac{\sum_{i\neq j} I_{iz}\gamma H_0 \hbar}{kT}\right)}$$

Here we separate the jth particle's contribution from the rest in the weight factor of the energy term. Obviously, the sum over all possible state a is now decomposed into two parts: the term $\exp\left(\frac{\sum_{i\neq j} m_i\gamma H_0 \hbar}{kT}\right)$ will sum over all possible states with possible values of other particle m_i $(i \neq j)$, then it will multiply with the sum over all possible states of jth value with the term $m_j \exp\left(\frac{m_j\gamma H_0 \hbar}{kT}\right)$. These two sum are independent from each other. Therefore, the common sum of the term $\exp\left(\frac{\sum_{i\neq j} m_i\gamma H_0 \hbar}{kT}\right)$ on both numerator and denominator will cancel with each other, and we have:

$$M = N\gamma\hbar \frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| I_{jz} \exp\left(\frac{I_{jz}\gamma H_0 \hbar}{kT}\right) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp\left(-\frac{m_j\gamma H_0 \hbar}{kT}\right)}$$

$$= N\gamma\hbar \frac{\sum_a \left\langle m_1, m_2, \dots m_i, \dots m_N \middle| I_{jz}(1 + \frac{I_{jz}\gamma H_0 \hbar}{kT}) \middle| m_1, m_2, \dots m_i, \dots m_N \right\rangle}{\sum_a \exp\left(-\frac{I_{jz}\gamma H_0 \hbar}{kT}\right)}$$

When we do the evaluation of the trace, note that we need to count all possible combinations of all particles. We can evaluate the trace in the numerator over all possible states of jth particle, and then it will be repeated over all possible states of other particle, for each m_i, it will be repeated $2I + 1$ times over all its possible quantized values, therefore, the results of the sum over the states of jth particle will be repeated $(2I + 1)^{N-1}$. Let's do the sum over jth particle first:

$$M_j = N\gamma\hbar \frac{\sum_{m_j} \left\langle m_j \middle| I_{jz}(1 + \frac{I_{jz}\gamma H_0 \hbar}{kT}) \middle| m_j \right\rangle}{\sum_{m_j} \exp\left(-\frac{m_j\gamma H_0 \hbar}{kT}\right)}$$

$$= N\gamma\hbar \frac{\sum_{m_j} \left\langle m_j \middle| m_j + \frac{I_{jz}^2\gamma H_0 \hbar}{kT}) \middle| m_j \right\rangle}{\sum_{m_j}(1 + \frac{m_j\gamma H_0 \hbar}{kT})}$$

Here we need to apply some approximation using the conditions in our normal experiment: say the H_0 is 20 T, temperature is 300 K, $\gamma H_0 \hbar$=267.522x10^{6} rad/(T·s)x20 Tx 1.0546 x 10^{-27} erg·s= 5.64257x10^{-18} erg. In comparison the denominator kT=300K x1.380622x10^{-16} erg/K=4.14187x10^{-}

^{14} erg. So $\frac{m\gamma H_0\hbar}{kT}$ ~ 0.0001 «1. Hence we can apply so called high temperature approximation $\exp\left(-\frac{m\gamma H_0\hbar}{kT}\right) \cong 1 - \frac{m\gamma H_0\hbar}{kT}$.

The sum of the term m_j over all m_j states from –I to I, and will be zero. The unit at the bottom will also be summed over all possible values, and be repeated 2I+1 times, so we will just have:

$$M_j = N\gamma\hbar \frac{\sum_{m_j} \left\langle m_j \middle| \frac{I_{jz}^2 \gamma H_0 \hbar}{kT} \middle| m_j \right\rangle}{2I+1}$$

$$= \frac{N\gamma^2\hbar^2 H_0}{(2I+1)kT} \sum_{m_j} \langle m_j | I_{jz}^2 | m_j \rangle$$

The term I_{jz}^2 contains square of I_{jz}. Recall that $I_x^2 + I_y^2 + I_z^2 = I^2 = I(I+1)$, and $I_x^2 = I_y^2 = I_z^2$, so $I_{jz}^2 = \frac{1}{3} I(I+1)$:

$$M_j = \frac{N\gamma^2\hbar^2 H_0}{3(2I+1)kT} \sum_{m_j} \langle m_j | I(I+1) | m_j \rangle$$

$$= \frac{N\gamma^2\hbar^2 H_0 I(I+1)(2I+1)}{3(2I+1)kT}$$

$$M_j = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT} H_0 \tag{1.12}$$

Now, recall that we still need to sum over the possible states of other particle. However, that sum will be the same both in numerator and denominator, so it will not change the result.

So the magnetization of N non-interacting particles will be just $\frac{N\gamma^2\hbar^2 I(I+1)}{3kT} H_0$ in presence of an external magnetic field.

This is in fact the Curie's law. The part in front of H_0 is essentially the susceptibility χ. We can apply estimation to the proton in water (although water is diamagnetic), and treat N as number of proton per unit volume, remember that there are two protons per water molecule:

$$\chi_H = 2 \times \frac{1}{2} \times \frac{3}{4} \times 6.022 \times 10^{23}/Mol \times 1000 \frac{kg}{m^3} \div 18 g/Mol \times (2.675 \times 10^6 \frac{rad}{s \cdot T} \times 1.0546$$

$$\times 10^{-34} J \cdot s)^2 \div \left(3 \times \frac{300\text{kx}1.380643\text{x}10^{-23}\text{J}}{\text{k}}\right)$$

$$= 2.508 \times 10^{28}/m^3 \times (2.82106 \times \frac{10^{-28}J}{T})^2 \div (1.243\text{x}10^{-20}\text{ J})$$

$$\chi_H = 1.60576 \times 10^{-7}\text{J}/(\text{T}^2\text{m}^3)$$

Remember the energy of magnetic field is $E = \frac{1}{2}\int B \cdot HdV$; So 1 J= 1T· A/m ·m^3=1T· $A \cdot m^2$, therefore,

$$\chi_H = 1.60576 \times 10^{-7}\text{A}/(\text{Tm})$$

1.4 Typical sensitivity requirements in NMR detection

Of course, this rough estimation is not accurate for the water susceptibility. Water is diamagnetic, not paramagnetic. The per volume susceptibility of water is -9.051x10^{-9}, due to electronic orbital motions, not the magnetic moment of nucleus. But this estimation does show how weak even the proton in water can be.

$$V_{sig} = \omega_0 \frac{B_1}{I} MV \tag{1.13}$$

Here ω_0 is the Larmor frequency, I is the current in coil, V is the sample volume, M is the magnetization per volume of the sample. B_1 is the transverse magnetic field created in coil. Eq. 13 was given by D.I. Hoult and R.E. Richards in their paper “The signal-to-noise ratio of the nuclear magnetic resonance,” *Journal of Magnetic Resonance*, vol. 24, pp. 71-85, 1976.

How does this expression tell us about our NMR experiment sensitivity?

First of all, nucleus with higher Larmor frequency or signals in higher magnetic field is more sensitive due to the ω_0 factor in Eq. 13. That is why we would rather do carbon detection than nitrogen detection, and now we are trying proton detection. Secondly, higher B_1 field gives more sensitivity (smaller coil etc). Finally, more sample would also improve our NMR signal. In the same publication, D.I. Hoult and R.E. Richards also gave an expression for B_1:

$$B_1 = \sum_{i=1}^{N} \frac{\mu_0 I a^2}{4(a^2 + z^2)^{3/2}} \tag{1.14}$$

Where a is the coil radius, and z is distance of the round of the coil to the evaluated point.

Therefore

$$\frac{B_1}{I} = \sum_{i=1}^{N} \frac{\mu_0 a^2}{4(a^2 + z^2)^{3/2}} \tag{1.15}$$

We can use this to do a rough estimation of the voltage induced by a $\frac{\pi}{2}$ pulse in our NMR experiment. First let's estimate the B_1 field of a single-turn coil with a=1.6 mm, z= 2mm.

$$\frac{B_1}{I} = 1.257 \times 10^{-6}\, T \cdot m/A \times \frac{1.6^2}{4(1.6^2+2^2)^{3/2} mm} = 4.788 \text{ x } 10^{-5} \text{ T/A}$$

Here we can estimate how strong the current should be to produce a $\frac{\pi}{2}$ pulse of proton channel with $t_p = 2\ \mu s$, which is quite common in our ssNMR experiments.

$$\gamma B_1 \mathrm{t}_p = \frac{\pi}{2} \tag{1.16}$$

$$2\pi \times 42.5774 \times 10^6 Hz/T \times B_1 \times 2 \times 10^{-6} s = \frac{\pi}{2}$$

$$2\pi \times 42.5774 \times B_1 \times 2/\mathrm{T} = \frac{\pi}{2}$$

$$B_1 = 29\ G = 2.9 \times 10^{-3} T$$

Compared with the $\frac{B_1}{I}$ expression, we see the current necessary to generate such a field in the solenoid coil is ~ 60.6 A. This is a huge amount of current. (Now you see why we need hundreds to 1000 of Watts power in our transmitter amplifier.

If we want a $\frac{\pi}{2}$ pulse with $t_p = 4\ \mu s$ on carbon channel, what would be the B_1 field? And how much current is needed?

$$2\pi \times 10.7084 \times 10^6 Hz/T \times B_1 \times 4 \times 10^{-6} s = \frac{\pi}{2}$$

$$B_1 = 58.4\ G$$

So even larger currents are needed for lower channel with a decent $\frac{\pi}{2}$ pulse.

The magnetization of our 3.2 mm rotor with water, which is about 30 μL. Recall we estimated $\chi_H = 1.60576 \times 10^{-7} \mathrm{A/(Tm)}$ for water. In a 14 Tesla magnetic field, the total magnetization of a 3.2 mm rotor filled with water would be:

$$MV = \chi_H \cdot H = 1.60576 \times 10^{-7} A/(Tm) \times 14T \times 3 \times 10^{-8} m^3 = 6.7449\text{x}10 - 14 \text{ A} \cdot \text{ m}^2$$

$$V_{sig} = \omega_0 \frac{B_1}{I} MV = 2\pi \times 6 \times 10^8 Hz \times 4.788 \times 10^{-5} \frac{T}{A} \times 6.7449 \times 10^{-14} \mathrm{A} \cdot \mathrm{m}^2$$

$$V_{sig} = 1.21749 \times 10^{-8} \frac{T \cdot \mathrm{m}^2}{s}$$

Now we need to do some unit conversion:

1 Tesla=1 $\frac{J}{A \cdot m^2}$, 1 A=1C/s, 1 V= 1J/(A$\cdot$ s)= 1J/C, so

$V_{sig} = 1.21749 \times 10^{-8} \frac{J \cdot \mathrm{m}^2}{A \cdot m^2 \cdot s}$=$1.21749 \times 10^{-8} \frac{J}{\mathrm{C}} = 1.21749 \times 10^{-8} \mathrm{V}$

So you can see the voltage induced in the coil is about nV range, very small. Of course, here we used a one-cound coil to do the B field calculation. In reality, a 3.2mm probe coil may have 5-6 turns. But you get the point, the NMR signal is very tiny. But this is not the whole story.

What about noise?

Noise.

In RF electronic circuit, there are two kinds of noise: Shot noise and Johnson noise. Flicker noise at DC circuit is not significant in NMR circuit.

1. Shot noise: arises from the fluctuation of discreteness/quantized of charge carriers in DC current. It is independent from temperature and frequency, and described by Poisson distribution. Hence at normal current magnitude that consists of large number of charge carriers, it is insignificant compared to Johnson noise.

2. Johnson noise and shot noise.

What is white noise?

Johnson Noise, A.K.A. Johnson-Nyquist Noise, or Nyquist noise, or thermal noise, arises from the thermal motion of electrons or other charge carriers in the electrical conductors at equilibrium. It exist with or without the application of voltage. In ideal resistor, the power spectral density of Johnson noise is is nearly uniform over all frequency, so called white noise. When the bandwidth is limited, Johnson noise can be approximated by a Gaussian distribution. Its voltage variance per Hertz bandwidth $\overline{v_n^2}$ can be described by

$$\overline{v_n^2} = 4kTR \tag{1.17}$$

Where k is the Boltzmann constant, T is temperature in Kelvin, and R is resistance in Ohm. This noise reveals the major noise contribution to the Signal-to-Noise (SNR) in NMR solenoid coil. Hence we have cryo-probe that lowers the coil temperature from room temperature to 4K to reduce the Johnson noise in the detection coil. Theoretically, by going from 300 k to 4k, the voltage/Hz decreases by $\sqrt{300/4} = 75$ folds. Of course, the actual S/N enhancement of normal cryo-probe is much less, roughly about a factor of 4.

At room temperature,

$$\sqrt{\overline{v_n^2}} = 0.13\sqrt{R}\, nV/\sqrt{Hz} \tag{1.18}$$

Eq. 1.18 indicates the noise is proportional to both the resistance, and the bandwidth. So reduction of unnecessary detection bandwidth also helps SNR.

For example, assume that we are detecting a 10 ppm proton spectrum on a 600MHz spectrometer with a bandwidth of 10000 Hz, and the probe coil resistance is 1 Ohm, the standard deviation of Voltage due to the Johnson noise from the probe coil will be: 0.13*100=13 nV. This is about the same level of magnitude to the signal we estimated earlier. It demonstrates the low sensitivity weakness of NMR.

What should we do?

The answer is signal average. Why does signal average enhances S/N, and how? Suppose we acquire a 1D cross polarization spectrum with 4 scans, with SNR=2. We want to get a spectrum with SNR=4, how many scans should we go?

SNR=Signal/Noise. The randomness factor associated with the Johnson noise can be described by the normal distribution in statistics. According to the Central Limit Theorem (CLT) for normal distribution, the variance of N independent random variables will be decreased by N fold. Hence, when you accumulate N scans of NMR spectra, your signal $V_s(N)=NV_{sig}$, the variance of Johnson noise will be $N\overline{v_n^2}$. The corresponding standard deviation for noise amplitude will be $\sqrt{N\overline{v_n^2}}$, so now SNR(N scan)=$\frac{NV_{sig}}{\sqrt{N\overline{v_n^2},}} = \sqrt{N}\frac{V_{sig}}{\sqrt{\overline{v_n^2}}}$, which proves the SNR increases with $\sqrt{N}$, not N.

In addition to the signal average, NMR also exploits the RLC resonance circuit for signal excitation and sensitive detection. We will give a brief introduction in Chapter 2.

Chapter 2 Introduction to principles of NMR hardware

We will cover some basic concepts regarding the building blocks for NMR spectrometer, and NMR probe. This knowledge will help you understand some more advanced literature regarding probe design. We will start with the discussion of factors contributing to NMR sensitivity, and give a brief introduction about some basic properties of coaxial cable. Detailed derivation will be given for two typical RLC circuits, which are the fundamental blocks in probe design. The final section will cover the concept of balanced circuit design exploited in most NMR probes.

2.1 Basic building blocks of NMR detection hardware.

We showed that the NMR signal arises from the change of the macroscopic magnetic moment (which is NMR signal) is very small, so NMR is a low sensitivity method compared to techniques like X-ray diffraction or cryoEM. At the same time, to improve the sensitivity and produce good quality signal, we need high power transmitter to excite NMR. Here is why:

The rotating field strength B_1 in gauss can be also related to the transmitter parameter (Experimental pulse NMR a Nuts and Bolts Approach by Eiichi Fukushima and Stephen Roeder, P.378):

$$B_1 \cong 3\sqrt{\frac{PQ}{V v_0}} \cong 3.7\sqrt{\frac{PT_R}{V}} \tag{2.1}$$

Where P is the transmitter power, Q is the quality factor, V is the volume of the coil in cm^3, v_0 is the frequency in MHz, and T_R is the ringdown time in the coil in μs. The strength of B_1 field determines not only the decoupling efficiency. (of course we can decouple too hard) but the associated E-field strength can heat up our biological samples:

$$Q_{RF} = \omega \varepsilon'' \varepsilon_0 E^2 \tag{2.2}$$

Q_{RF} is the heat power per volume generated by dielectric heating by E field. It is a dominant avenue for heating for materials with conductivity $\sigma \ll \omega\varepsilon''$, just like the microwave to heat up our food.

From Eq, 2.1, it is clear why we want to have high P, as it helps the sensitivity of detection (Receiver) shown in Eq. 1.13. In addition, we want short pulses to change the orientation of magnetization, to minimize the effect of relaxation (T_1 and T_2).

The quality factor Q

What is Q by definition? In a typical RF circuit, Q is the ratio of power stored versus power loss(dissipated in heat) per frequency cycle:

$$Q = 2\pi \frac{Power\ stored}{Power\ dissipated} = \frac{\frac{1}{2} L I_{peak}^2}{\frac{I_{rms}^2 R}{f_0}} = \frac{\omega_0 L}{R} = \frac{2\pi \nu_0 L}{R} = \frac{2\pi}{R}\sqrt{\frac{L}{C}} = \frac{f_0}{\Delta f} \tag{2.3}$$

Where f_0 or ν_0 is the resonance frequency and Δf is the FWHM. L, C, and R are the inductance, capacitance and resistance of the resonant circuit.

We can see that a large Q is favorable for SNR. Meanwhile, a large Q has some unwanted side effect as well. Normally a high Q of our NMR probe does not cause any issue in terms of the FWHM Δf, which should be at least bigger than the bandwidth of useful signal detection (Why?), but a high Q will cause a long transient response (or dead-time for detection) after the transmitter delivers the high power pulses to the probe for signal excitation. This dead time is normally multiple fold (7-20) of the time constant τ of the RLC resonant circuit. During this time, you can't start signal detection (you will overload/saturate/burn the preamp, as the receiver is to amplify microvolt signal by design). If let into your receiver, the large transient ringdown of pulses can also distort your signal at the least (the NMR signal will starts regardless of the ringdown). So that is why we have receiver blanking/delay time (check your setup, there is always about 4-8 μs delay between transmitter pulsing and receiver gate open). The ringdown time (or system recovery time is more serious at lower frequency than higher frequency. In some serious cases, we need to apply left-shift to truncate the contaminated signal by ringdown before Fourier transform. In any case, there will always be a dead-time of at least one half of the transmitter pulse length.

Therefore, we have to take a compromise by choosing an appropriate Q that is not too big/small. (Homework, measure your probe Q). Normally, the Q of your probe is between 50 to 500.

The resistance of the Q factor is mostly from the coil (there is also contribution from non-ideal inductor(coil) and capacitor (parasitic resistance). The coil needs to be mounted very carefully, otherwise, additional microphonics and spurious ringing can arise (Why? Recall that $\vec{F} = q\vec{v} \times \vec{B}$. When a large current is delivered to a coil in the magnetic field, it will induce this large force and make the coil to vibrate. Recall the large noise during MRI examination, this mechanical vibration will set off acoustic standing waves in the coil, which also increases the recovery time). Therefore, the mount of NMR coil needs to be robust (reinforced by epoxy, RTV, or wrap around some sturdy supporting structure, or use thick stranded wire).

In addition, the homogeneous B_1 field is critical for ssNMR, as experiments such as cross polarization requires precise matching the magnitude of RF fields between different channels.

The common method to test the B_1 field uniformity is to measure the decay of magnetization by a train of $\frac{\pi}{2} + 2n\pi$ pulses, which is the Fourier transform of the B_1 inhomogeneity if the $T_2^* \ll T_2$.

The imperfection of pulses is inevitable, however. We can achieve better accuracy of tipping angle with composite pulses than a single pulse. A $\frac{\pi}{2_x} - \pi_y - \frac{\pi}{2_x}$ combo can be used to replace a single π_y pulse.

Crossed diodes

A pair of silicon diodes with antiparallelly aligned are widely used in NMR. Each diodes will only pass current with the direction consistent with its diode conduction direction with a voltage larger than 0.5 Volt. Such a pair of crossed diodes thus act as an on switch for large RF signals and at the same time behaves as open circuit for small signals.

Crossed diodes are put in front of the sensitive preamp and work as a shunt to the ground for protection of the receiver circuit.

Diodes are also put in series on the transmitter side to disconnect the transmitter from the probe and the preamp, so the small NMR signal (10^{-6} V) will not leak back into the transmitter side, but exclusively goes from the probe (tank circuit) to the receiver.

By adding the crossed diodes to ground before the receiver, we guarantee the receiver will not see anything larger than 0.5 volts during transmitter pulsing. The transient pulse in an overcritically damped circuit will take 7 time constant to decay.

However, the cross-diodes only helps to protect the receiver from anything larger than 0.5 Volt, it does not reduces the ringdown time, which is determined by the transmitter circuit. Smart designs such as a Q spoiler has been used successfully to reduce the ringdown by drain off the oscillating current in an RLC circuit. As its name indicates, the Q spoiler works by reducing the circuit Q factor.

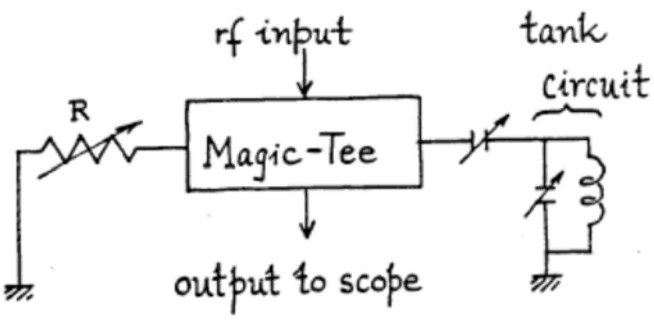


Figure 2.1. Magic T setup in NMR circuit. Adapted from Eiichi Fukushima and Stephen B.W. Roeder's Experimental Pulse NMR, A nuts and bolts approach.

Note that silicon diodes work well at lower frequency than 100 MHz. In complimentary, PIN diodes works well at frequency higher than 100 MHz. This is what I gathered from the classical book Experimental Pulse NMR, A nuts and bolts approach, which is pretty old now. There might be better devices now for this purpose.

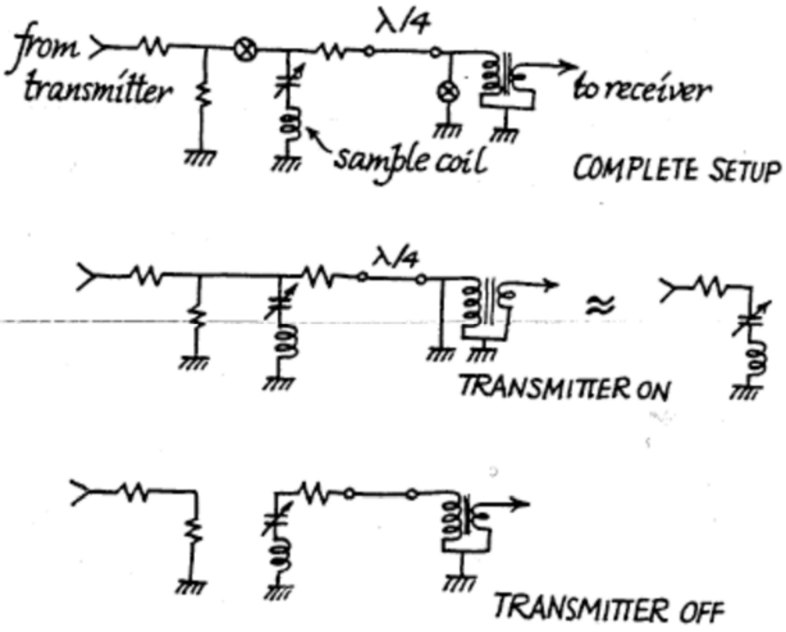


Figure 2.2. Use quarter wave cable to decouple transmitter and receiver in NMR circuit. Adapted from Eiichi Fukushima and Stephen B.W. Roeder's Experimental Pulse NMR, A nuts and bolts approach.

In addition to the crossed diodes, a Magic T or directional coupler (Fig. 2.1) can be used as duplexer to isolate transmitter and receiver. Cables of appropriate lengths are also used in single-coil probe, such as the quarter wave cable (Fig. 2.2), which can transform its input and output impedance according to equation:

$$|Z|^2 = Z_i Z_o \tag{2.4}$$

Where Z is the characteristic impedance of the cable(50, 75, or 300 Ohms normally), Z_i and Z_o are the input and output impedance at each end of the cable.

Please try to see if you can figure out why does the quarter wave cable have this impedance transformation property? Do you know how to calculate quarter wave cable length?

At 600MHz, the length L of the $\frac{\lambda}{4}$ cable =1/4x0.66x3x10^8 m/s x1/(6x10^8Hz)=8.25 cm,

Where 0.66 is the RF wave velocity factor compared to velocity of the wave (light) in vacuum. In RG-223/U, the speed factor is about 0.6. It depends on the dielectric materials of the cable.

However, the quarter wave cable also has its downside. It is not broadband, and works only for the selected frequency(±10%)/nuclei. Also, if your circuit impedance is different than that of the cable's, you need a different one. Thirdly, at low frequency(the $\frac{\lambda}{4}$ cable at 20 MHz is 2.475 m), the length of the cable can be very long. It is not convenient and can be lossy for our precious signal.

To circumvent these limitations, capacitors and inductors can be paired as L and the π circuit to do just the same with tunable frequency as impedance transformer. There are many popular websites that provides automatic calculation of all the parameters to construct a L or π circuit.

There are many interesting properties of transmission line, including the standing wave ratio, characteristic impedance of transmission line. You can find detailed instruction about these topics on many websites or openstack courses for electrical engineering major. An interesting thing we can explain is the impedance of free space.

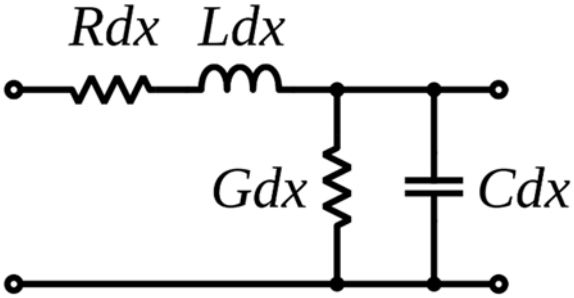


Figure 2.3.Schematic plot for the characteristic impedance of transmission line. Adapted from Wikipedia.

Here R, L, G, C are the per unit length value of resistance, inductance, conductance of dielectric and capacitance in transmission line. For example, a cable with 50 Ohm characteristic impedance has a capacitance of about 1pF/cm (30 pF/foot).

If j is imaginary unit and ω is the angular frequency of the RF wave, following the approach by Tim Healy (http://www.ee.scu.edu/eefac/healy/char.html), the characteristic impedance Z_0 of the transmission line is:

$$Z_0 = (R + j\omega L)dx + \frac{1}{(G+j\omega C)dx+\frac{1}{Z_0}};$$

$$Z_0 + Z_0^2(G + j\omega C)dx = (R + j\omega L)dx + Z_0(R + j\omega L)dx(G + j\omega C)dx + Z_0$$

Ignore the terms with two dx as they are higher order terms:

$$Z_0 + Z_0^2(G + j\omega C)dx = (R + j\omega L)dx + Z_0$$

We have the characteristic impedance of the transmission line as:

$$Z_0 = \pm\sqrt{\frac{R + j\omega L}{G + j\omega C}} \tag{2.5}$$

For ideal lossless transmission lines where R and G both =0,

$$Z_0 = \pm \sqrt{\frac{L}{C}} \tag{2.6}$$

Here we see that the characteristic impedance Z_0 does not depend on frequency.

If the load impedance matches the characteristic impedance, the transmitted wave will respond as if the cable is continuous to infinite length with the same impedance everywhere. The magnitude of the voltage and current along the line will be constant everywhere (with a phase factor). If the load impedance mismatches the characteristic impedance of a transmission line or waveguide, standing wave will be established by the reflected wave superimposing on the incident RF wave. The sanding wave ratio (SWR) is then a measure of the impedance mismatch, as the maximum and minimum AC voltage along the transmission line.

So how do you measure a quarter wave cable (besides you can calculate its length theoretically?) Imagine you leave one end of the cable open, hook its other end up with a frequency generator on one end, with a T and an oscilloscope. At the exact frequency matches the quarter wave length, the open end with it at the quarter wave frequency will have a $Z_o = \infty$. Therefore, the connected end will be just like a shunt, a short circuit, and you will see minimum resistance.

Another way to transform the impedance is shown below:

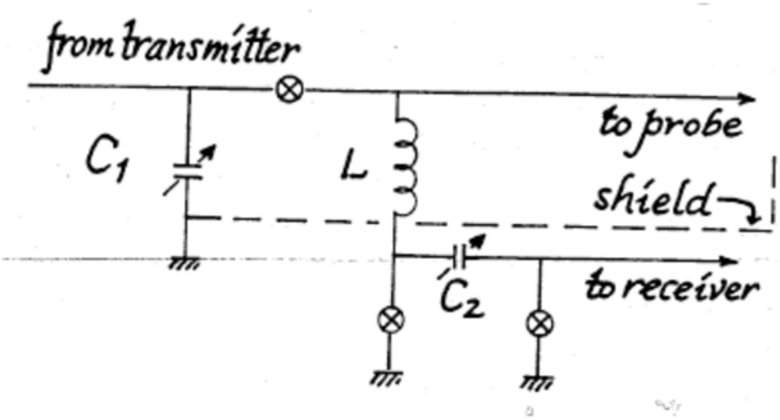


Figure 2.4. Impedance transformation using parallel and series LC circuit for Transmitter and Receiver side respectively. Figure adapted from Adapted from Eiichi Fukushima and Stephen B.W. Roeder's Experimental Pulse NMR, A nuts and bolts approach.

To understand this circuit, we need to first introduce the basic building blocks of RLC circuit: the RLC in series, and in parallel. All other circuits can be converted to combinations of these two basic blocks.

2.2 Simple probe introduction: RLC in series and in parallel circuit.

Owing to the frequency dependent characteristics of inductor L and capacitor C, a RLC in series will have its minimum resistance at resonance. This can be shown by sum the total frequency dependent impedance:

$$Z = R + j\omega L - \frac{j}{\omega C} \tag{2.7}$$

So the magnitude of the impedance is:

$$|Z| = \sqrt{R^2 + \left(\frac{1}{\omega C}\right)^2 (\omega^2 LC - 1)^2} \tag{2.8}$$

As you can see, at $\omega = \frac{1}{\sqrt{LC}}$, we reaches the resonance condition where the imaginary contribution is zero and $|Z|_{min} = R$. We will have largest current given a power source.

If you plot the frequency dependence of the impedance, you can show that $Q = \frac{\Delta f}{f_0}$, where Δf is the FWHM, representing the frequency selectivity of the circuit. In addition, can you show that the voltage across the coil is $V_{coil} = QV_{input}$, which means the voltage is amplified Q folds.

In comparison, when RLC are in parallel, at resonance, the impedance will be maximized. Let's look at the coil in parallel with a capacitor. The coil has inductance L and a small resistance r, and the capacitor has capacitance C. The total impedance is:

$$\frac{1}{Z} = \frac{1}{r + j\omega L} + j\omega C = \frac{(1 - \omega^2 LC) + j\omega rC}{r + j\omega L} \tag{2.9}$$

$$Z = \frac{r + j\omega L}{(1 - \omega^2 LC) + j\omega rC} = \frac{[r + j\omega L][(1 - \omega^2 LC) - j\omega rC]}{(1 - \omega^2 LC)^2 + (\omega rC)^2}$$

Let $A = (1 - \omega^2 LC)^2 + (\omega rC)^2$, we have:

$$Z = \frac{[r + j\omega L][(1 - \omega^2 LC) - j\omega rC]}{A} = real(Z) + j \cdot im(Z) \tag{2.10}$$

Where $real(Z) = \frac{r}{A}$; and

$$im(Z) = \frac{1}{A}(\omega L - \omega^3 L^2 C - \omega r^2 C)$$

At resonance, the imaginary part of the impedance should be zero:

$$\omega L - \omega^3 L^2 C - \omega r^2 C = 0$$

$$1 - \omega^2 LC - r^2 \frac{C}{L} = 0$$

Which gives us the condition at resonance:

$$\omega^2 LC = 1 - r^2 \frac{C}{L}$$

And

$$\omega^2 = \frac{1}{LC} - \frac{r^2}{L^2} \tag{2.11}$$

Here we recall the quality factor Q of the circuit(yes, it happens to be the same with the Q of RLC in series for the circuit with the resistor and inductor in series, and then together in parallel with the capacitor). However, if R, L, C are in parallel, then the Q expression is inversed, please see if you can prove it) is:

$$Q = \frac{\omega L}{r}$$

So the last condition at resonance is:

$$1 = \frac{1}{\omega^2 LC} - \frac{1}{Q^2}$$

Because the Q is normally quite big, from 50-500, so this means at resonance we can approximate

$$1 \cong \frac{1}{\omega^2 LC}$$

Which leads to the same resonance condition as RLC in series:

$$\omega = \frac{1}{\sqrt{LC}}$$

Put this resonance condition to A, we have:

$$A = (1 - \omega^2 LC)^2 + (\omega r C)^2 = (r^2 \frac{C}{L})^2 + (rC)^2 (\frac{1}{LC} - \frac{r^2}{L^2})$$

$$A = r^4 \frac{C^2}{L^2} + \frac{r^2 C}{L} - r^4 \frac{C^2}{L^2} = \frac{r^2 C}{L}$$

Recall that:

$$Q = \frac{\omega L}{r} = \frac{1}{r}\sqrt{\frac{L}{C}}$$

Hence we can pick the capacitance with a given coil and desired Q:

$$C = \frac{L}{Q^2 r^2}$$

$$A = \frac{r^2 C}{L} = \frac{1}{Q^2}$$

Hence at resonance, the pure resistive impedance is

$$real(Z) = \frac{r}{A} = Q^2 r \tag{2.12}$$

Normally the resistance of the coil is ~ 1 ohm, and Q is between 50-500. Therefore, the resistance of the parallel RLC tank is maximized at resonance condition.

Again, you can prove that $Q = \frac{\Delta f}{f_0}$. So the frequency selectivity of RLC in parallel stays the same as that of the RLC in series.

The total current of the circuit at resonance is:

$$I_t = \frac{V_{input}}{Q^2 r} \tag{2.13}$$

This is essentially saying the parallel RLC boosts the resistance of the circuit by a factor of Q^2, in comparison with the pure resistance of the coil. The current in the capacitor is:

$$I_c = \frac{V_{input}}{Z_c} = \frac{V_{input}}{1/\omega C} = \frac{V_{input}}{1/\sqrt{\frac{C}{L}}} = \frac{V_{input}}{Qr} \tag{2.14}$$

So we see that for the RLC in parallel, it is the current that gets amplified by Q. We can calculate the current through the RL branch:

$$I_{RL} = I_t - I_c = \frac{V_{input}}{Qr}(\frac{1-Q}{Q}) \tag{2.15}$$

So the current across the RL branch is opposing the direction of that through the capacitor, with nearly the same magnitude, since Q»1.

In real NMR probe, we often see series tuned and parallel matched or parallel tuned and series matched tank circuit. When the spectrometer frequency is selected to be slightly lower than the probe's resonance frequency where the parallel RLC's real part of impedance matches with the characteristic resonance Z of the circuit (normally 50 Ohm), the parallel RLC's imaginary part of impedance is positive (inductive), and then the probe adds another high quality capacitor to cancel this inductive residue and render the combined impedance purely real. This is called parallel tuned and series matched. As a homework, you can do the calculation by following the above given formulas:

$$Z_0 = real(Z) = \frac{r}{(1-\omega^2 LC)^2 + (\omega r C)^2} \tag{2.16}$$

The matching capacitor should then cancel the impedance:

$$\frac{1}{\omega C_M} = im(Z) = \frac{1}{(1-\omega^2 LC)^2 + (\omega rC)^2}(\omega L - \omega^3 L^2 C - \omega r^2 C) \tag{2.17}$$

Alternatively, we can use RLC in series to tune to the resonance frequency, and use another capacitor in parallel to match the impedance. This scheme is called series tuned and parallel matched.

BTW, why do we have to match the impedance of our tank circuit to transmitter and receiver? You can simply show that when a load has the same resistance with the source, maximum power will be delivered from the source to the load.

2.3 Balanced RLC circuit

Our NMR probe normally uses the same coil for multiple channels, so it means we have to design multiple resonances with the same set of coil and capacitors. Hence, parallel tuned LC and series tuned LC sets are incorporated as trap/shunt to help separate different channels, since they behave as infinite resistance like an open circuit and minimal resistance like a short circuit at their respective resonance conditions.

In addition, another common trick called balanced circuit is often used to reduce the voltage across the coil and the possibility of arching:

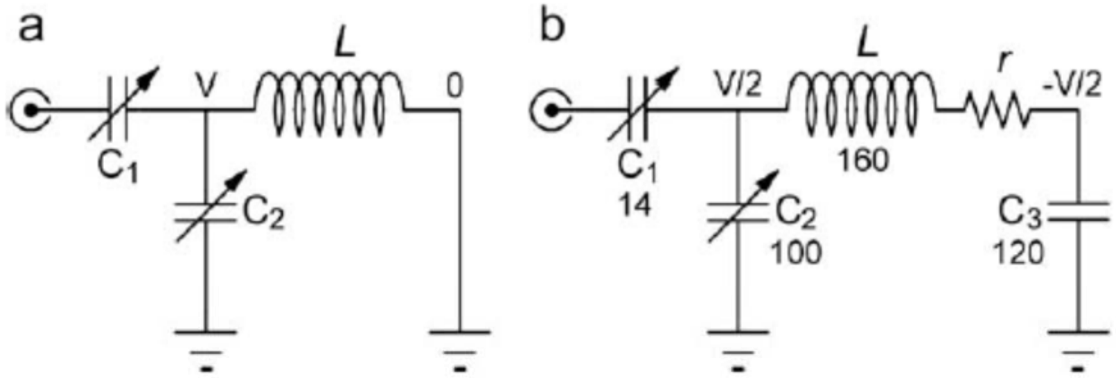


Fig. 1. (a) conventional and (b) voltage-balanced LC resonant circuit approaches for low-γ nuclei. The balanced circuit reduces the peak rf voltage from V to $V/2$. The shown values (pF and nH) are for a 4 mm MAS probe tuned to ^{25}Mg (50.8 MHz at 19.6 T) with $Q \approx 80$.

Figure 2.5.Comparison between conventional and voltage balanced LC resonant circuit. The shown values (pF and nF) are for a 4 mm MAS probe tuned to 25Mg 50.8 MHz at 19.6 T with Q ~ 80. the balanced circuit reduces the peak rf from ZH. Gan. et al. JMR 200, 2-5 (2009).

The scheme on the right of the figure is to insert C_3 to insure the mid-point of coil is virtually grounded.

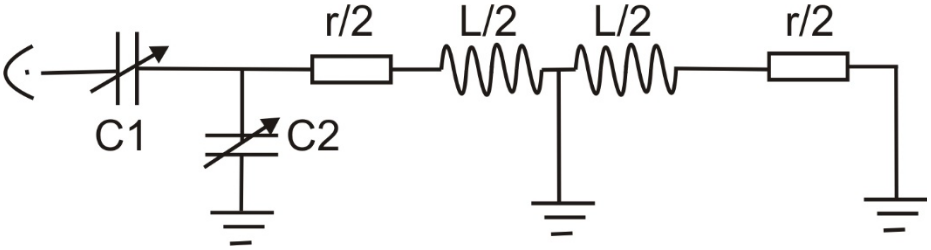


Figure 2.6. Equivalent circuit diagram to previous figure b.

Therefore the voltage across each half the coil will have equal magnitude but negative direction as that across C_3 at resonance:

$$\omega_0 L/2 = \frac{1}{\omega_0 C_3} \tag{2.18}$$

$$C_3 = \frac{2}{\omega_0^2 L} = \frac{2}{(2\pi \times 50.8 \times 10^6)^2 \times 160 \times 10^{-9}} = 123\, pF$$

Then to the left half of the circuit, the positive reactance from this half of the coil should cancel the combined negative reactance of C_1 and C_2. We can neglect the small resistance from the coil for now in the analysis or if we do proceed with rigorous analysis, it will be like this, and we have C_2 in parallel with half of the coil, then in series with C_1. The purpose of C_1 is to match the positive reactance from the parallel part. So the voltage due to reactance on the parallel part should be equal to the voltage on C_1. From our previous analysis of the parallel RLC circuit, we know that C_2 then should have a very close negative reactance (but still smaller) to the positive reactance of the left half of the coil, which means $\omega_0 L \sim \frac{1}{\omega_0 C_2}$.

$$-Z_{C1} = im(Z_{\frac{1}{2}Coil}) \tag{2.19}$$

$$-j\omega_0 C_1 = im(\frac{2}{j\omega_0 L + r} + \omega_0 C_2)$$

$$-j\omega_0 C_1 = im(\frac{2 - \omega_0^2 L C_2 + j\omega_0 C_2 r}{j\omega_0 L + r})$$

Here we will take some approximation. Since we know Q = $\frac{\omega_0 L}{r} \gg 1$, the bottom is $j\omega_0 L + r \sim j\omega_0 L$. The top $j\omega_0 C_2 r$ is roughly $jr/\omega_0 L \sim j/Q$, also much smaller than 2 or $\omega_0^2 L C_2$. Hence the above equation can be approximated by:

$$-j\omega_0 C_1 = im(\frac{2-\omega_0^2 LC_2}{j\omega_0 L})$$

$$\omega_0^2 LC_1 = 2-\omega_0^2 LC_2$$

$$\omega_0 L/2 = \frac{1}{\omega_0(C_1+C_2)} \tag{2.20}$$

If we had ignored the small resistance of the coil, we would have reached this conclusion sooner. Combined, at this stage we have:

$$C_3 = C_1 + C_2 \tag{2.21}$$
$$\omega_0 L/2 \sim \frac{1}{\omega_0 C_2}$$

Please note this is an approximation condition.

Now we just have to make sure the real part of impedance match 50 Ohm:

$$real\left(\frac{1}{\frac{1}{j\omega_0 L + r + 1/j\omega_0 C_3} + j\omega_0 C_2}\right) = 50 \tag{2.22}$$

$$real\left(\frac{1}{\frac{1}{j\omega_0 L/2 + r} + j\omega_0 C_2}\right) = 50$$

The inside is:

$$\frac{1}{\frac{2}{j\omega_0 L + 2r} + j\omega_0 C_2} = \frac{j\omega_0 L + 2r}{(2-\omega_0^2 LC_2) + 2j\omega_0 C_2 r}$$

$$\omega_0^2 LC_2 = \omega_0 L\omega_0 C_2 = \frac{2\omega_0 C_2}{\omega_0 C_3} = \frac{2C_2}{C_3}$$

$$\frac{j\omega_0 L + 2r}{(2-\omega_0^2 LC_2) + 2j\omega_0 C_2 r} = \frac{j\omega_0 L + 2r}{\left(2-\frac{2C_2}{C_3}\right) + 2j\omega_0 C_2 r} = \frac{j\omega_0 LC_3 + 2C_3 r}{(2C_3 - 2C_2) + 2j\omega_0 C_2 C_3 r}$$

recall the relation $\omega_0 L/2 = \frac{1}{\omega_0 C_3}$, and Q = $\frac{\omega_0 L}{r}$, the above equation can be turned into:

$$= \frac{j\omega_0 LC_3 + 2C_3 r}{2C_1 + 2jC_2\frac{2}{\omega_0 L}r} = \frac{jQrC_3 + 2C_3 r}{2C_1 + 4j\frac{C_2}{Q}}$$

Normalize:

$$\frac{(jQrC_3+2C_3r)\left(2C_1-4j\frac{C_2}{Q}\right)}{\left(2C_1+4j\frac{C_2}{Q}\right)\left(2C_1-4j\frac{C_2}{Q}\right)}=\frac{C_1C_3r+C_2C_3r}{C_1^2+4(\frac{C_2}{Q})^2}+j\frac{C_1C_3Qr-4\frac{C_2C_3r}{Q}}{2C_1^2+8(\frac{C_2}{Q})^2}$$

$$\frac{C_1C_3+C_2C_3}{(C_1)^2+(\frac{2}{Q}C_2)^2}r=50$$

The imaginary part should cancel with the reactance of C1:

$$\frac{C_1C_3Qr-4\frac{C_2C_3r}{Q}}{2C_1^2+8(\frac{C_2}{Q})^2}=\frac{1}{\omega_0C_1}$$

$$2C_1^2+8(\frac{C_2}{Q})^2=\omega_0C_3C_1^2Qr-4\frac{\omega_0C_3C_1C_2r}{Q}=\omega_0C_3C_1^2\omega_0L-4\frac{2}{\omega_0L}\frac{C_1C_2r}{Q}=2C_1^2-8\frac{C_1C_2}{Q^2}$$

Obviously this equation can’t be true. The approximation would be $2C_1^2 \gg 8(\frac{C_2}{Q})^2, 8\frac{C_1C_2}{Q^2}$.

In this problem as shown by the Fig. 2.5. The Q is ~ 80, so r can be estimated by $\frac{\omega_0L}{Q}=\frac{2\pi\times50.8\times10^6\times160\times10^{-9}}{80}=0.638372\ Ohm.$

$C_1^2 \gg \frac{C_2^2}{800}$, $C_1 \gg \frac{C_2}{1600}$, which gives us $C_1 \gg \frac{C_2}{28}$

This means the approximation condition C_3=C_1+C_2 is not compatible with the match and tune condition of the circuit at the same time.

We need to make some sacrifice. The priority is to satisfy tune and match first. Recall that our derivation of the parallel RLC. Our current circuit is essentially half of the coil’s inductance in parallel with C2 and then in series with C1, since the other half of the coil’s inductance is balanced by C3 to set the virtual ground at the middle of the coil, therefore, we can apply what we derived for parallel RLC. For a RLC circuit with coil’s inductance L paired in series with resistance r and then in parallel with a second capacitor C, the expression of impedance is given by Eq. 2.10:

$$Z=\frac{[r+j\omega L][(1-\omega^2LC)-j\omega rC]}{(1-\omega^2LC)^2+(\omega rC)^2}$$

Where

$$Z_0=50\ Ohm=real(Z)=\frac{r}{\left(1-\omega^2\frac{L}{2}C_2\right)^2+(\omega rC_2)^2}$$

$$im(Z)=\frac{\left(\omega\frac{L}{2}-\omega^3\frac{L^2}{4}C_2-\omega r^2C_2\right)}{\left(1-\omega^2\frac{L}{2}C_2\right)^2+(\omega rC_2)^2}=\frac{1}{\omega C_1}$$

Here we can replace the inductance with $\frac{L}{2}$ and C by C_2.

The real part of impedance needs to match to 50 Ohm, from which we can solve C_2:

$$\left(\omega^4\frac{L^2}{4}+\omega^2r^2\right)C_2^2-\omega^2LC_2+\left(1-\frac{r}{50}\right)=0$$

$$\left(\omega^4\frac{L^2}{4}+\omega^2r^2\right)C_2^2-\omega^2LC_2+(1-\frac{r}{50})=0$$

$$\omega^2r^2\left(\frac{\omega^2L^2}{4r^2}+1\right)C_2^2-\omega^2LC_2+(1-\frac{r}{50})=0$$

$$\omega^2r^2\left(\frac{1}{4}Q^2+1\right)C_2^2-\omega^2LC_2+(1-\frac{r}{50})=0$$

Apply the approximation that $Q\gg 1$,

$$\frac{1}{4}\omega^2r^2Q^2C_2^2-\omega^2LC_2+1-\frac{r}{50}=0$$

$$C_2=\frac{\omega^2L\pm\sqrt{\omega^4L^2-\omega^2r^2Q^2\left(1-\frac{r}{50}\right)}}{\frac{1}{2}\omega^2r^2Q^2}=\frac{\omega^2L\pm\sqrt{\omega^4L^2-\omega^2r^2\left(\frac{\omega L}{r}\right)^2\left(1-\frac{r}{50}\right)}}{\frac{1}{2}\omega^2r^2\left(\frac{\omega L}{r}\right)^2}$$

$$=\frac{\omega^2L\pm\sqrt{\omega^4L^2-\omega^4L^2(1-\frac{r}{50})}}{\frac{1}{2}\omega^4L^2}=\frac{\omega^2L\pm\sqrt{\omega^4L^2\frac{r}{50}}}{\frac{1}{2}\omega^4L^2}$$

$$C_2=\frac{2}{\omega^2L}(1\pm\sqrt{\frac{r}{50}})\tag{2.23}$$

Among the two solutions of C_2, the smaller one will give a total inductive impedance of the parallel circuit, while the larger solution will give a capacitive impedance. We will pick the smaller solution, since it will be matched by the capacitive impedance of capacitor C_1:

$$C_2 = \frac{2}{\omega^2 L}(1 - \sqrt{\frac{r}{50}})$$

$$C_2 = \frac{2}{(2\pi \times 50.8 \times 10^6)^2 \times 160 \times 10^{-9}}\left(1 - \sqrt{\frac{0.638}{50}}\right)$$

$$C_2 \cong 108.834\, pF$$

Recall C_3=123 pF calculated earlier, $C_1 = C_3 - C_2 = 14\, pF$.

Just hold on, we said the condition $C_1 + C_2 = C_3$ is an approximation. How can we use this to solve C_1?

Well, if you say so, we can try to solve the exact condition C_3 using the imaginary part of the impedance should be zero (matching condition):

$$im(Z) = \frac{\left(\omega \frac{L}{2} - \omega^3 \frac{L^2}{4} C_2 - \omega r^2 C_2\right)}{\left(1 - \omega^2 \frac{L}{2} C_2\right)^2 + (\omega r C_2)^2} = \frac{1}{\omega C_1}$$

$$\frac{\left(\omega \frac{L}{2} - \omega^3 \frac{L^2}{4} C_2 - \omega r^2 C_2\right)}{\frac{r}{50}} = \frac{1}{\omega C_1}$$

$$C_1 = \frac{r}{50} \frac{1}{(\omega^2 \frac{L}{2} - \omega^4 \frac{L^2}{4} C_2 - \omega^2 r^2 C_2)}$$

$$\omega C_2 = 2\pi \times 50.8 \times 10^6 \times 108.834 \times 10^{-12} = 0.347383\, Ohm$$

$$\omega \frac{L}{2} = 2\pi \times 50.8 \times 10^6 \times 80 \times 10^{-9} = 25.5349\, Ohm$$

$$\omega^2 \frac{L}{2} = 2\pi \times 50.8 \times 10^6 \times 25.5349 = 8.15 \times 10^9\, Ohm \cdot rad/s$$

$$C_1 = \frac{0.638}{50} \times \frac{1}{8.15 \times 10^9 - (8.15 \times 10^9)^2 \times 108.834 \times 10^{-12} - 0.347383^2 \times 0.638^2}$$

$$= \frac{0.638}{50} \times \frac{1}{8.15 \times 10^9 - 7.229 \times 10^9 - 0.04912} = \frac{0.638}{50 \times 9.21 \times 10^8}$$

$$C_1 = 13.8545\, pF$$

So you can see to match perfectly C_1 very close to the value to balance the circuit. In reality, we need to strike a compromise in between. We can check how much off matching if C_1 is taken as 14 pF.

$$\Delta Z_{C1} = \frac{1}{\omega C_1} - \frac{1}{\omega C_1'} = \frac{1}{2\pi \times 50.8 \times 10^6 \times 13.8545 \times 10^{-12}} - \frac{1}{2\pi \times 50.8 \times 10^6 \times 14 \times 10^{-12}}$$

$$= 2.35018 \text{ Ohm}$$

So this means we will have 2.35018 Ohm of reactance while the resistance is 50 Ohm. So roughly at this point due to the mismatch, we will have a SWR of $\sqrt{50^2 + 2.35^2}/50$=1.0011.

Without deriving the formula, the power loss ML_{dB} (in unit of dB) due to mismatched impedance is:

$$ML_{dB} = 10log_{10}(\frac{P_i}{P_d}) \tag{2.24}$$

Where P_i is the incident power, P_d is the delivered power:

$$\frac{P_d}{P_i} = 1 - |\rho|^2 \tag{2.25}$$

Where ρ is the reflection coefficient. It is a complex number, related to the load impedance Z_L and source impedance Z_s by:

$$\rho = \frac{Z_L - Z_s}{Z_L + Z_s} \tag{2.26}$$

So in our case:

$$\rho = \frac{50 + 2.35j - 50}{50 + 2.35j + 50} = \frac{2.35j}{100 + 2.35j} = j2.35 \times 10^{-2} + 5.5 \times 10^{-4}$$

So $|\rho|^2 \sim 5.5 \times 10^{-4}$

$$ML_{dB} = 10log_{10}\left(\frac{1}{1 - 5.5 \times 10^{-4}}\right) = 2.39 \times 10^{-3}\ dB$$

Or expressed in a more familiar manner for our tune and match curve:

$$MD_{dB} = 10log_{10}\left(\frac{P_d}{P_r}\right) = 32.59\ dB$$

In general, 20 dB dip in the tune and match curve is Ok:

$$MD_{dB} = 20 = 10log_{10}\left(\frac{P_d}{P_r}\right)$$

$$\frac{P_d}{P_r} = 100$$

Which means you will lose about 1% of power due to reflection. You can also see that a 15dB tune and match is sometimes thought as an acceptable condition, with about 3.2% power is lost.

The tune and match condition goes both ways. It not only determines the loss of power due to reflection during transmission, our minuscule NMR signal will also suffer such a proportional loss. So that is why it is essential to achieve tune and match condition as good as you can get.

Could you use the above knowledge to make some sense of the circuit for a two channel probe below?

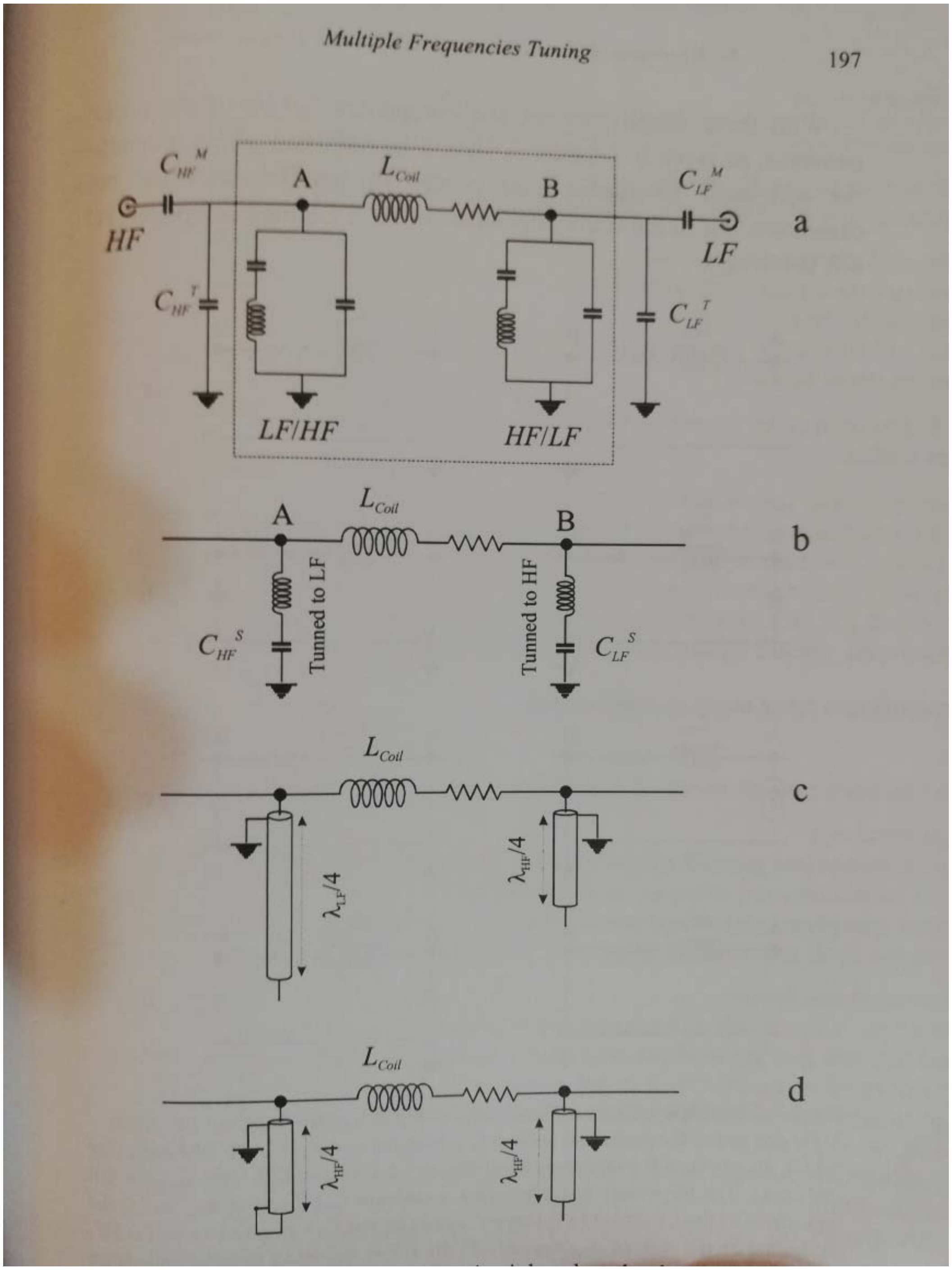


Figure 2.7.Double tuned probe circuit. Adapted from Fig. 6.6 of NMR Probeheads for Biophysical and Biomedical Experiments.

Chapter 3 Introduction to interactions between nucleus spin and RF pulse

By now, we can appreciate the ensemble of nucleus spins give rise to macroscopic magnetic moment as we shown in Chapter 1. Why would we use radio frequency (RF) pulses to excite NMR?

In this chapter, we will introduce some of the most frequently utilized skills in NMR: rotating frame transformation, in both classical and quantum mechanical perspective. It helps us visualize the motions of magnetization by removing the interference of Larmor frequency precessing. Detailed derivation will show the resonance offset effect, which will be one of the most common adversaries for many recoupling or decoupling sequence. Another common trick called tilted frame transformation will be introduced to simplify our discussion of the motion of magnetization in the presence of resonance offset. Following this, we will explain what is quadrature detection and how does it work. We will end this chapter with some qualitative discussion of relaxation phenomena.

3.1 Classical picture of rotating frame.

According to classical mechanics, the RF pulses in a solenoid coil will produce a magnetic field $\vec{H}_1 = 2H_1\overrightarrow{e_x}\cos\omega t$. We will see why I put 2 in the coefficient in a minute. Together with the external static magnetic field $\vec{H}_0$, they will produce a torque change the orientation of $\vec{\mu}$:

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma(H_0\overrightarrow{e_z} + 2H_1\,\overrightarrow{e_x}\cos\omega t) = \vec{\mu} \times \gamma\vec{H} \tag{3.1}$$

If we just have one static field $\vec{H}_0$, the interaction is very easy to visualize: $\vec{H}_0$ will produce a torque to rotate the magnetic moment $\vec{\mu}$ around $\vec{H}_0$. The frequency of rotation will be just the Larmor frequency $\omega_0 = -\gamma H_0$.

Now we have an additional alternating field produced by the alternating RF current in solenoid. The direction of external field is orthogonal to that of the alternating field. So the spins/magnetic moment is in fact rotated by the effective field $\vec{H}_{eff}$ combining $\vec{H}_0$ and $\vec{H}_1$, and process around this effective field. $\vec{H}_1$ field is oscillating as time goes by in the cosine function, which means its magnitude is oscillating and its direction is alternating between positive and negative x direction.

Well, this linearly alternating field can be decomposed into circular alternating field:

$$H_1\cos\omega t = \frac{1}{2}H_1(e^{i\omega t} + e^{-i\omega t}) \tag{3.2}$$

This way, we can exploit the trick in classical mechanics: if you have a vector $\vec{A}$ with constant magnitude that is rotating at frequency ω, then its time dependent variation is just $\omega \times \vec{A}$. Here we have two frequencies, one positive and one negative. Let's take the negative frequency, for which the direction of rotation is consistent with those nuclei with a positive gyromagnetic ratio γ. Let's see how this trick will help us, if we change our reference frame of observation to a frame whose z axis coincides with that of our lab frame, but x and y axis are rotating at $\vec{\omega} = -\gamma\vec{H}_0$, then the magnetic field is $\vec{H}_0$ along z, and $\vec{H}_1$ field is static with respect to x axis of this rotating frame of reference. Assume $\vec{\imath}, \vec{\jmath}, \vec{k}$ are the unit vector along x, y, and z direction in this rotating frame. Our goal is to understand how $\vec{\mu}$ moves. In maths, it is to solve:

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma H = \frac{\partial \mu_x}{\partial t}\vec{\imath} + \frac{\partial \mu_y}{\partial t}\vec{\jmath} + \frac{\partial \mu_k}{\partial t}\vec{k} + \left(\mu_x \frac{\partial i}{\partial t} + \mu_y \frac{\partial j}{\partial t} + \mu_k \frac{\partial k}{\partial t}\right) \tag{3.3}$$
$$= \frac{\partial \vec{\mu}}{\partial t} + \vec{\omega} \times \vec{\mu}$$

$\frac{\partial \mu}{\partial t}$ will be the time dependence of the magnetic moment in this new rotating frame. The new time dependence of magnetic moment $\vec{\mu}$ shall assume a simpler form, as $\frac{\partial i}{\partial t} = -\gamma \vec{H}_0 \times i$; $\frac{\partial j}{\partial t}$=$-\gamma \vec{H}_0 \times j$; $\frac{\partial k}{\partial t}$=0.

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \vec{H} = \frac{\partial \mu}{\partial t} + \vec{\omega} \times \vec{\mu}$$

$$\frac{\partial \mu}{\partial t} = \vec{\mu} \times \gamma \vec{H} - \vec{\omega} \times \vec{\mu} = \vec{\mu} \times \gamma \vec{H} + \vec{\mu} \times \vec{\omega} = \vec{\mu} \times (\gamma \vec{H} + \vec{\omega})$$

Therefore, the motion of magnetic moment $\vec{\mu}$ in the rotating frame obeys the same format, except that we need to replace the magnetic field in static lab frame with the field plus the frequency of rotation:

$$\frac{\partial \mu}{\partial t} = \vec{\mu} \times \left[\gamma\left(H_0 \vec{k} + H_1 \vec{\imath}\right) + \omega \vec{k}\right] = \vec{\mu} \times [(\gamma H_0 + \omega)\vec{k} + \gamma H_1 \vec{\imath}] \tag{3.4}$$

If the frequency of the rotating from equals to that of the nuclear Larmor frequency $\omega = -\gamma H_0$:

$$\frac{\partial \mu}{\partial t} = \vec{\mu} \times \gamma H_1 \vec{\imath} \tag{3.5}$$

So after transforming into the rotating frame, things become much simpler: we only have one “static” $\vec{H}_1$ field. It will induce a torque to rotate the magnetic moment and precess with a frequency $\omega_1 = \gamma H_1$.

What this is? Discuss how magnetic moment moves in the rotating frame at the resonance condition. This is the angular frequency of magnetic moment to follow pulses we apply. We have used this to calculate so called $\pi / \frac{\pi}{2}$ pulses length $\theta = \gamma H_1 t_p$.

To sum it up, we originally have the magnetic field as a sum of external magnetic field along z direction and alternating field $\vec{H}_1$ along x direction at frequency of the RF currents. If the RF frequency equals to the Larmor frequency, the magnetic moment will be rotated from z direction following the $\vec{H}_1$ field. If the frequency doesn’t match, then we don’t have this coherent motion.

You may ask what happens to the other circular polarized component of the $\vec{H}_1$ with positive $\vec{\omega}_0 = \gamma \vec{H}_0$? It is far away from resonance, but does contribute to a higher order term named Bloch-Siegert shift $\sim \frac{\omega_1^2}{\omega_0}$, normally negligible in most NMR experiments.

3.2 Quantum mechanical picture of rotating frame:

From the quantum mechanical perspective, we need to define the system Hamiltonian first:

$$\widehat{H} = -\vec{\mu} \cdot [H_0\overrightarrow{e_z} + H_1\,(\overrightarrow{e_x}\cos\omega t + \overrightarrow{e_y}\sin\omega t)]$$

$$= -\gamma(I_x\overrightarrow{e_x} + I_y\overrightarrow{e_y} + \overrightarrow{I_z e_z}) \cdot [H_0\overrightarrow{e_z} + H_1\,(\overrightarrow{e_x}\cos\omega t + \overrightarrow{e_y}\sin\omega t]$$

$$= -\gamma H_1(I_x\cos\omega t + I_y\sin\omega t) - \gamma H_0 I_z$$

$$\widehat{H} = -\gamma H_1 e^{-iI_z\omega t} I_x e^{-iI_z\omega t} - \gamma H_0 I_z \qquad (3.6)$$

Here we used the formulus:

$$e^{-iI_z\omega t} I_x e^{-iI_z\omega t} = I_x\cos\omega t + I_y\sin\omega t \qquad (3.7)$$

The motion of the state $|\psi\rangle$ is determined by the Schrodinger's equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = H|\psi\rangle \qquad (3.8)$$

$$= (-\gamma H_1 e^{-iI_z\omega t} I_x e^{iI_z\omega t} - \gamma H_0 I_z)\,|\psi\rangle$$

Now if we replace the state $|\psi\rangle = e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle$:

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = i\hbar\frac{\partial}{\partial t}\left(e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi''\rangle\right) = i\hbar\left[\frac{\partial}{\partial t}\left(e^{i\frac{\gamma H_0 I_z}{\hbar}t}\right)|\psi'\rangle + e^{i\frac{\gamma H_0 I_z}{\hbar}t}\frac{\partial}{\partial t}|\psi'\rangle\right]$$

$$= i\hbar\left[i\frac{\gamma H_0 I_z}{\hbar}e^{-i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle + e^{i\frac{\gamma H_0 I_z}{\hbar}t}\frac{\partial}{\partial t}|\psi'\rangle\right] = -\gamma H_0 I_z e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle + e^{i\frac{\gamma H_0 I_z}{\hbar}t}\frac{\partial}{\partial t}|\psi'\rangle$$

The right side of Eq. 3.8 will be:

$$H|\psi\rangle = \left(-\gamma H_1 e^{-iI_z\omega t} I_x e^{iI_z\omega t} - \gamma H_0 I_z\right)e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle$$

$$= -\gamma H_1 e^{-iI_z\omega t} I_x e^{\left[iI_z t\left(\omega + \frac{\gamma H_0}{\hbar}\right)\right]}|\psi'\rangle - \gamma H_0 I_z\, e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle$$

Therefore,

$$-\gamma H_0 I_z e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle + e^{i\frac{\gamma H_0 I_z}{\hbar}t}\frac{\partial}{\partial t}|\psi'\rangle$$

$$= -\gamma H_1 e^{-iI_z\omega t} I_x e^{\left[iI_z t\left(\omega + \frac{\gamma H_0}{\hbar}\right)\right]}|\psi''\rangle - \gamma H_0 I_z\, e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle$$

$$e^{i\frac{\gamma H_0 I_z}{\hbar}t}\frac{\partial}{\partial t}|\psi'\rangle = -\gamma H_1 e^{-iI_z\omega t} I_x e^{[iI_z t(\omega + \gamma H_0/\hbar)]} e^{i\frac{\gamma H_0 I_z}{\hbar}t}|\psi'\rangle$$

If we multiply both side from the left with $e^{-i\frac{\gamma H_0 I_z}{\hbar}t}$:

$$\frac{\partial}{\partial t}|\psi'\rangle = -\gamma H_1 e^{-i\frac{\gamma H_0 I_z}{\hbar}t} e^{-iI_z\omega t} I_x e^{[iI_z t(\omega + \gamma H_0/\hbar)]}|\psi'\rangle$$

$$\frac{\partial}{\partial t}|\psi'\rangle = -\gamma H_1 e^{-[iI_z t(\omega+\gamma H_0/\hbar)]} I_x e^{[iI_z t(\omega+\gamma H_0/\hbar)]}|\psi'\rangle$$

So now if the frequency is chosen as the Larmor frequency $\omega = -\gamma H_0/\hbar$, we have:

$$\frac{\partial}{\partial t}|\psi'\rangle = -\gamma H_1 I_x|\psi'\rangle \tag{3.9}$$

It means the new Hamiltonian $\hat{H}' = -\gamma H_1 I_x$. It eliminates the field along z direction. This agrees with the transformation in the classical picture.

The motion of magnetic moment then is described by density matrix, which will be introduced in Chapter 4:

$$\rho(t) = U(t)\rho(0)U^{-1}(t) = e^{-i\frac{\hat{H}}{\hbar}t}\rho(0)e^{i\frac{\hat{H}}{\hbar}t} = e^{i\gamma H_1 I_x t}\rho(0)e^{-i\gamma H_1 I_x t} \tag{3.10}$$

If we have $\gamma H_1 = \omega_1$; and from Eq. 1.12 in Chapter 1, the initial condition

$$\rho(0) = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT}H_0 I_z = CH_0 I_z$$

Hence:

$$\rho(t) = e^{i\omega_1 I_x t}CH_0 I_z e^{-i\omega_1 I_x t} = CH_0(I_z\cos\theta + I_y\sin\theta) \tag{3.11}$$

Afterwards, the change of magnetization in the coil will induce an emf, which gives us the detected NMR signal.

Right after the pulse, if there is no interactions between nucleus and other factors, after a $\frac{\pi}{2}$ pulse, we have the magnetic moment aligning with the y axis in the rotating frame, with no magnetization along x axis in the rotating frame. The magnetization after the pulse will precess around the H_0 along z axis for ever. However, the interaction with environments (relaxation) will have the condition spoiled. Some nuclei will have slightly lower or higher Larmor frequency, and their superposition will decoherently add up, which give rise to the decay of NMR signal in transverse plane and at the same time return the magnetization to z axis.

3.3 Resonance offset, effective field and tilted frame of reference

What if the z direction H_0 field has a bit of offset?

In classic picture, this is described by:

$$\frac{\partial\mu}{\partial t} = \vec{\mu}\times\left[(\gamma H_0+\omega)\vec{k}+\gamma H_1\vec{\imath}\right] = \vec{\mu}\times(\Delta\omega\vec{k}+\gamma H_1\vec{\imath}) \tag{3.12}$$

In quantum mechanics, the Hamiltonian in the rotating frame is:

$$\hat{H}' = -\Delta\omega I_z - \gamma H_1 I_x \tag{3.13}$$

Just to recap, this so called rotating frame transformation is to multiple the original Hamiltonian in the lab frame with:

$$\widehat{H'} = \exp(i\,\widehat{H_0}t)\hat{H}\exp(-i\,\widehat{H_0}t) \tag{3.14}$$

Where $\widehat{H_0} = -\,\gamma H_0 I_z$.

This off resonance effect can be simplified by a similar transformation with another common transformation called the tilted frame transformation. The goal is to replace the two orthogonal fields by a single field along the effective field direction. The new Hamiltonian in the tilted frame of reference is:

$$\widehat{H_t} = \exp\left(i\,I_y\theta\right)\hat{H}\exp\left(-i\,I_y\theta\right) \tag{3.15}$$

Where $\tan\theta = \frac{\gamma H_1}{\Delta\omega}$. Apply Eq. 3.15 to Eq. 3.13:

$$\widehat{H_t} = \exp\left(i\,I_y\theta\right)(-\Delta\omega I_z - \gamma H_1 I_x)\exp\left(-i\,I_y\theta\right) \tag{3.16}$$

$$= -\Delta\omega\exp\left(i\,I_y\theta\right)I_z\exp\left(-i\,I_y\theta\right) - \gamma H_1\exp\left(i\,I_y\theta\right)I_x\exp\left(-i\,I_y\theta\right)$$

$$= -\Delta\omega(I_z\cos\theta - I_x\sin\theta) - \gamma H_1(I_x\cos\theta + I_z\sin\theta)$$

Now we combine the coefficients for operators:

$$\widehat{H_t} = I_z(-\Delta\omega\cos\theta - \gamma H_1\sin\theta) + I_x(\Delta\,\omega\sin\theta - \gamma H_1\cos\theta)$$

Since $\tan\theta = \frac{\gamma H_1}{\Delta\omega}$, $\sin\theta = \frac{\gamma H_1}{\sqrt{\Delta\omega^2 + (\gamma H_1)^2}} = \frac{\gamma H_1}{\gamma H_e}$; $\cos\theta = \frac{\Delta\omega}{\sqrt{\Delta\omega^2 + (\gamma H_1)^2}} = \frac{\Delta\omega}{\gamma H_e}$, where

$H_e = \sqrt{(\frac{\Delta\omega}{\gamma})^2 + (\gamma H_1)^2}$ is the magnitude of the effective field in the rotating frame.

Therefore:

$$\Delta\,\omega\sin\theta - \gamma H_1\cos\theta = \Delta\omega\frac{\gamma H_1}{\gamma H_e} - \gamma H_1\frac{\Delta\omega}{\gamma H_e} = 0 \tag{3.17}$$

The Hamiltonian in the tilted frame of reference contains just a single term

$$\widehat{H_t} = I_z(-\Delta\omega\cos\theta - \gamma H_1\sin\theta) = -(\Delta\omega\cos\theta + \gamma H_1\sin\theta)I_z = -(\frac{(\Delta\omega)^2}{\gamma H_e} + \frac{(\gamma H_1)^2}{\gamma H_e})I_z$$

$$\widehat{H_t} = -\gamma\sqrt{\left(\frac{\Delta\omega}{\gamma}\right)^2 + (H_1)^2 I_z} = -\gamma H_e I_z \tag{3.18}$$

This matches exactly with the classical picture. Therefore, the above derivation justifies the vector picture to visualize the motion of magnetic moment. This transformation will be used to understand cross polarization with static sample in Sect. 4.12 and sample at magic angle spinning condition.

3.4 Quadruture detection

Well, when $\Delta\omega = 0$, the motion of magnetic moment is easy to visualize. The magnetic moment projection in the rotating frame will be just $M_t = M_0\vec{j}\sin\theta$, where $\theta = \gamma H_1 t_p$ is the tip angle of the pulse. There will be no magnetization along the x axis direction in the rotating frame. But in real NMR experiments, normally there are more than one carbon/nitrogen of interests with different resonance frequencies, we can't set our spectrometer frequency to match all sites simultaneously. So resonance offset effect is inevitable, and is a strong limiting factor for many recoupling and decoupling pulse sequences. So what is the consequence of the resonance offset? Let's use the classical picture to derive it first.

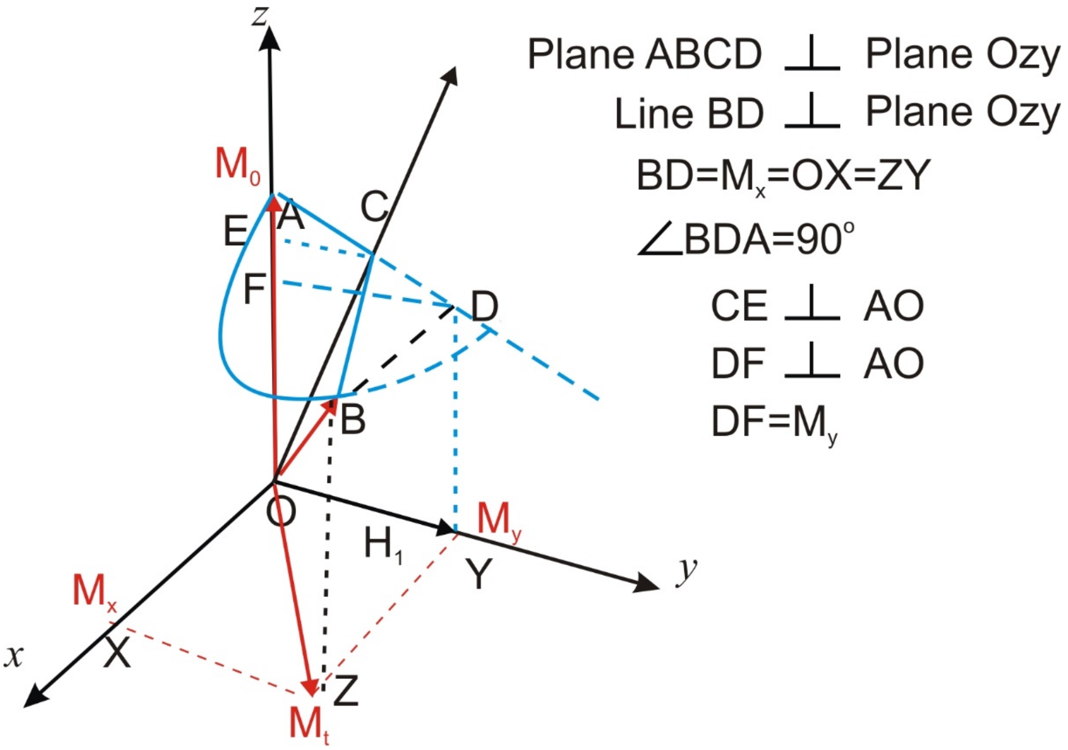


Figure 3.1. Classical picture of resonance offset effect.

Assume we are done with transformation to rotation frame. H_1 field aligns along the y axis. In addition, there is an H_{off} along z axis due to the resonance offset. The angle of the combined effective field with respect to the z axis can be described by:

$$\tan\theta = \frac{H_1}{H_{off}} = \frac{H_1}{\left|H_0 - \frac{\omega}{\gamma}\right|} = \frac{1}{x} \tag{3.19}$$

$$\sin\theta = \frac{1}{\sqrt{1 + x^2}} \tag{3.20}$$

Then in contrast to the on resonance situation where the magnetization aligned along the z axis, instead of precessing around H_1 field, it now precesses around the combined effective field $H_{eff} = \sqrt{H_1^2 + (H_0 - \frac{\omega}{\gamma})^2}$. After time t, the angle of precessing is:

$$\phi = \gamma H_{eff} t_p$$

Let's call

$$\phi_0 = \gamma H_1 t_p$$

Then we have:

$$\phi = \phi_0 \frac{H_{eff}}{H_1} = \phi_0 \sqrt{1 + x^2}$$

Let's trace the plane of nutation of the tip of the magnetization M_0, which starts at point A long z axis, the center of the nutation trajectory plane formed by the tip of M_0 is pointing C along the effective field direction along OC line(please remember OC line is in the plane of Ozy axes). If M_0 precesses an angle π, it will ends at some point in the Ozy plane, and this point should at the extrapolation line of AC and form a perfect half circle. At some arbitrary time t_p, the magnetization arrives at point B. Then $\phi = \angle ACB$. The projection of B to the plane Oxy is at point Z, which is the transverse magnetization M_t, and M_t's projection onto x and y axis are M_x and M_y at point X along x axis and point Y along y axis, respectively.

We can immediately see now that we should have a reading of magnetization along both x and y axis, instead of a pure M_x in the absence of resonance offset.

What is M_x and M_y?

In the plane of the half circle tracing the nutation trajectory of M_0, draw a line starting from point B, perpendicular to line AC, it crosses the extrapolation of AC at point D. The BD line is the distance of B to the plane Oyz, which means BD is equal to M_x.

Why?

Obviously, $BD \perp AC$. Also, line $OC \perp Oyz\ plane$, so $OC \perp BD$. Since BD is perpendicular to two non parallel lines in the plane Oyz, BD is perpendicular to the plane Oyz, which equals to M_x.

$$M_x = BD = BC \sin \angle BCD = BC \sin \angle ACB \qquad (3.21)$$
$$M_x = BC \sin \phi = BC \sin(\phi_0 \sqrt{1 + x^2})$$

Now we just have to find out what is BC?

Since AO $= M_0$, $\angle AOB = \theta$, $BC = AC = AO \sin \theta = M_0 \sin \theta = \frac{M_0}{\sqrt{1+x^2}}$

Therefore,

$$M_x = \frac{M_0}{\sqrt{1+x^2}} \sin(\phi_0 \sqrt{1+x^2}) \tag{3.22}$$

We can see that as long as tip angle ϕ_0 is not zero or multiples of π, and x is not zero(resonance offset is not zero), we are very likely to get a nonzero reading along x axis in the rotating frame.

How about the axis reading M_y? Surely it is no longer zero. By definition M_y is the distance of a point to Oxz plane. Now we have the projection of B in plane Oyz as D in the Oyz plane. So if we draw a line $FD \perp AO$ (which is the z axis), FD is equivalent to M_y,

$$M_y = FD = AD \sin \angle OAD \tag{3.23}$$

$$\angle OAD = \frac{\pi}{2} - \theta$$

$$M_y = FD = AD \cos\theta = AD \frac{x}{\sqrt{1+x^2}} = (AC + CD) \frac{x}{\sqrt{1+x^2}}$$

Since we know $AC = AO \sin\theta = M_0 \sin\theta$

$$CD = BC \cos \angle BCD = BC \cos(\pi - \angle ACB) = BC \cos(\pi - \phi) = BC \cos\left(\pi - \phi_0 \sqrt{1+x^2}\right)$$

In addition, $BC = AC = AO \sin\theta = M_0 \sin\theta$,

$$M_y = M_0 \frac{x}{\sqrt{1+x^2}} \left(1 + \cos\left(\pi - \phi_0 \sqrt{1+x^2}\right)\right)$$

Now apply half angle formula $2\cos^2\frac{\varphi}{2} = 1 + \cos\varphi$, so:

$$1 + \cos\left(\pi - \phi_0 \sqrt{1+x^2}\right) = 2\cos^2 \frac{\pi - \phi_0 \sqrt{1+x^2}}{2} = 2\sin^2 \frac{\phi_0 \sqrt{1+x^2}}{2}$$

Which gives us:

$$M_y = M_0 \frac{2x}{\sqrt{1+x^2}} \sin^2 \frac{\phi_0 \sqrt{1+x^2}}{2} \tag{3.24}$$

So in summary, with the standard tip angle we calibrated for on resonance pulse along y axis:

$$\phi_0 = \gamma H_1 t_p$$

For offset $\left|H_0 - \frac{\omega}{\gamma}\right| = xH_1$, we will observe signal along both x and y axis in the rotating frame:

$$M_x = \frac{M_0}{\sqrt{1+x^2}} \sin(\phi_0 \sqrt{1+x^2})$$

$$M_y = M_0 \frac{2x}{\sqrt{1+x^2}} \sin^2(\frac{\phi_0\sqrt{1+x^2}}{2})$$

Recall that we calculated the H_1 field for a $\frac{\pi}{2}$ pulse of 4 μs on the carbon channel is about 58 G. At a 600MHz (14.1 T field) spectrometer, assume that we set the carrier frequency at 90 ppm. The offset $\left|H_0 - \frac{\omega}{\gamma}\right|$ is about 90 ppm size, which is 12.7G. So $x = \frac{12.7}{58} = 0.219$. Assume that we have $\phi_0 = \frac{\pi}{2}$ along y axis for on resonance condition, the signal at 90 ppm away from the resonance will

$$\frac{M_x}{M_0} = \frac{1}{1.02369} \sin(\frac{\pi}{2} \times 1.02369) = 0.976$$

$$\frac{M_y}{M_0} = \frac{2 \times 0.219}{1.02369} \sin^2(\frac{\pi}{4} \times 1.02369) = 0.221856$$

M_x and M_y are normally called absorption and dispersion signal. The angle between M_x and M_y is roughly linear to x. This is why we can apply a first order phase correction in FT spectrum over the range. Another source of the first order phase correction is the dead time between transmitter and receiver. As the phase shift theorem of FT, the delay in the start of detection introduces the phase linear to the frequency:

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t}\, dt \tag{3.25}$$

$$\int_{-\infty}^{\infty} f(t-a) e^{-i\omega t}\, dt = \int_{-\infty}^{\infty} f(t') e^{-i\omega t'} e^{-i\omega a}\, d(t-a) = e^{-i\omega a} F(\omega) \tag{3.26}$$

It is of great importance that we can detect both x and y component of magnetization in the transverse plane.

First of all, it helps to distinguish the sense of precessing (the offset relative to the chosen carrier frequency), is it positive or negative?

If only M_x or M_y is detected, we can't figure out if the nutation of magnetization is faster or slower than the rotating frame frequency. In experiment, it is equivalent to the aliasing in pulse NMR. Historically, this problem is resolved by intentionally setting the carrier frequency higher or lower than the lowest or highest component of the spectrum, and use only half of the bandwidth to record the signal. So the complete spectrum occupies only half of the bandwidth. This wastes the transmitter power for excitation, and makes irradiation of any small range of the spectrum more difficult. The total admitted noise is actually doubled since the Johnson noise is linear to the bandwidth, as shown by Eq. 1.18 in Chapter 1. Hence quadrature detection is adopted.

Now due to the off-resonance effect, the calibrated $\frac{\pi}{2}$ pulse for on resonance conditions applied at 90 ppm will not only get you nearly all signal along x for CO site, but also some significant nonzero value along y. What is the consequence in our application? How about the acquisition method State we use to select x and y component for indirect dimension?

But first, how do we detect both x and y axis in rotating frame, with just one solenoidal coil?

Imagine the signal is a sinusoidal signal:

$$V_s = V_0 \sin(\omega_s t + \phi_s) \tag{3.27}$$

We will mix it with a sinusoidal reference signal:

$$V_s = V_0 \sin(\omega_s t + \phi_s)\, V_f \sin(\omega_r t + \phi_r)$$

$$V_s = \frac{V_0 V_f}{2}\cos((\omega_s + \omega_r)t + \phi_s + \phi_r) - \frac{V_0 V_f}{2}\cos((\omega_s - \omega_r)t + \phi_s - \phi_r) \tag{3.28}$$

We normally pick the frequency of reference to be close to that of signal, so $(\omega_s + \omega_r)$ will be way way higher than the frequency of interest, and the first term will be filtered out by the low pass filter in the circuit. In contrast, the second term will have its frequency $(\omega_s - \omega_r) \sim 0$, as a slow modulation of wave-package, and detected by phase sensitive detector.

Now let's mix the same signal with a reference that is $\frac{\pi}{2}$ out of phase of previous reference $V_f \sin(\omega_r t + \phi_r)$, which is:

$$V_f \sin\left(\omega_r t + \frac{\pi}{2} + \phi_r\right) = V_f \cos(\omega_r t + \phi_r) \tag{3.29}$$

Then after mixing we have:

$$V_s = V_0 \sin(\omega_s t + \phi_s)\, V_f \cos(\omega_r t + \phi_r)$$

$$V_s = \frac{V_0 V_f}{2}\sin((\omega_s + \omega_r)t + \phi_s + \phi_r) + \frac{V_0 V_f}{2}\sin((\omega_s - \omega_r)t + \phi_s - \phi_r) \tag{3.30}$$

Again the first term exhibit too high a frequency and will be removed by our low pass filter. The second term will be recorded. As you can see, it is $\frac{\pi}{2}$ out of phase relative to the first mixing result. Combined, they gave us quadrature detection of both M_x and M_y components in the rotating frame simultaneously. It essentially boosts the SNR by $\sqrt{2}$. Hence we lose this SNR boost in each of the indirect dimension acquiring multidimensional spectra. By locking the phase difference with respect to the known reference signal, the sensitivity can be enhanced as well, this is the basic principle of so called PHASE SENSITIVE DETECTOR.

3.5 Simple introduction of relaxation

This section heavily quotes or repeats contents from Experimental Pulse NMR A nuts and Bolts Approach by Eiichi Fukushima and Stephen Roeder. You should expand your reading if you have access to this book.

So we know now how to visualize an ensemble of non interacting spins behave in $\vec{H}_0$ and also follow their motion in the presence of an alternating field $\vec{H}_1$ at Larmor frequency. Now we have to consider, if we applied an on resonance $\frac{\pi}{2}$ pulse along the y axis in the rotating frame, what happens after the pulse is off? If there is no dissipation, we will have all the spins aligned along the y axis, and rotate together in phase around z axis, for ever. This will induce an ever lasting emf signal in our NMR solenoid coil.

But the reality is, our NMR signal decays very fast, which is called free induction decay. The decay of the signal is attributed to two processes, the spin lattice relaxation with characteristic time T_1, and spin-spin relaxation with characteristic time T_2.

The spin lattice relaxation is the process where the magnetization gradually returns back to the original $\vec{H}_0$ direction, after perturbation. The corresponding time of this process is called T_1.

To know why and how spin lattice relaxation process arises, we have to think from the microscopic perspective. Originally when the spins are aligned along the $\vec{H}_0$ direction at thermal equilibrium, as we derived in the previous chapter, the macroscopic magnetization comes from the inequivalent distribution of spin up $|\alpha\rangle$ and down state $|\beta\rangle$. Because of the Maxwell Boltzmann distribution, more spins will align along the $\vec{H}_0$ direction than antiparallel. We note that the system exists in the eigenstates of spin I_z at thermal equilibrium, as the system Hamiltonian is $\hat{H}_0 = -\vec{\mu} \cdot \vec{H}_0 = -\gamma H_0 I_z = -\omega_0 I_z$. When the magnetization is tipped into the transverse plan by the $\frac{\pi}{2}$ pulse, no macroscopic magnetization projection along the z direction anymore. Quantum mechanically, it means the $\frac{\pi}{2}$ pulse induces transition between the eigenstates of I_z, which is easy to understand, since the pulse corresponds to a perturbation Hamiltonian $\hat{H}_1 = -2\gamma H_1 I_y \cos \omega_0 t$. After transformed into rotating frame, $\hat{H}_1 = -\gamma H_1 I_y$. I_y does not commute with the Zeeman interaction Hamiltonian $-\gamma H_0 I_z$, so it will induce transitions between the original eigenstates of I_z, and perturb the equilibrium population distribution according to the Fermi's golden rule $\frac{2\pi}{\hbar}\left|\langle\alpha|\hat{H}_1|\beta\rangle\right|^2$. The persistent result of this $\hat{H}_1$ will lead to equal spins parallel and antiparallel to the $\vec{H}_0$ field.

After the pulse is turned off, the extra number of spins at the higher energy states needs to relax back to the lower energy states. There are two ways for this to happen, spontaneous emission or stimulated emission. If by spontaneous emission, the probability is proportional to ω_0^3. At the NMR frequency, this is too small and will give too long a T_1 compared to experimental observation. The source of actual spin lattice relaxation is dominated by stimulated emission.

What is the stimulation, then? Basically, anything interacting with nuclei to produce a transverse field at the Larmor frequency will do, just like our artificial excitation pulse. There are two sources, one is the fluctuating magnetic fields that interact with the dipolar moment of nuclei spins. The other is the electric field gradient (EFG) that can interact with the electric quadrupole moment of the nuclei. Since in protein NMR we mostly work with spin ½ nuclei with no quadrupolar moment, we will not discuss the second source here.

Before we go further about the details of the spin lattice relaxation, we will take a brief look at the spin spin relaxation. It describes the gradual decay of NMR signals in the transverse plane. Of course, the spin lattice relaxation will also contribute to the decay of transverse signal. It implies that all those mechanisms contributing to the spin lattice relaxation will also induce spin spin relaxation. The decay of transverse magnetization will have additional contribution. Intuitively, we can imagine that variations of local magnetic fields lead to variations of precessing frequencies of different spins. Some will precess faster while some precess slower. Thus their projection onto the x and y axis in the rotating frame will decrease due to the loss of coherence, and give rise to the decay of transverse signal. But this decoherence won't change the projection along z axis, and won't affect the spin lattice relaxation. So T_2 is usually shorter than T_1.

The common mechanism behind both relaxation is the fluctuating magnetic fields. The fluctuation arises from all kinds of motions. So in simple picture, if there is motion, being it rotation, vibration, or translation, the motion of molecules will have the magnetic field associated with the spins of its nuclei fluctuates at the site of neighboring nuclei. It is the combined effect of the motion and the field on the molecule/atom to create fluctuating fields at the nucleus of interest. If the field is at the Larmor frequency, and its instantaneous direction is in the transverse plane, it will also stimulate the spin lattice relaxation. Therefore, by measuring the spin lattice relaxation, we can probe the motion/dynamic information of the system, which is a unique strength of NMR.

What exactly are these fluctuations? Fluctuation means fast change and sometimes random changes that we can't predict. Indeed, all these sources of relaxation are related to the motions of the nuclei and the environments. For example, the Browning motions in solution at ps to ns scale, or the exchange interaction at μs to ms scale. Different kinds of the interactions will give different relaxation mechanism, with a common fluctuation source, the motion. Let's just name a few common mechanisms: interactions with neighboring spins will induce relaxations due to nucleus dipole-dipole interaction; interactions with the electrons outside the nucleus can induce the relaxation due to chemical shielding or chemical shift anisotropy; interactions with nearby unpaired electrons can induce the paramagnetic relaxation; interactions with adjacent nuclei through bonding electrons can induce relaxation via scalar coupling; and interactions with the molecular magnetic moment can induce spin rotation relaxation. The details of such interactions will be revealed in our discussion of decoupling in Chapter 7, where we will see that the cross terms corresponding to each of such sources will give rise to $I^{\pm}$ operators representing spin diffusion process.

Due to the differences of the interactions, the corresponding relaxation will carry its own dependence on physical parameters such as temperature, viscosity, molecular weight, electron orbitals, or the concentration of that relaxation center. But we have to remind ourselves that all these interactions only provide a fixed magnitude and direction of local magnetic field at the site of the nucleus of interest, which most likely does not coincide with the Larmor frequency, and won't induce relaxation by themselves.

For example, the dipolar interaction:

$$\hat{H}_D = \frac{\hbar^2\gamma_I\gamma_S}{r^3}\left[I\cdot S - 3\frac{(I\cdot\vec{r})(S\cdot\vec{r})}{r^2}\right] \qquad (3.31)$$

The separation between a proton and carbon atoms covalently bonded in the protein is 1.12 Å. Can you calculate the coefficient of strength of dipolar interaction by computing $\frac{\mu_0\hbar\gamma_I\gamma_S}{4\pi r^3}$? The factor $\frac{\mu_0}{4\pi}$ is added to convert from cgs unit to SI unit. The answer is roughly 21.5 kHz.

$$\frac{\mu_0\hbar\gamma_I\gamma_S}{4\pi r^3} = \frac{1\times 10^{-7}T\cdot m/A \times 1.05457\times 10^{-34}J\cdot s\times 267.522\times 10^{6}rad\cdot s^{-1}T^{-1}\times 67.2828\times 10^{6}rad\cdot s^{-1}T^{-1}}{(1.12\times 10^{-10}m)^3}$$

$$= 1.3510\times 10^{5}\frac{rad^2\cdot J\cdot m}{A\cdot T\cdot s\cdot m^3}$$

Now we have to convert unit T and J. Recall the energy density of magnetic field is:

$$E = \int\frac{B^2}{2\mu_0}dV = \int\frac{1}{2}H\cdot B\,dV$$

So we have:

$$J = T\cdot A/m\cdot m^3$$

So $\frac{rad^2\cdot J\cdot m}{A\cdot T\cdot s\cdot m^3} = s^{-1}$. Radian is the unit for angle, which is actually unitless. To convert this to Hz from s^{-1}, we need to divide by 2π:

$$\frac{\mu_0\hbar\gamma_I\gamma_S}{4\pi r^3} = \frac{1.3510\times 10^5}{2\pi}s^{-1} = 21.5033\,kHz \qquad (3.32)$$

Can you calculate what is the interaction strength in unit of Hz of a chemical shift anisotropy σ =240 ppm of CO carbon at 600MHz field?

$$\frac{\gamma_I H_0\sigma}{2\pi} = \frac{67.2828\times 10^{6}rad\cdot s^{-1}T^{-1}\times 14.1\,T\times 240\,ppm}{2\pi} \qquad (3.33)$$

$$= 36.237kHz$$

The chemical shifts anisotropy of other carbons are normally in tens of ppm (Chaohui Ye et al. Magnetic Resonance in Chemistry 31, 699-704 (1993)), thus much smaller than that of CO carbon. The size of other interactions such as scalar J couplings or the spin rotation will be even smaller. Their magnitude is much smaller compared to the Larmor frequency in standard superconductive magnetic fields.

By these interactions alone, they aren't very effective to induce the relaxation. Just like the pulse we send into probe to excite NMR signals, if the fields are not at the resonance frequency, the contribution to NMR is negligible, such as the positive frequency component for the Bloch-Siegert shift.

The other determinant of the efficiency of the relaxation source is the motion. The motions of nuclei and the motions of the parties involved in the interactions can modulate the interactions over a very broad range of frequencies, including Larmor frequency, which will directly determine if the interactions can efficiently excite "resonance" and induce relaxations. So we need to know how to characterize the motion and the interactions at the same time, before we can characterize the relaxation. We have a fairly good understanding how the interactions contribute to relaxation, as we can present their respective Hamiltonians or at least describe the physics picture, such as dipolar interaction or chemical shifts, we know what its coefficient, dependence on geometry involves, but how do we get some sense of the motions? Especially the random motions of molecules in gas or liquids?

For molecular motion, the random (sometimes it is not completely random, as the motion in solids are restricted, anisotropic or limited) motions will modulate the energy associated with the parties of interaction due to the change of orientations or distances.

Let's still take the dipolar interaction as an example. When the corresponding parties that carry the spins I and S are in motion, the translation will change the distance r between them and modulate the magnitude of the dipolar interaction energy. The rotational motion will change their respective orientation, and the angle between the directional vector $\vec{r}$ and their spin quantum alignment, which also cause the change of the dipolar interaction energy. But you can't make the distance between nuclei much shorter than the bond length of 1.12 Å. You most likely will get an attenuated dipolar strength due to such motional effect. For example, in solution, we have zero dipolar effect manifested and had to use external media to enforce the anisotropic alignment to induce the residue dipolar interaction for structural study. In solid state, we intentionally use magic angle spinning and decoupling pulse to reduce the broadening due to dipolar interaction for resolution purpose. So how exactly doe motional modulation of these weak interaction (compared to Larmor frequency) induce frequency contribution as high as resonance?

The molecular motion is very complicated, there is no way we can get an analytic solution for the motion of molecules (we can only solve the one-electron hydrogen atom's orbital motion, we can't even get an analytical solution for the energy states of atoms with multiple electron atoms). However, we don't need the exact complete characterization of the motion to evaluate the contribution to relaxation, as we only need to know the frequency distribution of the motion. This information is in the spectral density of the motion.

This is due to the conjugated relationship between time and frequency. If you have a physical quantity, no matter how small its magnitude is, as long as it fluctuates versus time, it will generate energy over a range of frequency from high to low. The power of the energy distribution over the frequency range is the Fourier transformation of the fluctuation over time. Therefore, the fluctuation over time and its frequency dependence has an inverse Fourier transformation relationship. If the quantity varies slowly over time, its power spectrum will comprise mostly low frequency components. If the quantity varies fast over time, its power spectrum will have more weight over the high frequency components. We can evaluate the interaction energy of two molecules in close vicinity, and the interaction will oscillate as a function of time together with the motion. Therefore, we actually do not need to know the exact trajectory of the motion, and can get this frequency distribution of interaction energy by Fourier analysis of the correlation, which measures the change of interaction in time. This greatly simplifies the problem to understand relaxation.

3.6 Spectral density.

The spectral density $J(\omega)$ is the Frequency spectrum (or Fourier analysis) of the time dependent signal. It is obtained by Fourier transformation of the time dependent signal. Particularly in our cases, the spectral density $J(\omega)$ is the FT of autocorrelation function $G(t)$:

$$G(t) \propto h(t) \cdot h(0) \propto \exp\left(-\frac{t}{\tau_c}\right) \tag{3.34}$$

Where $h(t)$ and $h(0)$ are the local fields at the site of nucleus produced by the interaction that we want to analyze at time t and 0, respectively. The τ_c is the time for the correlation to decay, and it exhibits an exponential fashion in the case of random motion. Therefore, the autocorrelation function assumes an exponential dependence on time, the FT of an exponential is a Lorentzian function $\frac{\tau_c}{1+\omega^2\tau_c^2}$. At the fixed correlation time τ_c, $G(t)$ has most of its power at low frequency, but its long tail extends over very high range of frequency, and thus can overlap with Larmor frequency and contribute to relaxation.

Let's explain a bit more detail of the common mechanism/interactions to NMR relaxation:

1. Paramagnetic relaxation: If there are unpaired electrons around the nucleus spin, the motion (Browning tumbling motion in liquids, or purely thermal agitation of the electronic spins in solids) will modulate the magnetic fields associated with the dipolar moments of the unpaired electrons. Since the gyromagnetic ratio of electron is 1836 folds larger than nucleus spins, the strength of the field is very strong. The component at the corresponding nucleus resonance frequency will stimulate spin lattice relaxation, which can be very strong. Ishii, Y. and Jaroniec, C. used this mechanism to intentionally suppress signals near the inserted paramagnetic centers for structure assignments and speed up the recycle delay between repetitive acquisition.

An interesting question is, what if there is no Browning motion in liquids (for free molecular rotation and translation), and no hindered motion of rotation or translation in solids, only vibration in solid, would there still be strong spin lattice relaxation? If there is no paramagnetic center, the frequency of vibration is much higher than nucleus Larmor frequency, so the contribution to help spin lattice relaxation is very ineffective. However, if there is still paramagnetic center such as unpaired electrons, you will still get good spin lattice relaxation, as the size of electronic moment is too big. This is the case in metals with lots of conduction electrons or insulators with paramagnetic impurities. In metals, the relaxation is so powerful you will get $T_1 \sim T_2$ similar to that in liquids. In insulators, at high temperature, the contribution from fluctuations of dipolar moments due to molecular motions can be the dominant mechanism to T_1 effect, but at lower temperature as the motion freezes out, the paramagnetic impurity center will become the dominant effect, which will then exhibit a weak temperature dependence.

2. Magnetic dipolar interactions: As we attribute the fields to the magnetic dipoles, we can look at the fluctuations of fields between two nuclear spins with distance R between them due to random rotation. There will be three different categories, as we will show in our derivation in Sect 4.6 in Chapter 4: zero quantum (no net spin flips or one flip and the other flop), single quantum (one spin quantum change), and double quantum. Each of these give rise to $J^0(\omega), J^1(\omega), and\ J^2(\omega)$. In weak collision limit ($\tau_c < T_2$ spin spin relaxation time), they have fixed ratio, as shown by Soda and Chihara in 1974 (J. Phys. Soc. Japan 36, 954-958 (1974)):

$$J^0(\omega) = \frac{24}{15R^6}(\frac{\tau_c}{1+\omega^2\tau_c^2}) \tag{3.35}$$

$$J^0(\omega):J^1(\omega):J^2(\omega) = 6:1:4 \tag{3.36}$$

By perturbation theory, they can be calculated. The contribution to both T_1 and T_2 relaxation rates from dipolar interaction of nearby spins due to rotation is:

$$\frac{1}{T_1} = \frac{3}{2}\gamma^4\hbar^2 I(I+1)[J^1(\omega) + J^2(2\omega)] \tag{3.37}$$

$$\frac{1}{T_2} = \gamma^4\hbar^2 I(I+1)[\frac{3}{8}J^0(0) + \frac{15}{4}J^1(\omega) + \frac{3}{8}J^2(2\omega)] \tag{3.38}$$

We can see the expression for spin spin relaxation rate contains $J^0(\omega)$, which is absent from that of the spin lattice relaxation. The physics picture corresponding to $J^0(\omega)$ is microscopic process with zero quantum change along z direction, which obviously doesn't change the total magnetization and affect magnetization. However, it does affect the dephasing in the transverse plane that speed up the T_2 process. This explains why normally T_2 is shorter than T_1 in most solids.

In motionally narrowed limit $\omega\tau \ll 1$, $J^0(0) = \frac{24\tau_c}{15R^6}$, $J^1(\omega) = \frac{4\tau_c}{15R^6}$, $J^2(2\omega) = \frac{16\tau_c}{15R^6}$. You can show that $\frac{1}{T_1} = 2\frac{\gamma^4\hbar^2 I(I+1)\tau_c}{R^6} = \frac{1}{T_2}$.

So when fast reorientation is present such as in gas or non viscous liquids, we have identical T_1 and T_2.

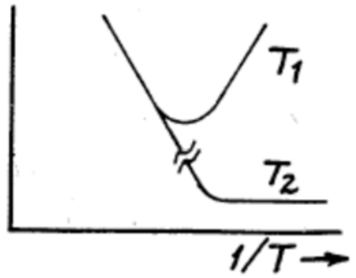


Figure 3.2. Temperature dependence of spin lattice. Adapted from Eiichi Fukushima and Stephen B.W. Roeder's Experimental Pulse NMR, A nuts and bolts approach.

Another interesting behavior is the temperature dependence of $J^0(\omega), J^1(\omega), and\ J^2(\omega)$. As temperature decreases, the frequency of the motion will decreases, and the correlation time τ_c will increase. So the Lorentzian function in the spectral density for $J^1(\omega), and\ J^2(\omega)$ will have smaller and smaller value as $\omega\tau$ becomes larger and larger. This means the contribution from $J^1(\omega), and\ J^2(\omega)$ will become smaller and smaller, which will lead to different values of T_1 and T_2 at lower temperature. $1/T_2$ will continue to have larger contribution from $J^0(0) = \frac{24\tau_c}{15R^6}$ as τ_c increases with decreasing temperature, so $1/T_2$ will have smaller and smaller value. Therefore, we will see the typical temperature dependence of T_1 and T_2 rate shown in Fig. 3.2. We note that the relaxation will have similar dependence on other physical parameter, if that parameter induces similar changes of molecular motions as temperature, such as change of viscosity, or the molecular weight.

Can you prove the T_1 minimum corresponds to the condition where $\omega\tau = 1$? Can you draw a schematic plot for the field dependence of the T_1 and T_2 vs temperature curve shown in Fig. 3.2(how will the curve shift at different fields?)

3. Chemical shift anisotropy: The chemical shift anisotropy comes from the auxiliary field arising from the orbital motion of electrons outside the nucleus in an external magnetic field. The direction and magnitude of this auxiliary field depends on the special distribution of the electron orbitals. The random motion will change the orientation and magnitude of this field and contribute to the relaxation through the coupling to external magnetic field. If the chemical shift anisotropy has an axial symmetry, with an anisotropy of $\Delta\sigma$:

$$\frac{1}{T_1} = \frac{1}{15}\gamma^2 H_0^2 \Delta\sigma^2 \frac{\tau_c}{1+\omega^2\tau_c^2} \tag{3.39}$$

$$\frac{1}{T_2} = \frac{1}{90}\gamma^2 H_0^2 \Delta\sigma^2 [\frac{6\tau_c}{1+\omega^2\tau_c^2} + 8\tau_c] \tag{3.40}$$

We can see that at motionally narrowed limit $\omega\tau \ll 1$, the two rates are not equal, which differs from the dipolar relaxation.

4. Scalar coupling: For the scalar coupling, it arises from the interaction of two nuclei spins mediated via the bonding electrons $I \cdot A \cdot S$, as commonly seen in the solution NMR. It can gives rise to relaxation, when a nucleus I exchanges with another inequivalent spin S at high exchange rate τ_e.

$$\frac{1}{T_1} = \frac{2}{3}A^2S(S+1)\frac{\tau_e}{1+(\omega_I-\omega_s)^2\tau_e^2} \tag{3.41}$$

Here A is 1/3 the trace of the scalar coupling tensor. For example, it is about 50 Hz between directly bonded proton and carbon, thus it is much smaller than previous mechanism.
You can see when I and S are the same species of nucleus, the expression is very simple:

$$\frac{1}{T_1} = \frac{2}{3}A^2S(S+1)\,\tau_e \tag{3.42}$$

5. Spin rotation interaction: This mechanism arises from the magnetic interaction between nucleus spin and the magnetic moment associated with the angular momentum of rotating molecules. This is only important for small spherical molecules in relatively free rotation when other relaxation mechanisms are not present. It is most common in gaseous state such as in AMO experiments, but may also manifest in liquids and some solids. For example, some of the rotating moiety can exhibit angular momentum, such as the aromatic groups. When the molecule experiences collisions, the angular momentum will exhibit fluctuations and gives rise to relaxation. So its relaxation mechanism couples with the correlation time of angular momentum τ_J instead of rotational correlation time τ_c in that of dipolar and chemical shift anisotropy. It also depends on the moment of inertia I of the molecule, and $C_e/3$, the average of the principle values spin rotation tensor C:

$$\frac{1}{T_1} = \frac{2}{3}IkT\hbar^2(2\pi C_e)\tau_J \tag{3.43}$$

We note that τ_J exhibits an opposite temperature dependence to τ_c: $\tau_J\tau_C = \frac{I}{6}kT$. As temperature increases, the density drops and gives less collision to change angular momentum and τ_J increases, while τ_c decreases with faster rotation at higher temperature. At lower temperature, the motion slows down and so τ_c becomes longer. However, each collision becomes less effective to change angular momentum at this extreme, so τ_J becomes longer.

3.7 The Bloch Equation

So now we understand the transverse magnetization signals will decay after it is produced by an RF pulse, due to both spin lattice and spin spin relaxation. In his seminar paper published on Phys. Rev. 70, 4604-4673 (1946), Felix Bloch introduced a set of phenomenological equations to describe the time dependence of magnetization can be summed as:

$$\frac{dM_z}{dt} = -\frac{M_z-M_0}{T_1} + \gamma(M\times H)_z \tag{3.44}$$

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} + \gamma(M\times H)_x \tag{3.45}$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} + \gamma(M\times H)_y \tag{3.46}$$

We can derive the solution of transverse magnetization by $M_{+} = M_{x} + iM_{y}$combining the 2nd and 3rd equations, using the 2nd add the third times I:

$$\frac{dM_x}{dt} + i\frac{dM_y}{dt} = -\frac{M_x + iM_y}{T_2} + \gamma[(M \times H)_x + (M \times H)_y] \tag{3.47}$$

Here we assume the resonance offset $h = H_0 + \frac{\omega}{\gamma}$:

$$\frac{dM_+}{dt} = -\frac{M_+}{T_2} + \gamma\left[M_y h - iM_x h\right] + i\gamma M_z H_1 = -\frac{M_+}{T_2} - i\gamma h M_+ + i\gamma M_z H_1 \tag{3.48}$$

When the alternating field H_1 is off, we can solve the magnetizations:

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} \tag{3.49}$$

$$\frac{dM_+}{dt} = -\frac{M_+}{T_2} - i\gamma h M_+ \tag{3.50}$$

The solution of these equations give the phenomenological description of longitudinal and transverse magnetization:

$$M_z(t) = M_0 + (M_z(0) - M_0)e^{-\frac{t}{T_1}} \tag{3.51}$$

$$M_+(t) = M_+(0)e^{-\frac{t}{T_2}}(\cos\gamma ht + i\sin\gamma ht) \tag{3.52}$$

This shows the relaxation will gradually return $M_z(t)$ to equilibrium magnetization along z and $M_+(t)$ decays in transverse direction.

Chapter 4 Density matrix and its basic application to NMR

I hope you have some qualitative physical concepts and pictures about the fundamentals of NMR with the first three chapters. This chapter will kick start the quantitative analysis of NMR observables.

We will first give a brief introduction of relevant quantum mechanical techniques necessary for our NMR derivation, esp. the density matrix method. Then we will use density matrix to explain what is coherence, and why normally only -1 coherence is detected in our NMR setup. As an example, we will use density matrix to derive the most basic NMR pulse sequence, Hahn Echo.

Before we introduce the effect of internuclear interaction, we will show how to break down the dipolar interaction into different coherence component. Subsequently we will use the operator formalism, which is based on density matrix method, to explain some basic sequences including the Stimulated Echo, Solid Echo and adiabatic demagnetization. In this process, you will see how internuclear interaction modulates the evolution of the system.

Another new concept we will introduce is coherence transfer. This trick is frequently used in pulse sequences of both solution and solid state NMR. Based on this, we will introduce fictitious double and zero quantum operators, the simplest example of multiple quantum coherences. We will use these new operators to explain how to excite multiple quantum coherence and how to detect it. This is the foundation for many more advanced pulse sequence design philosophies that we will introduce in Chapter 6 and 7.

The fictitious spin operators will also help us explain how does cross polarization works, one of the most frequently applied signal enhancement trick in solid state NMR.

We will end our discussion with coherence pathway selection and how to understand the Cogwheel phase cycling, the most effective strategy to design the coherence pathway.

4.1 A crash course of quantum mechanics

Bloch equation can describe the evolution of magnetization with the assumption that there is no interaction between spins, or the interaction is so weak that we can ignore it. It is not sufficient for more complicated scenarios in many of our NMR pulse sequences, where we need to turn on and off the interaction by different methods, such as decoupling, magic angle spinning and recoupling sequences. We need a more accurate approach. Hence here we introduce the density matrix method.

In quantum mechanics, the status of a system is represented by a wave function ψ. ψ is the probability amplitude of the system, due to the particle-wave duality for microscopic particles, as they exhibit both particle and wave behaviors. The implication of the wave like behavior means that the property of the system is not entirely deterministic, but exhibits statistical probability like status. A famous implication or principle is the Heisenberg uncentainty principle: two canonical conjugated parameters cannot be precisely determined at the same time. In maths, it is expressed as:

$$\delta_A \delta_B \geq \frac{\hbar}{2} \tag{4.1}$$

Here δ_A and δ_B are the standard deviation of two parameters that are related by canonical conjugation. This is a bit difficult to explain. For example, the position $\vec{r}$ and momentum $\vec{p}$ are such a pair, or the energy E and time t are another pair. An easy way to get our head around this concept is that the pair of parameters enjoying the canonical conjugation relationship are related by Fourier transformation, such as frequency (energy) and time, and so do the position and momentum for microscopy particles. Due to this principle, when we want a broad bandwidth (large frequency), we need to step very tiny time steps in the NMR indirect dimension during acquisition (small time interval). If we want sharp resolution in the indirection dimension (small frequency interval), we have to extend our acquisition in the time dimension (large time value). You just can't get both ends of the deal at the same time.

As you probably noted, I didn't put an argument for the wave function ψ. The argument depends on the degrees of freedoms of the system, which correspond to the maximal number of commutable observables in quantum mechanics. As position $\vec{r}$ and momentum $\vec{p}$ are canonically related and not commutable, only one of them is used to define the system wave function. Normally we also want to know the time evolution of the system. Time is commutable with $\vec{r}$ or $\vec{p}$. So we can take t as the second argument/degree of freedom for the wave function. If the particle has spin, the spin will be the third degree of freedom/argument for the wave function. This is like how we would describe a person, if he is tall or short, fat or thin, and old or young. Each description captures a specific aspect of the subject property.

Therefore, we can represent the system's status by $\psi(\vec{r}, t, I)$ or $\psi(\vec{p}, t, I)$. The wave function is a complex function of the arguments and describes the probability amplitude how different degrees of freedom are correlated, given the status of the system. Once we obtain the wave function, all physical observables can be computed from it, as we will explain soon. So the wave function is a center piece of puzzle in quantum mechanics.

There are several important properties of the wave function: it satisfies the condition that the integration of the product of the wave function with its complex conjugate over all possible range of all degrees of freedom should be 1, which means the system truly exists somewhere if you search all the parameter space of the independent degrees of freedoms (total probability to find the system is 1:

$$\sum_m \int \psi^*(\vec{r}, t, I_m)\psi(\vec{r}, t, I_m) d\vec{r} dt = \sum_m \int |\psi(\vec{r}, t, I_m)|^2 d\vec{r} dt = 1 \tag{4.2}$$

This is also called the normalization condition. Here $|\psi(\vec{r}, t, I_m)|^2$ is the probability density of the system at a given $\vec{r}$, t, and spin I_m state. Now you see why we call $\psi(\vec{r}, t, I_m)$ probability amplitude, not probability.

How do we obtain the system wave function? As the system can change or evolve with time, their corresponding wave function is described by the Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t, I_m) = \hat{H}\psi(\vec{r}, t, I_m) \tag{4.3}$$

Where $\widehat{H}$ is the Hamiltonian of the system, an operator describes the interactions of the system. So the wave function of the system can be obtained by solving Eq. 4.1. When the system Hamiltonian does not depend on time, it can be written as a simpler form:

$$\widehat{H}\psi(\vec{r},t,\, I_m) = E\psi(\vec{r},t,\, I_m) \tag{4.4}$$

This is so called the stationary-state Schrodinger equation, which is easier to solve in many cases. Here E is the eigenvalue of $\widehat{H}$, which corresponds to the energy level of the system. ψ is the eigenfunction of $\widehat{H}$. In later chapters, we normally convert systems with time dependent $\widehat{H}$ to a Hamiltonian without explicit time dependence, which is simpler to solve using linear algebra.

However, it is not possible to solve Eq. 4.3 and 4.4 for systems with more than two interacting components. Different numerical methods are available to compute the approximated solutions. One commonly approach is to separate the system Hamiltonian into a dominant part plus a small perturbation. If we can solve the Schrodinger equation with the dominant part as the Hamiltonian, the wave function for the original system can be computed by perturbation theory. We will see this strategy is used over and over again in later chapters.

Assume we can solve the wave function of the system, then any physical parameters can be computed by operating the quantum mechanical operators representing corresponding physical observables on the wave function.

So what is the quantum mechanical operators for physical observables?

All the physical observables are represented by their corresponding operators in quantum mechanics. For example, if the chosen degrees of freedom $\vec{r}$ and t, the operator for position is $\vec{r}$, the operator for momentum $\vec{p}$ is $\vec{p} = -i\hbar\nabla = -i\hbar\left(\vec{e}_x\frac{\partial}{\partial x} + \vec{e}_y\frac{\partial}{\partial y} + \vec{e}_z\frac{\partial}{\partial z}\right)$, and orbital angular momentum is $\vec{L} = \vec{r}\times\vec{p} = -i\hbar(\vec{r}\times\nabla)$.

We use the same symbol to represent the physical observables in quantum mechanics as classical mechanics. There are various ways to differentiate quantum mechanical operators from their classical counter parts. For example, the small $\widehat{\ }$ ("hat sign") on top of the Hamiltonian operator $\widehat{H}$. In addition, the small $\overrightarrow{\ }$ on top of $\vec{r}$ is often used to indicate the parameter is a vector.

From now on, we will drop $\widehat{\ }$ sign for quantum mechanical operators, as it will be obvious if we are discussing the classical or quantum mechanical operators. Thus our expression will be much cleaner. We will use bolded $\boldsymbol{r}$ to indicate it represents the vector $\boldsymbol{r}$. In contrast, we use r to represent the pure magnitude of the vector $\boldsymbol{r}$.

The experimental measurement of a system to obtain a specific physical observable A, correspond to the operation of the quantum mechanical operator A onto the wave function of the system. If the system is in an eigenstate of the operator A (which means the operator commutes with the Hamiltonian operator H, and they share the common eigenfunctions), we will get a corresponding eigenvalue of the observable A. This is the result you should get if you perform a measurement on the system at that state:

$$A\psi(\boldsymbol{r},t,\ I_m) = A_m\psi(\boldsymbol{r},t,\ I_m) \tag{4.5}$$

As all observables should be real numbers, therefore all operators corresponding to physical observables are Hermitian:

$$A^{\dagger}\psi(\boldsymbol{r},t,\ I_m) = A_m\psi(\boldsymbol{r},t,\ I_m) \tag{4.6}$$

Which in plain words means that the complex conjugate of an operator is itself, if it is Hermitian. To derive the Hermitian conjugate $A^{\dagger}$ of A, if the operator is expressed as a matrix format in some chosen basis, such as the spin operator show in Eq. 4.8 to 4.9, we need to transpose the matrix, and then replace each entry of the matrix by its complex conjugate $(a + ib \rightarrow a - ib)$. The Hermitian operators have several important properties: diagonalizable, unitary, and with real eigenvalues. We can see now the property of diagonalizable with real eigenvalues makes Hermitian operators a natural choice represent observables in quantum mechanics.

The Hermitian requirement of quantum mechanical operators is also associated with the Schrodinger equation. As we know, if $\psi(\boldsymbol{r},t_0,\ I_m)$ is the solution to Eq. 4.2, then $\psi(\boldsymbol{r},t_0,\ I_m)e^{-i\frac{E}{\hbar}(t-t_0)}$ also satisfies Eq. 4.4. Here E is the eigenvalue of Hamiltonian H, corresponding to the system energy. However, the probability to find the particle at $\boldsymbol{r},t,\ I_m$ status, is not just $\psi(\boldsymbol{r},t,\ I_m)$, but $|\psi(\boldsymbol{r},t,\ I_m)|^2 = \psi(\boldsymbol{r},t,\ I_m)\psi^*(\boldsymbol{r},t,\ I_m)$, which is unique and does not depend on any arbitrary phase factor. This requires the solution to Eq. 4.1 or 4.2 should be a unitary matrix $(\psi\psi^* = I)$.

In addition to the position and linear momentum operator, the other important quantum mechanical operator in NMR is spin momentum $\boldsymbol{S}$, which does not have its counterpart in classical mechanics. As we will show, the spin momentum shares the properties with orbital angular momentum operator. In quantum mechanics, both the angular and the spin momentum $\boldsymbol{S}$ can only adopt quantized values indicated by their quantum number L and S, in contrast to the continuous values of $\boldsymbol{r}$. Thus their projection onto a given direction also assume a set of discrete values. Normally the projection in Cartesian coordinate system is noted as $L_x, L_y\ and\ L_z$ for angular momentum and $S_x, S_y\ and\ S_z$ for angular momentum. The corresponding values for each projection S_i will be from –S, -S+1,…S-1, S, in unit of $\hbar$. Specifically for spin $S = 1/2$ particles, the spin operator can be represented by Pauli matrices σ:

$$S = \frac{\hbar}{2}\sigma \tag{4.7}$$

with its Cartesian components:

$$S_i = \frac{\hbar}{2}\sigma_i, i = x, y, z \tag{4.8}$$

And the Paulie matrices are:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.9}$$

These individual components of spin or angular momentum operator satisfy the so called commutation relation:

$$[I_i, I_j] = I_iI_j - I_jI_i = i\hbar\varepsilon_{ijk}I_k \tag{4.10}$$

Here $\varepsilon_{ijk} = 1$, if $ijk = (1,2,3), (2,3,1)$ or $(3,2,1)$; $\varepsilon_{ijk} = -1$, if $ijk = (1,3,2), (2,1,3)$ or $(3,1,2)$; and $\varepsilon_{ijk} = 0$, if $i = j, or\ j = k, or\ i = k.$

Eq. 4.10 also can be used to show:

$$I_iI_j = -I_iI_j = \frac{i\hbar}{2}\varepsilon_{ijk}I_k \tag{4.11}$$

$$I^2\psi = \sqrt{I(I+1)}\psi \tag{4.12}$$

Where ψ is the eigenfunction of the angular/spin momentum operator. Eq.10 to 12 naturally leads to the relation we used in previous chapters:

$$I^2 = I_x^2 + I_y^2 + I_z^2 = 3I_x^2 = 3I_y^2 = 3I_z^2 = I(I+1) \tag{4.13}$$

In addition,

$$[I^2, I_i] = 0 \tag{4.14}$$

Which means that I^2 shares the same eigenfunction as its component I_i.

In addition, Eq. 4.10 means these component operators I_i are incommutable matrices, and implies that each I_i has its own eigenfunction. Thus these individual components cannot be determined simultaneously, just like the parameters related in the Heisenberg uncertainty relationship. This can be shown by solving the the eigenfunctions of the Paulie matrices in Eq. 4.9:

$$\psi_{x+} = \frac{1}{\sqrt{2}}\binom{1}{1}; \psi_{x-} = \frac{1}{\sqrt{2}}\binom{1}{-1} \tag{4.15}$$

$$\psi_{y+} = \frac{1}{\sqrt{2}}\binom{1}{i}; \psi_{y-} = \frac{1}{\sqrt{2}}\binom{1}{-i} \tag{4.16}$$

$$\psi_{z+} = \binom{1}{0}; \psi_{z-} = \binom{0}{1} \tag{4.17}$$

Naturally, this means:

$$[\boldsymbol{r}_i, \boldsymbol{p}_j] = i\hbar\delta_{ij} \tag{4.18}$$

And:

$$[\boldsymbol{r}_i, \boldsymbol{L}_j] = i\hbar\varepsilon_{ijk}\boldsymbol{r}_k \tag{4.19}$$

Similarly:

$$[\boldsymbol{p}_i, \boldsymbol{L}_j] = i\hbar\varepsilon_{ijk}\boldsymbol{p}_k \tag{4.20}$$

We often use the linear combination of I_x and I_y, and define the so called raising/lowering (or ladder) operators:

$$I^{\pm} = I_x \pm iI_y \tag{4.21}$$

The function of $I^{\pm}$ is to shift up or down the eigenfunction of the component I_i operator from that of k to $k \pm 1$, where k and $k \pm 1$ are both within the allowed eigenvalue range of I_i $[-I, -I + 1, \ldots I - 1, I]$. If the shift is performed out of the range, then it will return zero.

Now we would like to introduce a notation bra and ket. Since we have seen that the probability density of the system is described by $\psi^*(\vec{r}, t, I_m)\psi(\vec{r}, t,\ I_m)$, , we can define a short-handed notation:

$$|\psi\rangle = \psi(r, t,\ I_m) \tag{4.22}$$

$$\langle\psi| = \psi^*(r, t,\ I_m) \tag{4.23}$$

Where $\langle\psi|$ is called a bra, and $|\psi\rangle$ is called ket. So the bra is the complex conjugate of a ket. These bra and ket notations were introduced by Paul Dirac. They bring many conveniences, one of which is to make the inner product shown in Eq. 4.2 simple to express:

$$\sum_m \int \psi^*(r, t, I_m)\psi(x, t,\ I_m)dxdt = \sum_m \int |\psi(r, t,\ I_m)|^2 dxdt = \langle\psi|\psi\rangle \tag{4.24}$$

In NMR, we will see that the wave functions of a system is often expressed as column or row vectors in linear algebra. A bra is actually the row vector representation of the wave function in a given orthonormal basis. The corresponding ket is a column vector. These vector representation of system wave functions is formatted by acknowledging some specific set of vectors as the so called basis, or base vectors. So what are these basis?

This explicit wave functions obtained by solving Eq. 4.3 or 4.4 are often too complicated. Alternatively, we can use a complete set of functions as the unit of measurements to simplify the expression of wave functions and relevant operations.

If we make an analogy, this is like how to express a vector $\boldsymbol{A}$ on a flat plane. If we want to know all the information about this vector, a convenient method is to define the length and direction of the vector in a specific coordinate system. For example, if we establish a Cartesian coordinate system by setting up x and y axis, we can move the vector into the coordinate system, and align its starting point to the origin of the coordinate system, without changing its length and direction. Then this vector can be represented by the coordinate $(x_n\ y_n)$ denoting the coordinate of its ending point. x_n and y_n are the dot product of this vector with the unit vectors:

$$x_n = \boldsymbol{A} \cdot \boldsymbol{e}_x, \qquad y_n = \boldsymbol{A} \cdot \boldsymbol{e}_y \tag{4.25}$$

Along the same logic, we can imagine the wave function exists in a similar space like our geometric space called the Hilbert space. We can pick some x and y axis along the orthogonal directions (well, it is often more than just two axes for two orthogonal dimensions, depends on the degrees of freedom for the specific problem. If it is just a single spin with S=1/2, we will have two possible directions along the magnetic field with spin up or down, corresponding to each eigenfunction of the S_z. If there are two spins, then we will have four possible combinations), and choose corresponding basis vector/wave function $|i\rangle = |u_i\rangle = u_i(r, t,\ I_m)$ $(i = 1, \dots n)$ as unit vector $\boldsymbol{e_i}$. To ensure the chosen basis vectors to represent independent degrees of freedom, they have to satisfy orthogonal relationship just like in our geometric space $\boldsymbol{e_x} \cdot \boldsymbol{e_y} = 0$:

$$\langle j|i\rangle = \langle u_j|u_i\rangle = \delta_{i,j} = \begin{cases} 1, i = j \\ 0, i \neq j \end{cases} \tag{4.26}$$

Note here we often have the basis vectors normalized just like the unit vector $\boldsymbol{e_i} \cdot \boldsymbol{e_i} = 1$. Together this is called orthonormal.

Normally the basis vectors are chosen as the eigenfunctions of the dominant interactions. In most of our NMR problems, the basis vectors are chosen as the eigenfunctions of the Zeeman interaction:

$$H_{zeeman} = -\vec{\mu} \cdot \vec{H} = -\mu H_0 = -\gamma I_z H_0 = -\omega_0 I_z$$

which is normally orders of magnitude larger than any other interactions present in the system. Hence the basis vectors are just the eigenfunctions of operator I_z. In Dirac notation, the wave function is normally written in terms of the major quantum number S and S_z projection m_z:

$$|\psi\rangle = |S, m_z\rangle \tag{4.26}$$

In more complicated cases, the system consists of multiple spins, then:

$$H_{zeeman} = \sum_i -\omega_{0i} I_{zi}$$

The base vectors will be combinations of the I_{zi} states:

$$|\psi\rangle = \sum_i |S, m_z\rangle \tag{4.26}$$

Once the basis is chosen, any vector in this space can be expressed in the chosen basis, in the same way as we express a 2D vector in the x-y coordinate system. Therefore, our wave function can then be recorded by its projection onto these basis vectors as the numerical coordinates:

$$|\psi\rangle = \sum_i \langle\psi|u_i\rangle\, |u_i\rangle = \sum_{i=1}^{n} \int \psi^*(\boldsymbol{r}, t, I_m) u_i(\boldsymbol{r}, t,\ I_m) dxdt\ \ u_i(\boldsymbol{r}, t,\ I_m)$$

Which in Dirac's bra and ket notation can be written as:

$$|\psi\rangle = \sum_{i=1}^{n} c_i |u_i\rangle = \sum_{i=1}^{n} c_i |i\rangle \tag{4.27}$$

Hence we can see that the wave function in the chosen basis, can be written as a column vector with the entries comprising the inner product of the wave function in bra and the corresponding basis in ket:

$$|\psi\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \tag{4.28}$$

And the ket of the same wave function is just the complex conjugate of the bra:

$$\langle\psi| = (c_1^* \quad c_2^* \quad \dots \quad c_n^*) \tag{4.29}$$

So it is just the row vector consisting of the corresponding coefficients c_j^*. Therefore, the bra and ket notation in such kind of basis is simply numerical numbers in the format of matrices. The integration to find the probability then becomes matrix operation:

$$\langle\psi|\psi\rangle = \sum_{i,j=1}^{n} c_i c_j^* \langle u_j|u_i\rangle = \sum_{i=1}^{n} c_i c_j^* \delta_{i,j} = \sum_{i=1}^{n} |c_i|^2 \tag{4.30}$$

This transforms the wave mechanics into matrix operations for quantum mechanics. The matrix format allows us to exploit many properties in linear algebra to make our life much easier.

4.2 Density matrix, expectation value and trace

In reality, when we perform normal experiments to measure some physical quantity, the system consists of not just a single particle or a pure state, but an ensemble of particles or mixed state. For example, our NMR measurements need somewhere 10^{16} or more nuclei to produce sufficient detectable signals. All the particles are otherwise indistinguishable with energy distributed according to the Maxwell-Boltzmann (MB) distribution. For the example of proton signals in water, it essentially is an ensemble of proton nuclei with some at spin up and some spin down states. The actual wave function of the system is not a pure state, but the weighted sum of spin up and spin down states by MB distribution:

$$|\psi\rangle = \frac{P_1|\alpha\rangle + P_2|\beta\rangle}{P_1 + P_2} \tag{4.31}$$

Where P_1 and P_2 are positive numbers between 0 and 1 representing the normalized probability of the system at different spin states in a magnetic field, and $\frac{P_1}{P_2} = \exp(-\frac{\Delta E}{kT})$.

Hence generally, the actual state of the our NMR system is expressed as the sum of all possible pure states with their respective weight P_i:

$$|\bar{\psi}\rangle = \sum_{i=1}^{n} P_i \, |\psi_i\rangle \tag{4.32}$$

This is called a system of mixed state, compared to the simpler case where the system can be described by a pure quantum mechanical state wave function spin up $|\alpha\rangle$ or spin down $|\beta\rangle$. So how does the quantum mechanical prediction compare with our actual measurements in such mixed states?

The measurements we obtain for a physical observable $\boldsymbol{A}$ in such a system at a mixed state correspond to the expectation value of the operator, which is the average value of all possible eigenvalues of operator $\boldsymbol{A}$. It very possibly may be different from any of the eigenvalues of operator $\boldsymbol{A}$. This can be proved by the simple derivation as follow. Assume the operator corresponds to the physical observable is $\boldsymbol{A}$**,** then the measured value for this observable with a system in a pure state $\psi(x,t,\ I_m)$ of the operator is:

$$\int \psi^*(r,t,I_m)\boldsymbol{A}\psi(x,t,\ I_m)dxdt = \langle \boldsymbol{A}\rangle \tag{4.33}$$

Or in bra and ket notation can be simplified as:

$$\langle \boldsymbol{A}\rangle = \langle \psi|\boldsymbol{A}|\psi\rangle \tag{4.34}$$

If the system is not degenerate, and there are $i = N$ different eigenvalues A_i and eigenfunctions $|\psi_i\rangle$ of $\boldsymbol{A}$:

$$\langle \boldsymbol{A}\rangle_i = \langle \psi_i|\boldsymbol{A}|\psi_i\rangle \tag{4.35}$$

For a mixed state expressed in Eq. 4.32, the expectation value of the same observable is:

$$\langle \boldsymbol{A}\rangle = \sum_i P_i\,\langle \psi_i|\boldsymbol{A}|\psi_i\rangle \tag{4.36}$$

We see that the final expectation value corresponding to the experimental measurements is the weighted sum P_i of all possible pure state eigenvalues of observable $\boldsymbol{A}$, which very likely will be different from any of the pure state eigenvalues A_i.

Let's step back for one second. Assume we are dealing with a system at a pure state $|\psi\rangle$, which may not be an eigenstate of $\boldsymbol{A}$. We can still perform the measurement on the system, and quantum mechanically, it corresponds to compute the expectation value for observable $\boldsymbol{A}$, which should be just Eq. 4.34. However, since this pure state $|\psi\rangle$ may or may not be in the eigenstate of A, we need to express $|\psi\rangle$ in the eigenstates of $\boldsymbol{A}$, by expanding $|\psi\rangle$ in the basis of $\{|u_i\rangle\}$. can be done by plugging Eq. 4.6 and 4.27 into Eq. 4.34: this can be expanded as:

$$\langle \boldsymbol{A}\rangle = \langle \psi|\boldsymbol{A}|\psi\rangle = \sum_{i,j=1}^{n} c_j^*\langle u_j|\boldsymbol{A}c_i|u_i\rangle = \sum_{i,j=1}^{n} c_ic_j^*\langle u_j|\boldsymbol{A}|u_i\rangle \tag{4.37}$$

$$\langle \boldsymbol{A}\rangle = \sum_{i,j=1}^{n} c_ic_j^*\langle j|\boldsymbol{A}|i\rangle$$

Since $\{|u_i\rangle\}$ are the eigenfunctions of $\boldsymbol{A}$:

$$\boldsymbol{A}|i\rangle = A_i|i\rangle$$

So Eq.4.37 becomes:

$$\langle\boldsymbol{A}\rangle = \sum_{i,j=1}^{n} c_i c_j^* \langle j|\, A_i |i\rangle = \sum_{i,j=1}^{n} c_i c_j^* A_i \langle j|\, i\rangle = \sum_{i,j=1}^{n} c_i c_j^* A_i \delta_{ij} = \sum_{i=1}^{n} c_i c_i^* A_i \\ = tr\{A_i|c_i|^2\} \tag{4.38}$$

So we see the convenience of expansion any pure state in a suitable basis can turn the expectation value computation into a simple trace summation. This also shows the experimental value of a physical observable may not be any eigenvalues of the operator, even if the system is in the pure quantum mechanical state that is not the eigenstate of the operator. An example for this would be if you prepare a system in the eigenstate of I_z, but a measurement of I_x or I_y will return instead of the eigenvalue $\pm\frac{\hbar}{2}$. You can show this result by expanding the eigenstates of I_z in terms of those of I_x or I_y and follow the derivation shown above for Eq. 4.38.

Therefore, if we define a new operator called density operator ρ for a system in a pure state $|\psi\rangle$, the density operator is:

$$\rho = |\psi\rangle\langle\psi| \tag{4.39}$$

We notice that the ket and bra are now back to back, not like the face to face in the inner product expression shown in Eq. 4.30. This back to back style is called outer product, normally represented by "$\otimes$ " between two vectors, and the result of the operation is an operator. If you apply it to another ket $|\varphi\rangle$, ρ will have its bra side $\langle\psi|$ apply an inner product with $|\varphi\rangle$, which turns into a number, and this number will be the coefficient to multiply with the remaining ket $|\psi\rangle$ in ρ. In short, it means the operation of ρ onto a given wave function (vector $|\varphi\rangle$ in Hilbert space) will lead to another wave function (another vector $|\psi\rangle$ in Hilbert space). This actually is the definition of operators in quantum mechanics, and works for all other quantum mechanical operators:

$$\rho\big|\varphi\rangle = |\psi\rangle\langle\psi|\big|\varphi\rangle = (\langle\psi|\varphi\rangle)|\psi\rangle = C_{\varphi\psi}|\psi\rangle$$

Another approach to understand this new concept is its expression in the format of matrix. As we introduced earlier, all wave functions are vectors in Hilbert space. They can be expressed as row(brat) or column(ket) vectors, shown in Eq. 4.28 and 4.29. Their inner product operations turned to be the multiplication between row and column multiplication, which always ends up to be a single number. However, density matrix, just like other operators, are not vectors, but a matrix corresponding to the outer product. This can be shown more clearly if we expressed ρ in some basis $\{|u_i\rangle\}$:

$$\rho = \sum_{i,j=1}^{n} c_i c_j^* \, |u_i\rangle\langle u_j| \tag{4.40}$$

Therefore, its component ρ_{mn} can be expressed in this basis as matrix:

$$\rho_{mn} = \langle u_m|\rho|u_n\rangle = \sum_{i,j=1}^{n} \langle u_m|c_i c_j^* \, |u_i\rangle\langle u_j|u_n\rangle = c_i c_j^* \delta_{mi}\delta_{nj} = c_m c_n^* \tag{4.41}$$

Then the expectation value of an operator A on a system in a state $|\psi\rangle$ becomes:

$$\langle A\rangle = \langle\psi|A\psi\rangle = \sum_{i,j=1}^{n} c_i c_j^* \langle u_j|A|u_i\rangle = \sum_{i,j=1}^{n} \rho_{ij} A_{ji} \tag{4.42}$$

$$= \sum_{i,j=1}^{n} \langle u_i|\rho|u_j\rangle \, \langle u_j|A|u_i\rangle = \sum_{i,j=1}^{n} \langle u_i|\rho A| \, u_i\rangle = tr\{\rho A\}$$

Here $\{|u_i\rangle\}$ do not have to be the eigenfunctions of operator A. Therefore, to calculate the expectation value of any observable with operator A, we just need to calculate its trace with density operator in some chosen basis.

Similarly, if we are dealing with a system in a mixed state $|\bar{\psi}\rangle$ as defined in Eq. 4.32, the density operator for the mixed state is defined as:

$$\rho = \sum_i P_i \, |\psi_i\rangle\langle\psi_i| \tag{4.43}$$

Where P_i is the probability of the mixed state in each pure state $|\psi_i\rangle$. Then the expectation value of an operator A for such a system in this mixed state $|\bar{\psi}\rangle$ becomes:

$$\langle \boldsymbol{A}\rangle = \sum_i P_i \, \langle\psi_i|\boldsymbol{A}|\psi_i\rangle = \sum_{i,j} P_i \, \langle\psi_i|\psi_j\rangle\langle\psi_j|\boldsymbol{A}|\psi_i\rangle \tag{4.43}$$

Here we insert the identity operator:

$$I = \sum_j |\psi_j\rangle\langle\psi_j| \tag{4.44}$$

Recall that for pure state sets $\{|\psi_j\rangle\}$, we have the orthonormal condition:

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

So Eq. 4.43 turns into:

$$\langle \boldsymbol{A} \rangle = \sum_i P_i \langle \psi_i | \psi_i \rangle \langle \psi_i | \boldsymbol{A} | \psi_i \rangle$$

If we move the P_i inside the dot product:

$$\langle \boldsymbol{A} \rangle = \sum_i \langle \psi_i | P_i | \psi_i \rangle \langle \psi_i | \boldsymbol{A} | \psi_i \rangle$$

Now, in the middle of the matrix we can replay it by the definition of the density matrix for the mixed state:

$$\rho = \sum_i P_i \, |\psi_i\rangle\langle\psi_i|$$

Hence we have:

$$\langle \boldsymbol{A} \rangle = tr\{\rho \boldsymbol{A}\} \tag{4.45}$$

So for the mixed state, the expectation value computation adopts the same format with the help of density matrix.

4.3 Why do we define density matrix as an operator?

It seems that density matrix makes no actual difference for quantum mechanical calculation. Let's take a closer look at the density matrix. First of all, the diagonal elements of the density operator stand for the probability density at each state $|u_n\rangle$:

$$\rho_{nn} = \langle u_n | \rho | u_n \rangle = \sum_{i,j=1}^{n} \langle u_n | c_i c_j^* \, |u_i\rangle \langle u_j | u_n \rangle = c_i c_j^* \delta_{ni} \delta_{nj} = c_n c_n^* \tag{4.46}$$

The off diagonal elements $\rho_{mn} = c_m c_n^*$ are called coherences that connect state $|u_m\rangle$ and $\langle u_n|$. In NMR, $|u_m\rangle$ and $\langle u_n|$ are called coherence order m and n, as they correspond to the eigenstates of operator I_z, since the dominant Hamiltonian is Zeeman interaction. RF pulses can be used to induce transitions between different eigenstates of spin quantum number I_z. For example, when applied to an ensemble of spins with quantum number I, a $\frac{\pi}{2}$ pulse along y axis in the rotating will flips the magnetization from the z to x axis and induce a change of $\Delta I_z = 0 - 1 = -1$. The change of coherence is -1, and it connects the zero quantum to -1 quantum. In general, the coherence in NMR refer to the change of total I_z quantum number induced by the RF pulses. The diagram that records the change of coherences before and after RF pulses in a pulse sequence is called coherence pathway. It will always start with coherence order 0 corresponding to the magnetization along z axis. It will always ends with coherence order $|\pm 1|$, as the quadrature detection can only detect $I_x \pm i I_y$. The normal convention always has the pulse sequence ends with coherence order -1. We will show why this is the case after we complete the density matrix introduction.

Secondly, after introducing such an operator, the expectation value becomes the trace, which can bring computational convenience. From linear algebra we know the trace of any matrix does not change with respect to the representation/basis:

$$tr\langle A\rangle = \sum_{i=1}^{n} \langle\psi_i|A|\psi_i\rangle \tag{4.47}$$

This can be proved simply by inserting an identify operator in terms of another different basis $|\phi_m\rangle$:

$$\langle A\rangle = \langle\psi|A\psi\rangle = \sum_{i=1}^{n} \langle\psi_i| \textstyle\sum_{m=1}^{n} |\phi_m\rangle\langle\phi_m|\, A|\psi_i\rangle$$

Switch the summation order of i and m should not change the evaluation result:

$$\langle A\rangle = \sum_{i=1}^{n} \langle\psi_i| \textstyle\sum_{m=1}^{n} |\phi_m\rangle\langle\phi_m|\, A|\psi_i\rangle = \displaystyle\sum_{i,m=1}^{n} \langle\phi_m|\psi_i\rangle\langle\psi_i|A|\phi_m\rangle$$

Where inside we have the identity matrix in terms of basis $\{|\psi_i\rangle\}$, which can be omitted and we have

$$\langle A\rangle = \sum_{m=1}^{n} \langle\phi_m|A|\phi_m\rangle$$

This agrees with the fact that the measurements of any physical quantity of a fixed subject system should not change when you change your perspective (basis /representation). This is just an analogy to the vector example we mentioned earlier. The same vector should not change its property (length and actual orientation) if you change (rotate x and y axis) your coordinate system. Of course, by changing coordinate system, you will change the coordinate of the ending point. By choosing an appropriate coordinate system, you may have the vector align with the x or y axis. In similarity, by change the basis, the matrix corresponds to ρA can be dragonalized. The multiplication of diagonal matrices becomes simple number multiplication. Therefore, we can have the freedom to pick an appropriate system convenient for our computation.

Thirdly, in Schodinger's picture, the time dependence of the system is manifested on the state function of the system while the observable's operators are time independent. Thus, by defining the density matrix, it can carry all the time dependence of the system. When we compute the expectation value of a observable, its time dependence is directly manifested by the density operator:

$$\frac{d\rho}{dt} = \frac{d}{dt}(|\psi\rangle\langle\psi|) = \frac{d|\psi\rangle}{dt}\langle\psi| + |\psi\rangle\frac{d\langle\psi|}{dt} \tag{4.48}$$

Recall the Schrodinger's equation in Eq. 4.3:

$$i\hbar \frac{d|\psi\rangle}{dt} = H|\psi\rangle$$

If we take complex conjugate on both sides of the equation, we get:

$$-i\hbar \frac{d\langle\psi|}{dt} = \langle\psi|H^{+} = \langle\psi|H$$

Plug into Eq. 4.48:

$$\frac{d\rho}{dt} = \frac{H}{i\hbar}|\psi\rangle\langle\psi| + |\psi\rangle\frac{\langle\psi|H}{-i\hbar} = i\hbar(-H\rho + \rho H) = i\hbar[\rho, H] \tag{4.49}$$

This equation is also called the LvN rate equation, and it describes the time evolution of the density operator.

Following the Heisenberg picture style, we can write the time evolution of density matrix as:

$$\rho(t) = U\rho(0)U^{-1} \tag{4.50}$$

Where U is called the time evolution or time proporgation operator, which is unitary (whose norm is 1 and does not change the norm of the operator it works on):

$$\begin{gathered} U \\ = \exp[-\frac{i}{\hbar}\int_{t_{n-1}}^{t_n} H_n d\tau]H_n(\tau)]\exp[-\frac{i}{\hbar}\int_{t_{n-2}}^{t_{n-1}} d\tau H_{n-1}(\tau)] \\ \dots \exp[-\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau H_2(\tau)]\ \exp[-\frac{i}{\hbar}\int_{0}^{t_1} d\tau H_1(\tau)] \\ = \vec{T}\exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)] \end{gathered} \tag{4.51}$$

Here T is called the Dyson time-ordering operator. Please note that the first exponent operator at the right side with $H_1(\tau)$ corresponds to the Hamiltonian of the system in the earliest time interval, while last operator with $H_n(\tau)$ is the Hamiltonian of the system in the final time interval.

$$\rho(t) = U\rho(0)U^{-1} = \exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)]\ \ \rho(0)\ \exp[\frac{i}{\hbar}\int_0^t d\tau H(\tau)]$$

Here we demonstrate the system can have a sequence of Hamiltonian $H_1(\tau)$, $H_2(\tau)$, …$H_n(\tau)$ from time 0 to time t_n in sequential order.

Here I want to emphasize that this operation resembles the transformation of reference frame, but with a reverse sign in the operator U: $\widehat{H'} = \exp(i\,\widehat{H_0}t)\widehat{H}\exp(-i\,\widehat{H_0}t)$, Thirdly, when the system is in a mixed state, which is normally the case if you want to correlate to experiments, the expectation value of a physical observation in quantum mechanics is still the trace of the density matrix with the corresponding observable's operator, as shown in Eq. 4.48.

This can bring convenience and physical picture to life for many computations which otherwise may get obscured by quantum mechanical manipulation. For example, for our magnetization in NMR of an ensemble of spins, the spin states of a system is not in a pure state but in a mixed state with Maxwell Boltzmann distribution. Because internal interactions are small compared to Zeeman interactions, we can assume the system is in the eigenstates of the Zeeman interaction Hamiltonian and treat internal interactions as perturbations. The state function of the system will be:

$$\overline{|\psi\rangle} = \sum_{i=1}^{n} P_i\,|\psi_i\rangle = \frac{\sum_{i=1}^{n} e^{-\frac{E}{kT}}\,|\psi_i\rangle}{Z} \tag{4.52}$$

Where Z is the partition function as the weight, you can think it as the sum of all possible states with their respective distribution possibility:

$$Z = \sum_{i=1}^{n} e^{-\frac{E}{kT}}\,|\psi_i\rangle \tag{4.53}$$

$|\psi_i\rangle$ is the outer product of the eigenstates of each particle:

$$|\psi_i\rangle = |1\rangle \otimes |2\rangle \otimes \cdots |i\rangle \otimes \ldots |n-1\rangle \otimes |n\rangle$$

Since all particles are indistinguishable, identical and independent, we can perform the computation for one of the particle at a time, and the Z of the system will be the multiplication of the individual value: $Z = Z_1 Z_2 \ldots Z_n$, where

$$Z_i = \sum_{I_z=-I}^{I} e^{-\frac{E_i}{kT}} \tag{4.54}$$

We know that the energy is

$$E_i = -\gamma I_{zi} H_0$$

So

$$Z_1 = \sum_{m_i=-I}^{I} e^{m_i \frac{\gamma H_0}{kT}}$$

Where m_i is the quantum number for I_{zi}. Apply Taylor expansion and recall $\frac{\gamma H_0}{kT} \ll 1$ at room temperature:

$$Z_1 = \sum_{m=-I}^{I} [1 + m_i \frac{\gamma H_0}{kT} + (m_i \frac{\gamma H_0}{kT})^2 + \cdots] = (2I + 1) \tag{4.55}$$

So we can see that the partition function of a system with N identical noninteracting particles with spin quantum number I is: $Z = (2I + 1)^N$, which is a constant.

For the numerator, the value will be $e^{-\frac{E}{kT}}|\psi_i\rangle$. We can expand it as:

$$e^{-\frac{E}{kT}}|\psi_i\rangle = (1 + \sum_i m_i \frac{\gamma H_0}{kT})|\psi_i\rangle \tag{4.56}$$

Therefore, the density operator is just the outer product with $\langle\psi_i|$:

$$\rho = \frac{1}{Z}(1 + \sum_i m_i \frac{\gamma H_0}{kT})|\psi_i\rangle\langle\psi_i|$$

The first part is 1, together with the basis $|\psi_i\rangle\langle\psi_i|$, it becomes the identity operator, which does not make any difference.

The second part is proportional to the sum of each spin quantum number I_{zi} times the corresponding spin state, in addition to an extra coefficient $\frac{\gamma H_0}{kT}$. For the density matrix, this is further joint bythe outer product with the bra of the wave function:

$$\rho = \frac{1}{Z}\sum_i e^{-\frac{E}{kT}}|\psi_i\rangle\langle\psi_i| = \frac{N\gamma H_0}{kT(2I + 1)^N}\sum_{i=1}^{N} I_{zi} \tag{4.57}$$

The total particle number and the temperature of the system are kept a constant in most NMR experiments, with the orientation of the magnetization modulated by RF pulses. Hence, we can ignore the coefficient, and represent the state of the system using the total spin operator $\sum_{i=1}^{N} I_{zi}$, and if the system is uniform, we can just represent the density matrix by I_z.

The fourth advantage of the density matrix is to provide user extra information about the system. Given a density operator/matrix, we always have:

$$Tr\{\rho^2\} \leq 1 \tag{4.58}$$

If $Tr\{\rho^2\} = 1$, it means that the system is in a pure state, and all possible information about the system is known.

For example, if the system is in the eigenstate $|\varphi\rangle$ of an observable A, every time when we perform measurement about that system we will always obtain exactly the same value, which correspond to the eigenvalue of A on that eigenstate.

If $Tr\{\rho^2\} < 1$, then the system is in a mixed state, we only have partial information about the system. The minimum of $Tr\{\rho^2\} = \frac{1}{d}$, where d is the number of dimensions of the basis that span the wave vector space (for example, if we have two independent spins with $I = 1/2$ as a system, $d = (2I + 1)^N = (2 \times \frac{1}{2} + 1)^2 = 4$).

We will terminate our brief introduction to quantum mechanics here. This is barely sufficient to help you navigate through the remaining lecture note. We would encourage readers to take some undergraduate quantum mechanics course, or read through some online materials such as Wikipedia or various open course lecture notes. Another topic in quantum mechanics we will use frequently is the perturbation theory, both time dependent and independent form.

4.4 Why can we directly detect only -1 single quantum in NMR experiments?

Let's get back to the detection in NMR, why only single quantum is detected. The NMR quadrature detection is represented in the density matrix format by:

$$S = tr\{I^+\rho\} = tr\{R_z^{-1}(\theta)R_z(\theta)I^+\rho\} = tr\{R_z(\theta)I^+\rho R_z^{-1}(\theta)\} \qquad (4.59)$$

Where $R_z(\theta) = \exp(-i\theta I_z)$, it means a rotation of θ angle the z axis. Eq. 4.59 essentially equals to rotate the evaluation basis around the z axis by a random angle. Because the expectation value of the signal is the trace, which doesn't change if you change the representation according to linear algebra.

$$tr\{R_z(\theta)I^+\rho R_z^{-1}(\theta)\} = tr\{R_z(\theta)I^+R_z^{-1}(\theta)R_z(\theta)\rho R_z^{-1}(\theta)\} = tr\{\exp(-i\theta)I^+R_z(\theta)\rho R_z^{-1}(\theta)\}$$

Here we used identity:

$$\exp(-i\phi I_z)\, I^\pm \exp(i\phi I_z) = \exp(\mp i\phi)I^\pm \qquad (4.60)$$

To work out the $R_z(\theta)\rho R_z^{-1}(\theta)$, we use the identity for a coherence order p system, its density matrix is $\rho = |m\rangle\langle m'|$, where $m - m' = \pm p$:

$$\exp(-i\phi I_z)\, \rho \exp(i\phi I_z) = \exp(-ip\phi)\rho \qquad (4.61)$$

Without losing generality, let's say our system is in a mixed state, in an ensemble of pure states of different coherence order p_j with probability P_j according to the Maxwell Boltzmann distribution:

$$\rho = \sum_{j=1}^{n} P_j \rho^{p_j} \qquad (4.62)$$

So together we have:

$$S = tr\{I^+\rho\} = tr\left\{\exp(-i\theta)\, I^+ R_z(\theta) \sum_{j=1}^{n} P_j \rho^{p_j} R_z^{-1}(\theta)\right\} \qquad (4.63)$$

$$= tr\left\{\exp(-i\theta)\, I^+ \sum_{j=1}^{n} P_j \exp(-ip_j\theta)\, \rho^{p_i}\right\}$$

$$= tr\left\{I^+ \sum_{j=1}^{n} P_j \exp[-i(p_j+1)\theta]\rho^{p_j}\right\}$$

As we said, this operation should not change the value of the signal, therefore:

$$tr\left\{I^+ \sum_{j=1}^{n} P_j \exp[-i(p_j+1)\theta]\rho^{p_j}\right\} = tr\{I^+\rho\} = tr\{I^+ \sum_{j=1}^{n} P_j \rho^{p_j}\} \tag{4.64}$$

Should stand for arbitrary angle θ. The only possibility for this equation to be true is when $\exp\left[-i(p_j+1)\,\theta\right] = 1$ for all values of θ, which means $p_j + 1 = 0$, which is:

$$p_j = -1 \tag{4.65}$$

This explains why quadrature detection can only detect -1 quantum. However, we often see reports about multi quantum coherence in NMR experiments. If we can't see multiquantum coherences with our quadrature setup, what did they do to detect these multi quantum coherences? How to generate them?

We will use density matrix to explain how multiple quantum could be generated and detected indirectly. Before we explain those, let's look at some simple examples.

4.5 Density matrix analysis of Hahn Echo.

We have introduced with the application of a $\frac{\pi}{2}$ pulse at resonance Larmor frequency, we can induce NMR and observe the signal as FID.

However, there are some limitations with this method. Some NMR signals have very short T_2, thus very fast decay of FID. It could completely decay to zero within the dead/recover time of the system before receiver is ready to receive any signal. In addition, the actual decay time T_2^* of transverse magnetization can be shorter than the real T_2 due to relaxation:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma\Delta H_0 \tag{4.66}$$

For full width half maximum(FWHM) of a Gaussian shaped spectral line in the frequency domain:

$$f(\omega) \propto \exp\left(-\frac{\omega^2}{2\sigma^2}\right) \Leftrightarrow F(t) \propto \exp\left(-\frac{\sigma^2 t^2}{2}\right) \tag{4.67}$$

Then you can show that $FWHM = 2.36\sigma$. According to the definition of T_2 which is for the signal to decay to 1/e of F(0), we have $T_2 = \sqrt{2}/\sigma$, so we can get the estimate of a Gaussian line:

$$FWHM = \frac{3.33}{T_2}\ (Hz) \tag{4.68}$$

For an exponential line commonly present in liquids:

$$G(t) \propto \exp(-\frac{t}{T_2}) \Leftrightarrow g(\omega) \propto \frac{T_2}{1 + T_2^2\omega^2} \tag{4.69}$$

You can show:

$$FWHM = \frac{1}{\pi T_2}\ (Hz) \tag{4.70}$$

So we can see measurements of lineshape can get us direct estimation of relaxation and vice versa.

What can we do if FID is too short? As I was told by Erwin Hahn, His discovery of the Hahn Echo method was inspired by his experience working with sonar during WWII in US Navy.

Assume we first apply a $\frac{\pi}{2}$ pulse on resonance along the y axis in the rotating frame. After the pulse, the magnetization along the z axis would be flipped onto x axis. Soon, some fraction of the magnetization (spins), we call isochromat, will experience slightly higher field along the z direction, they will precess in transverse plane faster. Some isochromats will experience slightly lower magnetic field along the z axis and precess slower. This dephasing of the precessing spins will lead to decoherent addition of transverse magnetization along the x axis and the decay of the signal. The reasons for this loss of pacing are multifolds, as shown above by the T_2^* expression. The inhomogeneous external magnetic field, for example, in the range of the sample, will be one. The variety of spin spin lattice relaxation factors will be another.

However, if we let the dephasing proceed for a time τ after the $\frac{\pi}{2}$ pulse, and hit the system with another π pulse along the y axis, we will flip all the spins over. Thus those precessed faster and accumulated a larger precessing angle in transverse plane will be lagged behind the precessing, and those precessed slower will have exactly the opposite. But the isochromat with faster precessing will continue to precess faster, and the lagged angle will be compensated in the same time τ after the π pulse, and the same will happen to those at slower precessing frequency in the same time τ after the π pulse. So gradually we will see a build-up of the magnetization signal along the –x axis, and the signal will reach its maximum at exact time τ after the π pulse, which then will be followed by its decay as a mirror image just like the normal FID. This is called an Echo, which essentially is made up by a reversed FID followed by a normal FID.

Thus we can modulate the time τ to have the NMR signal stationed anywhere we like (well, before the completely decay due to relaxation), and away from the dead zone of the system recovery time. In short, all the decay of FID due to static field inhomogeneity will be recovered by the Echo. However, the decay due to normal relaxation mechanisms such as dipolar or chemical anisotropy associated with the motions, which are stochastic, cannot be recovered. But this limitation can be used by the Echo method to measure corresponding relaxation, such as Carr-Purcell-Meiboom-Gill (CPMG) sequence.

Here we will use density matrix to show how Hahn Echo works.

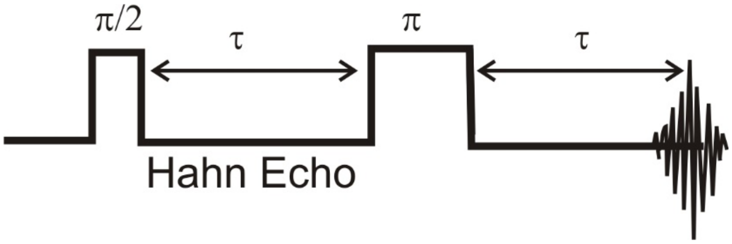


Figure 4.1. Hahn Echo pulse sequence.

The initial state of the system is at thermal equilibrium with magnetization along Z, so the density matrix of the system is:

$$\rho(0) = I_z \tag{4.71}$$

The RF pulse is essentially a rotation operation around the axis of the pulse, assume it is applied along the y axis for a time t with field strength ω for a time t_p, it will be a tip angle $\theta = \omega t_p$ pulse, and the magnetization along z will be modulated by:

$$\rho(t) = U\rho(0)U^{-1} = e^{-i\theta I_y} I_z e^{i\theta I_y} = I_z \cos\theta + I_x \sin\theta \tag{4.72}$$

For a $\frac{\pi}{2}$ pulse along y axis, it can be represented by:

$$U = e^{-i\frac{\pi}{2}I_y} \tag{4.73}$$

So the evolution will take the system to:

$$\rho\left(t_{\frac{\pi}{2}}\right) = e^{-i\frac{\pi}{2}I_y} I_z e^{i\frac{\pi}{2}I_y} = I_x \tag{4.74}$$

After rotated to I_x, the spins will continue to precess in the transverse plane. Let's ignore all interactions internal to the system, and just account for precessing due to difference of isotropic chemical shifts in the dominant Zeeman interaction with Hamiltonian $H = -\omega I_z$. The evolution operator U will be $U = \exp(-\frac{i}{\hbar}Ht)$. As the system will be in the eigenstates of I_z due to the dominant Hamiltonian is linear of I_z, the Hamiltonian will give us another $\hbar$. So from now on, we will drop the $\hbar$ in all our derivation unless otherwise noted. Hence we have $U(\tau) = \exp(-iH\tau) = \exp(i\omega I_z \tau)$. After time τ, the system will be:

$$\begin{aligned}\rho\left(t_{\frac{\pi}{2}} + \tau\right) &= U(\tau)\rho\left(t_{\frac{\pi}{2}}\right)U^{-1}(\tau) = \exp(-iH\tau)\, I_x \exp(iH\tau) \\ &= \exp(i\omega I_z \tau)\, I_x \exp(-i\omega I_z \tau) = I_x \cos\omega\tau - I_y \sin\omega\tau\end{aligned} \tag{4.75}$$

With the application of the π pulse along y axis:

$$\rho\left(t_{\frac{\pi}{2}}+\tau+t_{\pi}\right)=U(\tau)\rho\left(t_{\frac{\pi}{2}}+\tau\right)U^{-1}(\tau) \tag{4.76}$$
$$=e^{-i\pi I_y}\left(I_x\cos\omega\tau-I_y\sin\omega\tau\right)e^{i\pi I_y}$$
$$=\cos\omega\tau\ \ e^{-i\pi I_y}I_xe^{i\pi I_y}+\sin\omega\tau\ \ e^{-i\pi I_y}I_ye^{i\pi I_y}=-I_x\cos\omega\tau-I_y\sin\omega\tau$$

Then after the π pulse all spins will evolve under the normal isotropic chemical shifts with evolution operator $U(t)=\exp(-iHt)=\exp(i\omega I_z t)$, and the system after another time t is:

$$\rho\left(t_{\frac{\pi}{2}}+\tau+t_{\pi}+t\right)=\ U(t)\rho\left(t_{\frac{\pi}{2}}+\tau+t_{\pi}\right)U^{-1}(t)$$

$$=\exp(i\omega I_z t)(-I_x\cos\omega\tau-I_y\sin\omega\tau)\exp(-i\omega I_z t)$$

$$=-\cos\omega\tau\exp(i\omega I_z t)\,I_x\exp(-i\omega I_z t)-\sin\omega\tau\exp(i\omega I_z t)\,I_y\exp(-i\omega I_z t)$$

$$=-\cos\omega\tau\left(\ I_x\ \cos\omega t-I_y\ \sin\omega t\right)-\ \sin\omega\tau\ \ (I_y\cos\omega t+I_x\ \sin\omega t)$$

$$=-\ I_x(\cos\omega\tau\cos\omega t+\ \sin\omega\tau\sin\omega t)+\ I_y\ (\cos\omega\tau\ \sin\omega t-\ \sin\omega\tau\cos\omega t)$$

$$\rho\left(t_{\frac{\pi}{2}}+\tau+t_{\pi}+t\right)=-\ I_x\cos[\omega(\tau-t)]+\ I_y\ \sin[\omega(t-\tau)] \tag{4.77}$$

Hence we see at time $t=\tau$ after the π pulse, the system density matrix is:

$$\rho\left(t_{\frac{\pi}{2}}+\tau+t_{\pi}+\tau\right)=-I_x \tag{4.78}$$

The signal detection function in NMR is $S=I_x\pm iI_y$, the sign depends on the choice of setup. If we pick the convention as $S=I_x+iI_y$, the measured signal according to density matrix should be:

$$S=\langle S\rho\left(t_{\frac{\pi}{2}}+\tau+t_{\pi}+\tau\right)\rangle=Tr\{(I_x+iI_y)\cdot(-I_x)\} \tag{4.79}$$
$$=-Tr\{I_x^2\}-Tr\{I_xI_y\}$$

The second term $I_xI_y=-\frac{1}{2}I_z$, and I_z is traceless as we know. So it is zero.

Using the identity relationship Eq. 4.13: $I_x^2=I_y^2=I_z^2=\frac{1}{3}I^2=\frac{1}{3}I(I+1)$

We have:

$$S=-\frac{1}{3}I(I+1) \tag{4.80}$$

Therefore, we demonstrated with the density matrix method how to explain the Hahn Echo. As we will show later, density matrix will help many more complicated analyses.

Before we proceed further, we need to take a closer look at the dipolar interaction, as it will be present in many of our conversation.

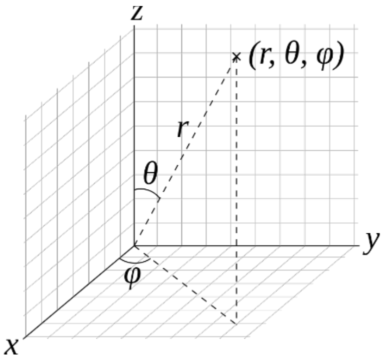


Figure 4.2. Polar angle θ and azimuth angle φ to indicate a vector ***r*** *in a spherical coordinate.*

4.6 Decomposition of dipolar interaction Hamiltonian

Between two adjacent spins with spin ***I*** and ***S***, they can interact via magnetic dipolar interactions:

$$H_D = \frac{\hbar^2\gamma_I\gamma_S}{r^3}[\boldsymbol{I}\cdot\boldsymbol{S} - 3\frac{(\boldsymbol{I}\cdot\boldsymbol{r})(\boldsymbol{S}\cdot\boldsymbol{r})}{r^2}] \tag{4.81}$$

Assume we adopt the spherical coordinate with polar angle θ and azimuthal angle φ.

$$H_D = \frac{\hbar^2\gamma_I\gamma_S}{r^3}[\boldsymbol{I}\cdot\boldsymbol{S}$$

$$-3\frac{(I_z r\cos\theta + \mathrm{r}\sin\theta\, I_x\cos\varphi + \mathrm{r}\sin\theta\, I_y\sin\varphi)(S_z r\cos\theta + \mathrm{r}\sin\theta\, S_x\cos\varphi + \mathrm{r}\sin\theta\, S_y\sin\varphi)}{r^2}]$$

$$= \frac{\hbar^2\gamma_I\gamma_S}{r^3}\{I\cdot S - 3[I_zS_z\cos^2\theta$$

$$+\sin^2\theta\,(I_xS_x\cos^2\varphi + I_yS_y\sin^2\varphi) + (I_xS_y + I_yS_x)\sin^2\theta\sin\varphi\cos\varphi$$

$$+\cos\theta\sin\theta\cos\varphi(I_zS_x + I_xS_z) + \cos\theta\sin\theta\sin\varphi\,(I_zS_y + I_yS_z)]\}$$

$$H_D = \frac{\hbar^2\gamma_I\gamma_S}{r^3}\{I\cdot S - 3\left[I_z\cos\theta + \frac{\sin\theta}{2}(I^+e^{-i\varphi} + I^-e^{i\varphi})\right]\left[S_z\cos\theta + \frac{\sin\theta}{2}(S^+e^{-i\varphi} + S^-e^{i\varphi})\right]\} \tag{4.82}$$

Where $I^\pm = I_x \pm iI_y$, and we used $I_x = \frac{1}{2}(I^+ + I^-), I_y = \frac{1}{2i}(I^+ - I^-)$, and similarly for S spins, to convert from second step to third step, or we use:

$$I^+S^+ + I^-S^- = (I_x + iI_y)(S_x + iS_y) + (I_x - iI_y)(S_x - iS_y) = 2(I_xS_x - I_yS_y) \tag{4.83}$$

$$I^+S^- + I^-S^+ = (I_x + iI_y)(S_x - iS_y) + (I_x - iI_y)(S_x + iS_y) = 2(I_xS_x + I_yS_y) \tag{4.84}$$

The above can be converted to:

$$= \frac{\hbar^2 \gamma_I \gamma_S}{r^3} [I_x S_x + I_y S_y + I_z S_z - 3 I_z S_z \cos^2\theta - \frac{3}{2} \sin\theta \cos\theta \, e^{-i\varphi} (I_z S^+ + S_z I^+)$$

$$- \frac{3}{2} \sin\theta \cos\theta \, e^{i\varphi} (I_z S^- + S_z I^-) - \frac{3}{4} \sin^2\theta \, (I^+ S^- + I^- S^+)$$

$$- \frac{3}{4} \sin^2\theta \, (I^+ S^+ e^{-2i\varphi} + I^- S^- e^{2i\varphi})]$$

Note the term:

$$\frac{3}{4} \sin^2\theta \, (I^+ S^- + I^- S^+) = \frac{3}{4} (1 - \cos^2\theta) 2 (I_x S_x + I_y S_y) = \frac{3}{2} (1 - \cos^2\theta)(I_x S_x + I_y S_y)$$

Combine with first two terms:

$$I_x S_x + I_y S_y - \frac{3}{2} (1 - \cos^2\theta)\left(I_x S_x + I_y S_y\right) = -\frac{1}{2} (1 - 3\cos^2\theta)\left(I_x S_x + I_y S_y\right)$$

$$= -\frac{1}{4} (1 - 3\cos^2\theta)(I^+ S^- + I^- S^+)$$

Combine $I_z S_z - 3 I_z S_z \cos^2\theta = I_z S_z \, (1 - 3\cos^2\theta)$,

Together, we have the format presented in C.P. Slichter's Principles of Magnetic Resonance:

$$H_D = \frac{\hbar^2 \gamma_I \gamma_S}{r^3} [A + B + C + D + E + F] \tag{4.85}$$

Where

$$A = I_z S_z \, (1 - 3\cos^2\theta)$$

$$B = -\frac{1}{4} (1 - 3\cos^2\theta)(I^+ S^- + I^- S^+)$$

$$C = \frac{3}{2} \sin\theta \cos\theta \, e^{-i\varphi} (I_z S^+ + S_z I^+)$$

$$D = C^\dagger$$

$$E = \frac{3}{4} \sin^2\theta \, I^+ S^+ e^{-2i\varphi}$$

$$F = E^\dagger$$

	Δm_I	Δm_S	$\Delta(m_I + m_S)$	
A	0	0	0	Zero quantum
B	± 1	± 1	0	Zero quantum
C	0, 1	1,0	1	Single quantum
D	0,-1	-1,0	-1	Single quantum

E	1	1	2	Double quantum
F	-1	-1	2	Double quantum

If I and S are like spins (the same species with the same gyromagnetic ratio), in most of NMR computation, we only consider A+B when dipolar interactions are involved:

$$H_D = \frac{\hbar^2\gamma_I^2}{r^3}(1-3\cos^2\theta)\, I_{zi}I_{zj} - \frac{1}{4}(I_i^+I_j^- + I_j^+I_i^-)] = \frac{\hbar^2\gamma_I^2}{r^3}(1-3\cos^2\theta)I_{zi}I_{zj}$$

$$-\frac{1}{4}\,2(I_{xi}I_{xj} + I_{yi}I_{yj}\,)]$$

$$= \frac{\hbar^2\gamma_I^2}{r^3}(1-3\cos^2\theta)\left[I_{zi}I_{zj} - \frac{1}{2}\left(I_{xi}I_{xj} + I_{yi}I_{yj}\right)\right]$$

$$= \frac{\hbar^2\gamma_I^2}{r^3}(1-3\cos^2\theta)[\frac{3}{2}I_{zi}I_{zj} - \frac{1}{2}(I_{xi}I_{xj} + I_{yi}I_{yj} + I_{zi}I_{zj})]$$

$$H_D = \frac{\hbar^2\gamma_I^2}{r^3}(\frac{1-3\cos^2\theta}{2})(3I_{zi}I_{zj} - I_i\cdot I_j) \tag{4.86}$$

This form we have $3I_{zi}I_{zj} - I_i \cdot I_j$ commute with the Zeeman interaction Hamiltonian

$$H_0 = -\omega(I_{zi} + I_{zj})$$

However, if I and S are unlike spins with different gyromagnetic ratio, then only A term will commute with the total Zeeman interaction Hamiltonian, and $I \cdot S$ does not commute anymore.

Then for these scenarios, we will have:

$$H_D = \frac{\hbar^2\gamma_I\gamma_S}{r^3}I_zS_z(1-3\cos^2\theta) \tag{4.87}$$

Pleas prove for yourself for like spins:

$$[(I_{zi} + I_{zj}), I_i \cdot I_j] = 0$$

For unlike spins:

$$[(I_z + S_z), I \cdot S] \neq 0$$

4.7 Product operator formalism for NMR to account for internuclear interactions

The operator formalism or in its full name, product operator formalism has been used in many NMR literature to work out pulse sequences. Here we will follow PK. Wang and CP. Slichter's tutorial "A pictorial operator formalism for NMR coherence phenomena" (Bulletin of Magnetic Resonance 8, 3-16 (1986)) to show how it can be used to account for simple cases of spin interactions, multiquantum coherence, solid echoes, and coherence transfer between heteronuclear.

Here we assume the system contains two spins I and S. Both I and S are spin ½ nuclei. In a magnetic field of $\boldsymbol{H_0} = H_0\boldsymbol{e_z}$, the system's dominant interaction is the Zeeman interaction with Hamiltonian:

$$\widehat{H}_0 = -\hbar H_0(\gamma_I I_z + \gamma_s S_z) \tag{4.88}$$

Recall we use $\hbar$ as unit for all interaction parameters, so we can drop the $\hbar$ in Eq. 4.88. Similarly, we account for their interaction by:

$$\widehat{H}_C = b_{IS} I_z S_z \tag{4.89}$$

This format can represent either the J coupling commonly discussed in solution NMR or the dipolar coupling between unlike spins in solids. For like spins in solids, the dipolar interaction can be represented by a format similar to Eq. 4.87:

$$\widehat{H}_C = b_{IS}(3I_{zi}I_{zj} - I_i \cdot I_j) \tag{4.90}$$

The two coupled spins can be either in singlet or triplet state, with total spin quantum number 0 or 1. If they are in singlet state, they will not contribute to magnetization. If they are in triplet state, $I \cdot S = 1/4$(can you show that? Can you also show what $I \cdot S$ is if two spins are singlet coupled? It should also be a constant, -1/4). Either way, we can drop the term as it is a constant, and use

$$\widehat{H}_C = b_{IS} I_z S_z$$

At time t=0, the system is at thermal equilibrium and the density matrix is:

$$\rho(0) = I_z + S_z \tag{4.91}$$

We will work in the rotating frame so that we can drop the Zeeman interaction $\widehat{H}_0$. To transform the system into rotating frame, as we demonstrated, we need to apply:

$$\widehat{H'} = \exp(i\,\widehat{H}_0 t)\widehat{H}\exp(-i\,\widehat{H}_0 t)$$

to the Zeeman Hamiltonian.

The Hamiltonian of RF pulse along the x axis is:

$$\begin{aligned}\widehat{H_1} &= -\gamma_I H_1\left(I_x \cos\omega t + I_y \sin\omega t\right) - \gamma_S H_1\left(S_x \cos\omega t + S_y \sin\omega t\right) \\ &= -\gamma_I H_1 \exp(i\omega_I I_z t) I_x \exp(-i\omega_I I_z t) - \gamma_S H_1 \exp(i\omega_s S_z t) S_x \exp(-i\omega_s S_z t)\end{aligned} \tag{4.92}$$

Apply the transformation, at resonance $\omega = \gamma H_0$, the exponential factors will be canceled out, and the Hamiltonian of RF pulses will be stationary in the rotation frame instead of the sinusoidal form as we demonstrated earlier in Chapter 2:

$$\widehat{H_1} = -\gamma_I H_1(I_x + S_x) \tag{4.93}$$

Transformation to rotating frame will not affect the coupling between I and S:

$$\widehat{H_C} = b_{IS} I_z S_z$$

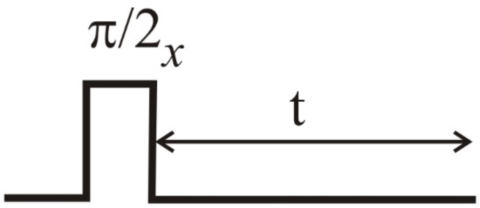
Since it commutes with Zeeman interaction of each nucleus.

To track the evolution of the system during the experiment, we can follow the density matrix:

$$\rho(t) = U\rho(0)U^{-1} = \exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)]\,\rho(0)\,\exp[\frac{i}{\hbar}\int_0^t d\tau H(\tau)]$$

All we need to do is to find out what is the Hamiltonian during each time interval.

Assume RF pulses generate stronger fields (tens of kHz to 100 kHz) than the coupling b_{IS} (dipolar is about 21 kHz between proton and ^{13}C, J is about tens of Hz) , so during RF pulses, we can ignore the effect of interactions between I and S.



$$\rho\left(t_{\frac{\pi}{2}} + t\right) = I_y \cos(\frac{b_{IS}t}{2}) - 2S_zI_x \sin\left(\frac{b_{IS}t}{2}\right) + S_y \cos\left(\frac{b_{IS}t}{2}\right) - 2I_zS_x \sin(\frac{b_{IS}t}{2})$$

Figure 4.3. Evolution of the density matrix under coupling between I and S

So the effect of RF pulses on I spin is very easy to represent:

$$U = \exp\left(-i(-\gamma_I H_1 I_i)t_p\right) = \exp\left(i\omega_1^I I_i t_p\right) = \exp(i\theta_I I_i) \tag{4.94}$$

Where θ_I represent the tip angle of the RF pulse on I spin. I_i represent the pulse is along the ith axis. The effect of RF pulses on spin S will be similar:

$$U = \exp\left(-i(-\gamma_I H_1 S_i)t_p\right) = \exp\left(i\omega_1^S S_i t_p\right) = \exp(i\theta_S S_i) \tag{4.95}$$

Note here the Hamiltonian during RF pulsing is $-\gamma_I H_1 I_i$ and $-\gamma_I H_1 S_i$. The negative sign in the front is from the Hamiltonian, same as the negative sign in the Zeeman interaction $\widehat{H}_0$. Note if it is along a negative axis, say –x axis, then we will replace I_i/S_i with $-I_x/-S_i$.

Thus if we have a $\frac{\pi}{2}$ pulse applied on both I and S spins along x axis, the density matrix will become:

$$\begin{aligned}\rho\left(t_{\frac{\pi}{2}}\right) &= \exp\left(i\frac{\pi}{2}I_x\right) I_z \exp\left(-i\frac{\pi}{2}I_x\right) + \exp\left(i\frac{\pi}{2}S_x\right) S_z \exp\left(-i\frac{\pi}{2}S_x\right) \\ &= I_y + S_y\end{aligned} \tag{4.96}$$

Now let's take a look at what the coupling between I and S will do after the pulse:

$$\rho\left(t_{\frac{\pi}{2}} + t\right) = \exp(-ib_{IS}I_zS_zt)\,(I_y + S_y)\,\exp(ib_{IS}I_zS_zt) \tag{4.97}$$

Let's work out the evolution on spin I:

$$\exp(-ib_{IS}I_zS_zt)\,I_y\exp(ib_{IS}I_zS_zt) = I_y\cos(b_{IS}S_zt) - I_x\sin(b_{IS}S_zt)$$

If we apply Taylor expansion:

$$\cos(b_{IS}S_zt) = \sum_{n=0}^{\infty}\frac{(b_{IS}S_zt)^{2n}}{(2n)!} = \sum_{n=0}^{\infty}\frac{(b_{IS}t)^{2n}}{(2n)!}({S_z}^2)^n$$

Recall Eq. 4.13: ${S_z}^2 = \frac{1}{3}S^2 = \frac{S(S+1)}{3}$, so for spin $S = 1/2$, ${S_z}^2 = 1/4$, and we have:

$$\cos(b_{IS}S_zt) = \sum_{n=0}^{\infty}\frac{(b_{IS}t)^{2n}}{(2n)!}(\frac{1}{4})^n = \sum_{n=0}^{\infty}\frac{(b_{IS}t)^{2n}}{(2n)!}(\frac{1}{2})^{2n} = \sum_{n=0}^{\infty}\frac{(\frac{b_{IS}t}{2})^{2n}}{(2n)!} \tag{4.98}$$

$$\cos(b_{IS}S_zt) = \cos(\frac{b_{IS}t}{2})$$

Similarly, we can show:

$$\sin(b_{IS}S_zt) = \sum_{n=0}^{\infty}\frac{(b_{IS}S_zt)^{2n+1}}{(2n+1)!} = 2S_z\sum_{n=0}^{\infty}\frac{\frac{1}{2}(b_{IS}t)^{2n+1}(S_z)^{2n}}{(2n+1)!} \tag{4.99}$$

$$= 2S_z\sum_{n=0}^{\infty}\frac{\frac{1}{2}(b_{IS}t)^{2n+1}(\frac{1}{2})^{2n}}{(2n+1)!}$$

$$= 2S_z\sum_{n=0}^{\infty}\frac{(b_{IS}t)^{2n+1}(\frac{1}{2})^{2n+1}}{(2n+1)!} = 2S_z\sum_{n=0}^{\infty}\frac{(\frac{b_{IS}t}{2})^{2n+1}}{(2n+1)!} = 2S_z\sin(\frac{b_{IS}t}{2})$$

Hence, the evolution of I spin under the coupling of two nuclei is:

$$\exp(-ib_{IS}I_zS_zt)\,I_y\exp(ib_{IS}I_zS_zt) = I_y\cos(\frac{b_{IS}t}{2}) - 2S_zI_x\sin(\frac{b_{IS}t}{2}) \tag{4.100}$$

For each spin, the first term will contribute to detectable signals with sinusoidal oscillation. The second term, when sum up the trace in the subspace of S_z (Eq. 4.8 and 4.9), we get zero. Alternatively, you can visualize that for every eigenvalue of I_x, it couples with every eigenvalue of S_z with quantized values from $S, S-1$, to $-S$, hence there is always a positive S_z corresponding to a $-S_z$, which always averages to zero and does not contribute any observable signal.

Similarly, for S spin, the result will be:

$$\exp(-ib_{IS}I_zS_zt)\,S_y\exp(ib_{IS}I_zS_zt) = S_y\cos(\frac{b_{IS}t}{2}) - 2I_zS_x\sin(\frac{b_{IS}t}{2}) \tag{4.101}$$

If the density matrix was I_x after the RF pulse, we can show in the same way that for two spins that evolve under the coupling is:

$$\rho\left(t_{\frac{\pi}{2}}+t\right)=\exp(-ib_{IS}I_zS_zt)\,(I_x+S_x)\exp(ib_{IS}I_zS_zt) \tag{4.102}$$
$$=I_x\cos(\frac{b_{IS}t}{2})+2S_zI_y\sin\left(\frac{b_{IS}t}{2}\right)+S_x\cos\left(\frac{b_{IS}t}{2}\right)-2I_zS_y\sin(\frac{b_{IS}t}{2})$$

We will use the above derived formula to explain the common topics below.

4.8 Product operator formalism analysis of adiabatic demagnetization

In thermodynamics, there is an adiabatic cooling process/decompression of gaseous materials: first compress the gas in a container while maintaining good thermal contact with external reservoir at a constant temperature T. The generate heat by compression will be conducted away from the gas to the external reservoir. After compression, the gas in the container is still at temperature T. Then, we implement thermal isolation between the gas and the environments, so no heat exchange can take place. Meanwhile, we will let the gas freely expand. During this free expansion process, the gas will do work to the external environments, which according to the first law of thermodynamics is:

$$dU=\delta Q-\delta W=\delta Q-pdV \tag{4.103}$$

Since we are in an adiabatic process, $\delta Q=0$. Therefore, the free expansion will lead to a negative dU, which means the system loses its internal energy, and its temperature will decrease.

Adiabitic demagnetization is a same process in physics. When we apply an external magnetic field B to a paramagnetic or diamagnetic materials, the materials acquire magnetization M which otherwise does not exist. For an ensemble of non-interacting spins, we showed in Eq. 1.12 in Chapter 1:

$$M=\frac{N\gamma^2\hbar^2I(I+1)}{3kT}H_0$$

Where we used symbol H_0 to represent the magnetic field. In fact, here it should be B, the magnetic induction or magnetic flux intensity, as it measures the response of a medium to applied magnetic field H_0 induced by current in vacuum:

$$B=\mu_0(H+M)=\mu_0(1+\chi_m)H=\mu_0\mu_rH \tag{4.104}$$

Where χ_m is the susceptibility. H in physics is reserved for magnetic field strength, in the same unit as magnetization M, but it represents the magnetic field strength directly associated from electrical currents, in vacuum.

In simple words, when we set up a circuit and pass a current, it will produce H in vacuum. However, if there is non-vacuum medium around the current, this medium will respond to H by acquiring its own magnetization M, depending on its susceptibility. If it is diamagnetic material, the induced M will be opposing to H within the medium. If it is paramagnetic material, the induced M will be aligning in the same direction as H. The total field flux intensity B is the superposition of both the induced magnetization M and the raw external field H due to the current.

Well, the change of the induced magnetization within the material actually takes work, just like for gas, if you keep the pressure constant and change the volume.

The work associated with the process is:

$$\delta W =- BdM \tag{4.105}$$

So for a magnetic system, the first law of thermal dynamics is:

$$dU = \delta Q + BdM \tag{4.106}$$

Immediately we can construct a similar adiabatic cooling process in magnetic materials similar to ideal gas system. The magnetic material first undergoes an isothermal process to build up the magnetization inside the materials by applying a strong external field. Due to the isothermal condition, the system is maintained in good contact with a thermal reservoir, so the extra energy due to the increase of magnetization BdM leaks out as heat δQ to the heat reservoir, and the system is kept at a constant temperature so $dU = 0$.

When the system is magnetized to the maximum degree, the thermal contact is disconnected with the external reservoir to initiate an adiabatic process. Subsequently, the external magnetic field is gradually decreased to zero. In this process, the system will also lose its magnetization, which means that the system does work to the environment according to Eq. 4.105. With $\delta Q = 0$ at adiabatic condition, the system will lose internal energy $dU = \delta W =- BdM < 0$. And temperature of the system will get colder as a result.

The physics behind this explanation is the exchange of energy reserved in the Zeeman interaction form with the dipolar interaction of the spin system. Thus the adiabatic demagnetization process can be demonstrated by RF pulses, as shown by Jeener-Broekaert: with a 90_x and 45_x pulse separated by τ, an interval about the order of the spin spin lattice relaxation time T_2. The system before the change has the maximum order reserved in Zeeman field due to the alignment of spins along the applied magnetic field H_0, we can call this Zeeman order. After the pulse, we remove the magnetization in the material which is equal to the destroy of the Zeeman order, by transferring the order to the dipolar field $b_{IS}I_zS_z$.

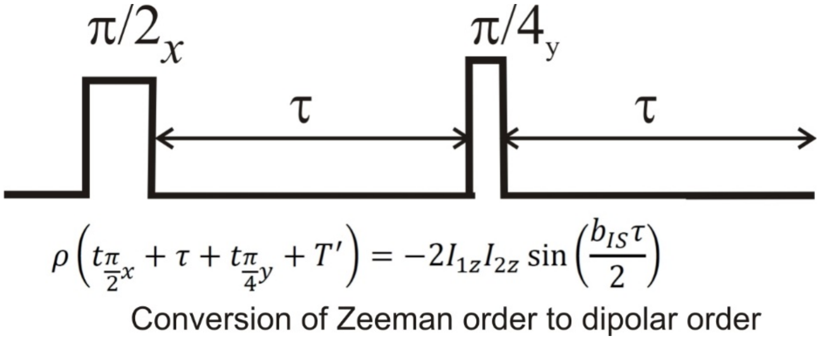


Figure 4.4. Conversion of Zeeman order to dipolar order by NMR pulses.

From Eq. 4.100 and 4.101, we know at time τ after the 90_x pulse, the system evolves under the H_c and becomes:

$$\rho\left(t_{\frac{\pi}{2}x}+\tau\right)=\exp(-ib_{IS}I_zS_z\tau)\left(I_y+S_y\right)\exp(ib_{IS}I_zS_z\tau)$$

$$=I_y\cos(\frac{b_{IS}\tau}{2})-2S_zI_x\sin\left(\frac{b_{IS}\tau}{2}\right)+S_y\cos\left(\frac{b_{IS}\tau}{2}\right)-2I_zS_x\sin(\frac{b_{IS}\tau}{2})$$

We can see that the magnetization along z direction is zero at this moment, so we destroyed the Zeeman order. However, we don't have the dipolar order yet. We do have $2S_zI_x\sin(\frac{b_{IS}\tau}{2})+2I_zS_x\sin(\frac{b_{IS}\tau}{2})$ terms due to the dipolar interaction.

To convert it into dipolar order, we need to change both terms to I_zS_z. If I and S are heteronuclei, we can do it by applying 90_y pulse on either nucleus channel. If we apply a 90_y pulse on I to convert the first term$-2S_zI_x\sin(\frac{b_{IS}\tau}{2})$ to $-2S_zI_z\sin(\frac{b_{IS}\tau}{2})$, the 90_y pulse on S will work on the second term and turn it into $-2I_xS_x\sin(\frac{b_{IS}\tau}{2})$. If I and S are homonuclear with the same gyromagnetic ratio, we can't apply a RF pulse to change the relative angle between the two as both will be affected simultaneously. Instead, we can apply a 45_y, and the system after the 45_y will become:

$$\rho\left(t_{\frac{\pi}{2}x}+\tau+t_{\frac{\pi}{4}y}\right)=\exp\left(i\frac{\pi}{4}I_y\right)\rho\left(t_{\frac{\pi}{2}}+\tau\right)\exp\left(-i\frac{\pi}{4}I_y\right)$$

$$=\exp\left(i\frac{\pi}{4}I_y\right)I_{y1}\exp\left(-i\frac{\pi}{4}I_y\right)\cos\left(\frac{b_{IS}\tau}{2}\right)-2\exp\left(i\frac{\pi}{4}I_y\right)I_{z1}I_{x2}\exp\left(-i\frac{\pi}{4}I_y\right)\sin\left(\frac{b_{IS}\tau}{2}\right)$$

$$+\exp\left(i\frac{\pi}{4}I_y\right)I_{y2}\exp\left(-i\frac{\pi}{4}I_y\right)\cos\left(\frac{b_{IS}\tau}{2}\right)-2\exp\left(i\frac{\pi}{4}I_y\right)I_{z2}I_{x1}\exp\left(-i\frac{\pi}{4}I_y\right)\sin(\frac{b_{IS}\tau}{2})$$

Here we switched I and S to I_1 and I_2 to indicate that they are the same spin species. You can apply similar analysis if I and S are different spins.

$$\rho\left(t_{\frac{\pi}{2}x}+\tau+t_{\frac{\pi}{4}y}\right)$$

$$= \cos\left(\frac{b_{IS}\tau}{2}\right)\left(I_{y1}+I_{y2}\right) - 2\sin\left(\frac{b_{IS}\tau}{2}\right)[\left(I_{z1}\cos\frac{\pi}{4} - I_{x1}\sin\frac{\pi}{4}\right)\left(I_{x2}\cos\frac{\pi}{4} + I_{z2}\sin\frac{\pi}{4}\right)$$
$$+ \left(I_{z2}\cos\frac{\pi}{4} - I_{x2}\sin\frac{\pi}{4}\right)\left(I_{x1}\cos\frac{\pi}{4} + I_{z1}\sin\frac{\pi}{4}\right)]$$

Recall that $\cos\frac{\pi}{4} = \sin\frac{\pi}{4} = \frac{\sqrt{2}}{2}$:

$$\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{4}y}\right) \tag{4.107}$$
$$= \cos\left(\frac{b_{IS}\tau}{2}\right)\left(I_{y1}+I_{y2}\right) - \sin\left(\frac{b_{IS}\tau}{2}\right)[(I_{z1}-I_{x1})(I_{x2}+I_{z2})$$
$$+ (I_{z2}-I_{x2})(I_{x1}+I_{z1})]$$

As most of solids exhibit $T_1 \gg T_2$, so any term containing I_x or I_y will diphase quickly by the spin spin relaxation. The terms with pure I_z terms will survive after T_2 and decay by the spin lattice relaxation. So after some additional time T', only dipolar order will survive and the system is:

$$\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{4}y} + T'\right) = -2I_{z1}I_{z1}\sin\left(\frac{b_{IS}\tau}{2}\right) \tag{4.108}$$

The maximal transfer will be achieved when $\sin\left(\frac{b_{IS}\tau}{2}\right) = 1$, which is $\tau = \frac{\pi}{b_{IS}}$.

However, this dipolar order does not induce observable NMR signal in quadrature detection for the same reason as we demonstrated earlier. To observe the dipolar order, we can convert the dipolar order back to Zeeman order by the reverse of the pulse sequence $45_{-y} - \tau - 90_{-x}$.

At the end of this pulse, we can add another 90_x pulse to observe the FID along y axis. However, this 90_x will cancel the preceding 90_{-x}. I will leave it as a homework for you to show that the detectable signal you will get is:

$$\rho(end) = -\frac{1}{2}(I_{y1}+I_{y2})\sin^2\left(\frac{b_{IS}\tau}{2}\right) \tag{4.109}$$

Which indicates the maximum efficiency is 1/2 of a direct FID detection from $I_{z1} + I_{z2}$, which is also the theoretical efficiency for a perfect adiabatic demagnetization.

How much cooling can we obtain from adiabatic demagnetization?

This can be proved by statistical thermodynamics. As the process is adiabatic, the entropy is conserved. According to thermodynamics, we do not have to solve the exact wave function of the state to evaluate the average observable/properties of a system, if we can evaluate its partition function Z:

$$Z = \sum_{i=1}^{n}\exp\left(-\frac{E_i}{kT}\right) = \sum_{i=1}^{n}\exp(-\beta E_i) \tag{4.110}$$

Here we replace $\frac{1}{kT}$ by β

Then the average energy of the system is:

$$\langle E\rangle = \frac{\sum_{i=1}^{n} E_i \exp(-\beta E_i)}{Z} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial \ln(Z)}{\partial\beta} \tag{4.111}$$

The entropy S is:

$$S = \frac{\langle E\rangle + kT\ln(Z)}{T} \tag{4.112}$$

In case of a system with Zeeman interaction as the dominant Hamiltonian, we can use the spin I_{zi}'s eigenstates to evaluate the system and treat other interactions as perturbations. This makes the evaluation of entropy as easy as the trace computation, which we did in Chapter 1 in the computation of magnetization, so:

$$E_i = -\gamma H_0 \sum_{i=1}^{N} I_{zi} \tag{4.113}$$

Here the trace involves the spin I_{zi} eigenstates of all N spins, in their joint outer product space. We can apply the high temperature approximation.

$$Z = \sum_{i=1}^{n} \exp(\beta\gamma H_0 I_{zi}) = Tr\{1 + \beta\gamma H_0 I_{zi} + \frac{1}{2}(\beta\gamma H_0 I_{zi})^2 + \cdots\} \tag{4.114}$$

$$Z = \sum_{i=1}^{n} \exp(\beta\gamma H_0 I_{zi}) = (2I+1)^N + \beta^2\gamma^2 {H_0}^2 \frac{I(I+1)}{6}$$

Here again all terms in odd power of I_{zi} will lead to $Tr\{\sum_{i=1}^{n} I_{zi}\} = 0$. Only even power terms will be nonzero due to the property in Eq.4.13: $I_{zi}^2 = \frac{1}{3}I(I+1)$.

If we include extra coupling between spins as:

$$\widehat{H_C} = b_{IS} I_z S_z$$

All the evaluation of Z, E and S will be the same format, just replace the system energy in Eq. 4.113:

$$E_i = -\gamma H_0 \sum_{i=1}^{N} I_{zi}$$

With:

$$E_i = -\gamma H_0 \sum_{i=1}^{N} I_{zi} + b_{IS} \sum_{i=1}^{N} \sum_{j=1}^{N} I_{zi} S_{zj} \tag{4.115}$$

We can take the same approach as in Eq. 4.113 to do a Taylor expansion in the high temperature approximation. The linear terms of I_{zi} or S_{zj} again become zero and only the quadratic terms remain in the approximation:

$$Z = \sum_{i=1}^{n} \exp(\beta\gamma H_0 E_i)$$

$$= (2I+1)^N + (2S+1)^N$$

$$+\beta^2 \left[N_I \gamma_I^2 {H_0}^2 \frac{I(I+1)}{6} + N_S \gamma_S^2 {H_0}^2 \frac{S(S+1)}{6} + N b_{IS}^2 \frac{I(I+1)S(S+1)}{18} \right]$$

$$Z = (2I+1)^N + (2S+1)^N + \frac{\beta^2}{2} \left[C_I {H_0}^2 + C_S {H_0}^2 + N b_{IS}^2 \frac{I(I+1)S(S+1)}{9} \right] \tag{4.116}$$

Here we have the Curie coefficients defined as:

$$C_I = N_I \gamma_I^2 {H_0}^2 \frac{I(I+1)}{6}, C_S = N_S \gamma_S^2 {H_0}^2 \frac{S(S+1)}{6} \tag{4.117}$$

Therefore, we can insert the expression of Z in Eq. 4.116 back to Eq. 4.111 to compute the system energy:

$$\langle E \rangle = -\beta \left[C_I {H_0}^2 + C_S {H_0}^2 + N b_{IS}^2 \frac{I(I+1)S(S+1)}{18} \right] \tag{4.118}$$

And we can insert Z in Eq. 4.116 back to Eq. 4.112 to compute the system entropy:

$$S = \frac{\langle E \rangle + \mathrm{kTln}(Z)}{T} \tag{4.119}$$

$$= -\frac{1}{T^2} \left[C_I {H_0}^2 + C_S {H_0}^2 + N b_{IS}^2 \frac{I(I+1)S(S+1)}{18} \right] + k ln\{(2I+1)^{N_I} + (2S+1)^{N_S}$$

$$+\frac{\beta^2}{2} \left[C_I {H_0}^2 + C_S {H_0}^2 + N b_{IS}^2 \frac{I(I+1)S(S+1)}{9} \right]\}$$

Note for the ln{} term, the first two terms $(2I+1)^{N_I}+(2S+1)^{N_S}$will be much greater than the remaining term, as the spin numbers in normal system are astronomically large. So we can say:

$$S=-\frac{1}{T^2}\left[C_I{H_0}^2+C_S{H_0}^2+Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}\right] \\ +kln\{(2I+1)^{N_I}+(2S+1)^{N_s}\} \tag{4.120}$$

We assume at the beginning of adiabatic demagnetization the temperature is T_i, and at the end of the process the temperature is T_f. As entropy is conserved in the process, we should have:

$$\frac{1}{T_i^2}\left[C_I{H_{0i}}^2+C_S{H_{0i}}^2+Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}\right] \\ =\frac{1}{T_f^2}\left[C_I{H_{0f}}^2+C_S{H_{0f}}^2+Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}\right]$$

$$\frac{T_f}{T_i}=\sqrt{\frac{C_I{H_{0f}}^2+C_S{H_{0f}}^2+Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}}{C_I{H_{0i}}^2+C_S{H_{0i}}^2+Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}}} \tag{4.121}$$

Hence, if we replace corresponding adiabatic demagnetization condition $H_{0i}=H_0, H_{0f}=0$:

$$\frac{T_f}{T_i}=\sqrt{\frac{Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}}{(C_I+C_S){H_0}^2+Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}}} \tag{4.122}$$

In addition, if we can satisfy $(C_I+C_S)H_0 \gg Nb_{IS}^2\frac{I(I+1)S(S+1)}{18}$, we will be able to cool the system to orders of magnitude lower than the initial temperature.

We note that $C_I=N\gamma_I^2\hbar^2{H_0}^2\frac{I(I+1)}{3}$ and $C_S=N\gamma_S^2\hbar^2{H_0}^2\frac{S(S+1)}{3}$ are just the Curie coefficient, which we can't change. However, if the interaction between I an S are dipolar:

$$b_{IS}=\frac{\hbar\gamma_I\gamma_S}{r^3}$$

It involves the separation between I and S. Therefore, in dilution fridge, we can increase the separation between ^{3}He (spin ½) by adding ^{4}He (spin 0) into ^{3}He to a mixture of about 93% ^{4}He and 7% ^{3}He, this helps reduces the coupling between ^{3}He, and combined with adiabatic demagnetization, the setup can be cooled to even lower temperature.

4.9 Product operator formalism analysis of Solid Echo

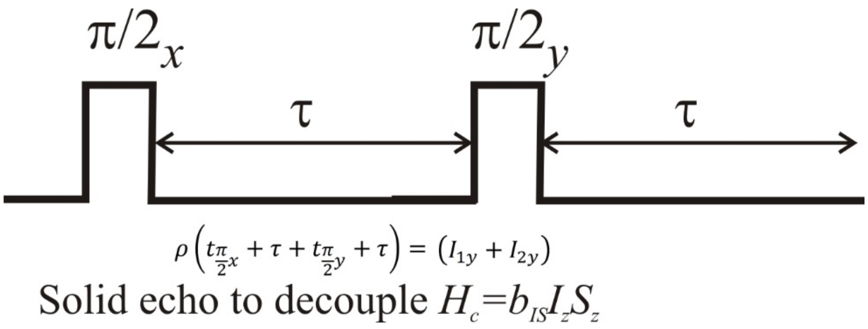


Figure 4.5. Solid Echo pulse sequence to decouple effect of internuclear interaction.

The solid echo technique with $90_x - \tau - 90_y$was discovered by Powles and Mansfield (Phys. Lett 2, 8 (1962)). In contrast to the Hahn Echo, the solid echo is to refocus the dipolar field, and also can be used to refocus quadrupolar interactions for spin-1 nuclei such as deuterium. We will demonstrate how this is achieved by the solid echo. Similarly, we pick up the system at time τ after 90_x, the system density matrix is:

$$\rho\left(t_{\frac{\pi}{2}x} + \tau\right) = \exp(-ib_{IS}I_{1z}I_{2z}\tau)\left(I_{1y} + I_{2y}\right)\exp\left(ib_{IS}I_zSI_{1z}I_{2z_z}\tau\right) \quad (4.123)$$
$$= \left(I_{1y} + I_{2y}\right)\cos(\frac{b_{IS}\tau}{2}) - 2\sin\left(\frac{b_{IS}\tau}{2}\right)(I_{1z}I_{2x} + I_{2z}I_{1x})$$

With the application of 90_y:

$$\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}y}\right) \quad (4.124)$$
$$= \exp\left(i\frac{\pi}{2}I_y\right)\left(I_{1y} + I_{2y}\right)\exp\left(-i\frac{\pi}{2}I_y\right)\cos\left(\frac{b_{IS}\tau}{2}\right)$$
$$-2\sin\left(\frac{b_{IS}\tau}{2}\right)\exp\left(i\frac{\pi}{2}I_y\right)(I_{1z}I_{2x} + I_{2z}I_{1x})\exp\left(-i\frac{\pi}{2}I_y\right)$$

$$= \left(I_{1y} + I_{2y}\right)\cos\left(\frac{b_{IS}\tau}{2}\right) - 2\sin\left(\frac{b_{IS}\tau}{2}\right)(-I_{1z}I_{2x} - I_{2z}I_{1x})$$

$$= \left(I_{1y} + I_{2y}\right)\cos\left(\frac{b_{IS}\tau}{2}\right) + 2\sin\left(\frac{b_{IS}\tau}{2}\right)(I_{1z}I_{2x} + I_{2z}I_{1x})$$

Here we see the signs for the two operator terms are reversed. After another time t, the system evolves under dipolar interaction:

$$\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}y} + t\right) \quad (4.125)$$
$$= \exp(-ib_{IS}I_{1z}I_{2z}t)\left(I_{1y} + I_{2y}\right)\exp(ib_{IS}I_{1z}I_{2z}t)\cos\left(\frac{b_{IS}\tau}{2}\right)$$
$$+2\sin\left(\frac{b_{IS}\tau}{2}\right)\exp(-ib_{IS}I_{1z}I_{2z}t)\,(I_{1z}I_{2x} + I_{2z}I_{1x})\exp(ib_{IS}I_{1z}I_{2z}t)$$

$$= \cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)(I_{1y}+I_{2y}) - 2\sin\left(\frac{b_{IS}t}{2}\right)\cos\left(\frac{b_{IS}\tau}{2}\right)(I_{1z}I_{2x}+I_{2z}I_{1x})$$

$$+2\sin\left(\frac{b_{IS}\tau}{2}\right)\left[I_{1z}\left(I_{2x}\cos\left(\frac{b_{IS}t}{2}\right) + 2\sin\left(\frac{b_{IS}t}{2}\right)I_{1z}I_{2y}\right) + I_{2z}\left(I_{1x}\cos\left(\frac{b_{IS}t}{2}\right)\right.\right.$$

$$\left.\left. +2\sin\left(\frac{b_{IS}t}{2}\right)I_{2z}I_{1y}\right)\right]$$

Recall for spin ½ nuclei $I_z^2 = \frac{1}{4}$

$$= \cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)(I_{1y}+I_{2y}) - 2\sin\left(\frac{b_{IS}t}{2}\right)\cos\left(\frac{b_{IS}\tau}{2}\right)(I_{1z}I_{2x}+I_{2z}I_{1x})$$

$$+2\sin\left(\frac{b_{IS}\tau}{2}\right)[I_{1z}I_{2x}\cos\left(\frac{b_{IS}t}{2}\right) + 2\sin\left(\frac{b_{IS}t}{2}\right)I_{2y}I_{1z}^2) + I_{2z}I_{1x}\cos\left(\frac{b_{IS}t}{2}\right) + 2\sin\left(\frac{b_{IS}t}{2}\right)I_{1y}I_{2z}^2)]$$

$$= \cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)(I_{1y}+I_{2y}) - 2\sin\left(\frac{b_{IS}t}{2}\right)\cos\left(\frac{b_{IS}\tau}{2}\right)(I_{1z}I_{2x}+I_{2z}I_{1x})$$

$$+2\sin\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)[I_{1z}I_{2x}+I_{2z}I_{1x}] + \sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)(I_{1y}+I_{2y})$$

When $t = \tau$, we have:

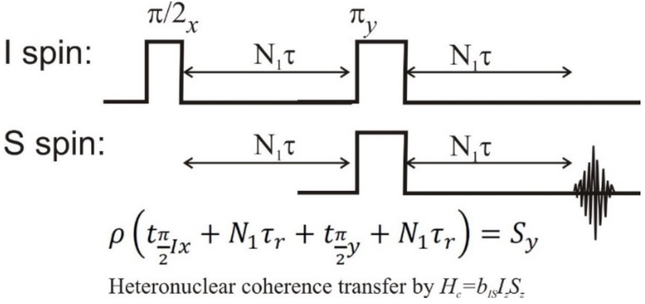
$$\begin{gathered} \rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}y} + \tau\right) \\ = \cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}\tau}{2}\right)(I_{1y}+I_{2y}) + \sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}\tau}{2}\right)(I_{1y}+I_{2y}) \\ = (I_{1y}+I_{2y}) \end{gathered} \tag{4.127}$$

Thus we completely removed the influence of dipolar field (so called refocus of the interaction).

Homework: if we concatenate another pair of $\tau - 90_{-y} - \tau - 90_{-x}$ after the solid echo, we get $\tau - 90_x - \tau - 90_y - 2\tau - 90_{-y} - \tau - 90_{-x} - \tau$, which is the famous WHUHA(named after Waugh, Huber, Haberlen) sequence for decoupling of dipolar interaction in solids. Can you work out the rest for WAHUHA.

4.10 Product operator formalism analysis of heteronuclear coherence transfer

Figure 4.6.Pulse seuqnce for heteronuclear coherence transfer by internuclear coupling.



For heteronuclear coherence transfer, we have a number of pulse sequences, such as INEPT (G. A. Morris and R. Freeman, JACS 101, 760-762 (1979)) via J coupling, or TEDOR(A.W. Hing, S. Vega, and J. Schaefer, JMR 96, 205-209 (1992)) via dipolar coupling. The physics of these sequences is the same. TEDOR is the back to back of REDOR (T. Guallion and J.Schaefer, JMR 81,196-200 (1989)) sequence: at Magic Angel Spinning, a series of rotor synchronized π pulses applied on the S spin channel recouples the dipolar interaction between I and S spins. This lasts a period of time $N_1\tau_r$. Then a π pulse is applied on the I spin in the middle of the sequence to refocus the chemical shifts without affecting the coupling between I and S, and followed by another series of rotor synchronized π pulses applied on the S spin channel in time $N_2\tau_r$. Assume at the beginning of the sequence we had a -90_x rotation (if the gyromagnetic ratio is positive, this needs apply the H_1 field along –x) on I spin so after the pulse the system is prepared with magnetization of I spin along y.

$$\rho\left(t_{\frac{\pi}{2}Ix}\right) = I_y$$

During $N_1\tau_r$, the dipolar interaction or J coupling is alive and evolves the density matrix:

$$\begin{aligned}\rho\left(t_{\frac{\pi}{2}Ix} + N_1\tau_r\right) &= \exp(-ib_{IS}I_zS_zt)\, I_y \exp(ib_{IS}I_zS_zt) \\ &= I_y \cos\left(\frac{b_{IS}N_1\tau_r}{2}\right) - 2S_zI_x \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\end{aligned} \tag{4.128}$$

Then the system is hit by a 90_y rotation on S channel and a 90_y on I channel simultaneously:

$$\rho\left(t_{\frac{\pi}{2}Ix} + N_1\tau_r + t_{\frac{\pi}{2}y}\right) = I_y \cos\left(\frac{b_{IS}N_1\tau_r}{2}\right) + 2S_xI_z \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right) \tag{4.129}$$

Then the system undergoes another $N_2\tau_r$ period of evolution under the coupling between I and S:

$$\begin{gathered}\rho\left(t_{\frac{\pi}{2}Ix} + N_1\tau_r + t_{\frac{\pi}{2}y} + N_2\tau_r\right) \\ = \exp(-ib_{IS}I_zS_zt)\, I_y \exp(ib_{IS}I_zS_zt) \cos\left(\frac{b_{IS}N_1\tau_r}{2}\right) \\ +2\exp(-ib_{IS}I_zS_zt)\, S_xI_z \exp(ib_{IS}I_zS_zt) \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\end{gathered} \tag{4.130}$$

$$\begin{gathered}= \cos\left(\frac{b_{IS}N_1\tau_r}{2}\right)\left[I_y \cos\left(\frac{b_{IS}N_2\tau_r}{2}\right) - 2S_zI_x \sin\left(\frac{b_{IS}N_2\tau_r}{2}\right)\right] \\ +2\sin\left(\frac{b_{IS}N_1\tau_r}{2}\right) I_z\left[S_x \cos\left(\frac{b_{IS}N_2\tau_r}{2}\right) + 2S_yI_z \sin\left(\frac{b_{IS}N_2\tau_r}{2}\right)\right] \\ = I_y \cos\left(\frac{b_{IS}N_1\tau_r}{2}\right)\cos\left(\frac{b_{IS}N_2\tau_r}{2}\right) - 2S_zI_x \sin\left(\frac{b_{IS}N_2\tau_r}{2}\right)\cos\left(\frac{b_{IS}N_1\tau_r}{2}\right) \\ +2I_zS_x \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\cos\left(\frac{b_{IS}N_2\tau_r}{2}\right) + 4S_yI_z^2 \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\sin\left(\frac{b_{IS}N_2\tau_r}{2}\right)\end{gathered}$$

Again we have $I_z^2 = \frac{1}{4}$ for spin ½ nuclei, so

$$\rho\left(t_{\frac{\pi}{2}Ix} + N_1\tau_r + t_{\frac{\pi}{2}y} + N_2\tau_r\right)$$

$$= I_y \cos\left(\frac{b_{IS}N_1\tau_r}{2}\right)\cos\left(\frac{b_{IS}N_2\tau_r}{2}\right) - 2S_zI_x \sin\left(\frac{b_{IS}N_2\tau_r}{2}\right)\cos\left(\frac{b_{IS}N_1\tau_r}{2}\right)$$

$$+2I_zS_x \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\cos\left(\frac{b_{IS}N_2\tau_r}{2}\right) + S_y \sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\sin\left(\frac{b_{IS}N_2\tau_r}{2}\right)$$

The middle two terms do not contribute to any detectable signals due to the traceless spin I_z and S_z. The last term is the coherence on S spin transferred from *I* spin. It reaches maximum transfer efficiency when $N_1\tau_r = N_2\tau_r$, since

$$\sin\left(\frac{b_{IS}N_1\tau_r}{2}\right)\sin\left(\frac{b_{IS}N_2\tau_r}{2}\right) = \frac{1}{2}[\cos b_{IS}\tau_r(N_1 - N_2) - \cos b_{IS}\tau_r(N_1 + N_2)]$$

Hence we have:

$$\rho\left(t_{\frac{\pi}{2}Ix} + N_1\tau_r + t_{\frac{\pi}{2}y} + N_1\tau_r\right) \tag{4.131}$$

$$= I_y\left[\frac{1+\cos(N_1b_{IS}\tau_r)}{2}\right] + \sin(b_{IS}N_1\tau_r)\,(I_zS_x - S_zI_x)$$

$$+ S_y\left[\frac{1-\cos(N_1b_{IS}\tau_r)}{2}\right]$$

$$= I_y\cos^2(\frac{N_1b_{IS}\tau_r}{2}) + \sin(b_{IS}N_1\tau_r)\,(I_zS_x - S_zI_x) + S_y\sin^2(\frac{N_1b_{IS}\tau_r}{2})$$

If we have the interaction recoupled period $N_1\tau_r$ satisfies: $N_1b_{IS}\tau_r = \pi$, we get $\cos(N_1b_{IS}\tau_r) = -1$ and

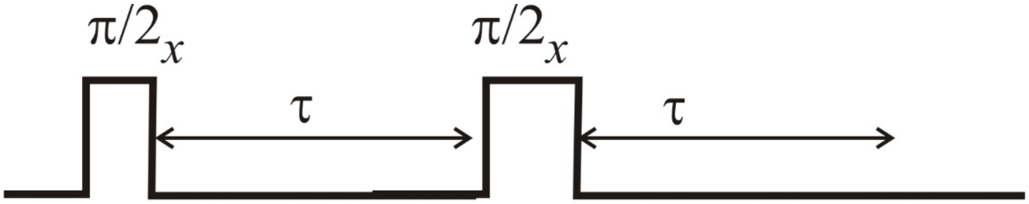
$$\sin(b_{IS}N_1\tau_r) = 0$$

So:

$$\rho\left(t_{\frac{\pi}{2}Ix} + N_1\tau_r + t_{\frac{\pi}{2}y} + N_1\tau_r\right) = S_y$$

There are various motivations for the coherence transfer. For example, *S* spin has a larger gyromagnetic ratio, and thus is more sensitive for detection. Or reversely, *I* spin has a larger gyromagnetic ratio or more abundant, but two strong coupling among *I* spins leave *I* channel not suitable for high resolution detection, and transfer the larger magnetization to *S* spin for detection with enhanced signals compared to direct detection from *S* channel.

4.11 Product operator formalism analysis of multiquantum coherence excitation and conversion



$$\rho\left(t_{\frac{\pi}{2}x}+\tau+t_{\frac{\pi}{2}x}\right)=-\cos\left(\frac{b_{IS}\tau}{2}\right)(I_z+S_z)+i\sin\left(\frac{b_{IS}\tau}{2}\right)(I^+S^+-\ I^-S^-)$$

Double quantum coherence excitation by $H_c=b_{IS}I_zS_z$

Figure 4.7. Excitation of double quantum coherence using internuclear coupling.

After a $\frac{\pi}{2}$ pulse on two spins, from the above derivations, two spins will evolve under the interactions between each other:

$$\rho\left(t_{\frac{\pi}{2}x}+\tau\right)=\exp(-ib_{IS}I_zS_z\tau)\left(I_y+S_y\right)\exp(ib_{IS}I_zS_z\tau) \tag{4.132}$$
$$=I_y\cos(\frac{b_{IS}\tau}{2})-2S_zI_x\sin\left(\frac{b_{IS}\tau}{2}\right)+S_y\cos\left(\frac{b_{IS}\tau}{2}\right)-2I_zS_x\sin(\frac{b_{IS}\tau}{2})$$

The second term and the fourth term are a mixture of two spins, but the operator I_z is zero quantum. So they are not double quantum. In fact, as we will show in Chapter 5, they can be decomposed into quantum 1 component (single quantum) of the rank 2 tensor formed by two spins.

Before we show how to convert these terms into double quantum, let's first see what is double quantum. Recall our work in the decomposition of dipolar interaction in Sect. 4.6:

$$I^+S^+ +\ I^-S^-=\left(I_x+iI_y\right)\left(S_x+iS_y\right)+\left(I_x-iI_y\right)\left(S_x-iS_y\right) \tag{4.133}$$
$$=2(I_xS_x-I_yS_y\ )$$

This is a double quantum operator. It flips or flops the spins to induce simultaneous change of the spin z component quantum by 1 for both spins.

$$I^+S^- +\ I^-S^+=\left(I_x+iI_y\right)\left(S_x-iS_y\right)+\left(I_x-iI_y\right)\left(S_x+iS_y\right) \tag{4.134}$$
$$=2(I_xS_x+I_yS_y\ )$$

This a zero quantum operator. It simultaneously flips one spin and flops the other spin so the combined change of spin z component quantum number is zero.

Now similarly, we can introduce another set of operators with reversed signs between the terms:

$$I^+S^+ -\ I^-S^-=\left(I_x+iI_y\right)\left(S_x+iS_y\right)-\left(I_x-iI_y\right)\left(S_x-iS_y\right) \tag{4.135}$$
$$=2i(I_xS_y+I_yS_x\ )$$

This is another double quantum operator. Similarly:

$$\begin{aligned} I^+S^- - I^-S^+ &= (I_x + iI_y)(S_x - iS_y) - (I_x - iI_y)(S_x + iS_y) \\ &= 2i(I_yS_x - I_xS_y) \end{aligned} \tag{4.136}$$

This is another zero quantum operator.

We can show that if we define:

$$\begin{aligned} I_2^x &= \frac{1}{2}(I^+S^+ + I^-S^-) = I_xS_x - I_yS_y \\ I_2^y &= \frac{1}{2i}(I^+S^+ - I^-S^-) = I_xS_y + I_yS_x \end{aligned} \tag{4.137}$$

Then, you can use the commutation relationship of spin I and S to prove:

$$[I_2^x, I_2^y] = \frac{i}{2}(I_z + S_z) \tag{4.138}$$

If we define:

$$I_2^z = \frac{1}{2}(I_z + S_z) \tag{4.139}$$

You can prove again that this set of operators satisfy:

$$[I_2^i, I_2^j] = i\hbar\varepsilon_{ijk}I_2^k, i, j, k = x, y, z \tag{4.140}$$

This means that this set of operators form a complete subspace themselves, just like the single spin operator set I_x, I_y and I_z.

As I_2^x and I_2^y operators consist of terms for simultaneous flipping or flopping of two spins that lead to the combined change of spin z component quantum number equal to 2, we say that this set of operators comprise a fictitious double quantum subspace, just like the single spin operator set I_x, I_y and I_z span their own single quantum space. Their eigenstates form a complete orthonomal basis of this subspace.

Likewise, we can construct a fictitious zero quantum subspace by two spins with a set of spin operators:

$$\begin{aligned} I_0^x &= \frac{1}{2}(I^+S^- + I^-S^+) = I_xS_x + I_yS_y \\ I_0^y &= \frac{1}{2i}(I^+S^- - I^-S^+) = I_yS_x - I_xS_y \\ I_0^z &= \frac{1}{2}(I_z - S_z) \end{aligned} \tag{4.141}$$

Here we call this set of operators span a zero quantum subspace, because I_0^x and I_0^y operators consist of terms of simultaneous flipping and flopping two spins that lead to the combined change of spin z component quantum number equal to 0. And you can also prove:

$$[I_0^i, I_0^j] = i\hbar\varepsilon_{ijk}I_0^k, i, j, k = x, y, z \tag{4.142}$$

Therefore, we will can excite double quantum from Eq. 4.132, if we can convert the second and fourth term $-2S_zI_x\sin\left(\frac{b_{IS}\tau}{2}\right) - 2I_zS_x\sin(\frac{b_{IS}\tau}{2})$ into $I_xS_y + I_yS_x$.

To do so, we can apply a 90_x, which will not touch the spin x component, but flip spin z component into y:

$$\begin{gathered}\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x}\right) \\ = \exp(i\frac{\pi}{2}I_x)\exp(i\frac{\pi}{2}S_x)\rho\left(t_{\frac{\pi}{2}x} + \tau\right)\exp(-i\frac{\pi}{2}I_x)\exp(-i\frac{\pi}{2}S_x) \\ = \exp\left(i\frac{\pi}{2}I_x\right)I_y\exp\left(-i\frac{\pi}{2}I_x\right)\cos\left(\frac{b_{IS}\tau}{2}\right) - 2\exp\left(i\frac{\pi}{2}S_x\right)S_zI_x\exp\left(-i\frac{\pi}{2}S_x\right)\sin\left(\frac{b_{IS}\tau}{2}\right) \\ +\exp(i\frac{\pi}{2}S_x)S_y\cos\left(\frac{b_{IS}\tau}{2}\right)\exp(-i\frac{\pi}{2}S_x) - 2\exp(i\frac{\pi}{2}I_x)I_zS_x\exp(-i\frac{\pi}{2}I_x)\sin(\frac{b_{IS}\tau}{2})\end{gathered} \tag{4.143}$$

Here we dropped respective evolution operator of I or S when they commute with all the operators. After a bit of rearrangements, we have:

$$\begin{gathered}\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x}\right) = -\cos\left(\frac{b_{IS}\tau}{2}\right)(I_z + S_z) - 2\sin\left(\frac{b_{IS}\tau}{2}\right)\left(S_yI_x + I_yS_x\right) \\ = -\cos\left(\frac{b_{IS}\tau}{2}\right)(I_z + S_z) + i\sin\left(\frac{b_{IS}\tau}{2}\right)(I^+S^+ - I^-S^-)\end{gathered} \tag{4.144}$$

Where the second term now corresponds to double quantum transitions, since each of the operator pairs changes the total spin z quantum number by two.

However, as we demonstrated earlier, only -1 single quantum can be detected. So we can let the double quantum evolve for some time. This creates an indirect dimension where coupled spins will evolve under the joint chemical shifts of double quantum first. Then we need to convert the double quantum back into -1 single quantum for detection, which all we need is the reverse what we did in the creation of this double quantum, with a 90_{-x} pulse.

If we let the system in double quantum evolve for time t' under the coupling:

$$\begin{gathered}\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x} + t'\right) \\ = \exp(-ib_{IS}I_zS_zt')\left[-\cos\left(\frac{b_{IS}\tau}{2}\right)(I_z + S_z)\right. \\ \left.+i\sin\left(\frac{b_{IS}\tau}{2}\right)(I^+S^+ - I^-S^-)\right]\exp(ib_{IS}I_zS_zt')\end{gathered} \tag{4.145}$$

$$= \exp(-ib_{IS}I_zS_zt')\left[-\cos\left(\frac{b_{IS}\tau}{2}\right)(I_z + S_z)\right.$$
$$\left.-2\sin\left(\frac{b_{IS}\tau}{2}\right)\left(S_yI_x + I_yS_x\right)\right]\exp(ib_{IS}I_zS_zt')$$

The term $I_z + S_z$ commutes with I_zS_z, so they will not be affected, and remain the same after t'.

For the second term, it will not be affected either, since it is double quantum, we can work it out using

$$\exp(-ib_{IS}I_zS_zt')\left(S_yI_x + I_yS_x\right)\exp(ib_{IS}I_zS_zt')$$
$$= \left[S_y\cos\left(\frac{b_{IS}t'}{2}\right) - 2I_zS_x\sin\left(\frac{b_{IS}t'}{2}\right)\right]\left[I_x\cos\left(\frac{b_{IS}t'}{2}\right) + 2S_zI_y\sin\left(\frac{b_{IS}t'}{2}\right)\right]$$
$$+\left[I_y\cos\left(\frac{b_{IS}t'}{2}\right) - 2S_zI_x\sin\left(\frac{b_{IS}t'}{2}\right)\right]\left[S_x\cos\left(\frac{b_{IS}t'}{2}\right) + 2I_zS_y\sin\left(\frac{b_{IS}t'}{2}\right)\right]$$
$$= \left(S_yI_x + I_yS_x\right)\cos^2\left(\frac{b_{IS}t'}{2}\right) - 2\sin\left(\frac{b_{IS}t'}{2}\right)\cos\left(\frac{b_{IS}t'}{2}\right)\left(S_yS_zI_y - I_zS_xI_x + I_yI_zS_y - S_zI_xS_x\right)$$
$$-4\sin^2\left(\frac{b_{IS}t'}{2}\right)(I_zS_xS_zI_y + S_zI_xI_zS_y)$$

Now recall:

$$I_iI_j = \frac{i}{2}\hbar\varepsilon_{ijk}I_k$$

We can show:

$$S_yS_zI_y - I_zS_xI_x + I_yI_zS_y - S_zI_xS_x = \frac{i}{2}(S_xI_y - I_yS_x + I_xS_y - I_xS_y) = 0$$
$$I_zS_xS_zI_y + S_zI_xI_zS_y = \frac{i}{2}I_x\frac{i}{2}S_y + \frac{i}{2}S_x\frac{i}{2}I_y = -\frac{1}{4}(I_xS_y + S_xI_y)$$

Therefore

$$\exp(-ib_{IS}I_zS_zt')\left(S_yI_x + I_yS_x\right)\exp(ib_{IS}I_zS_zt') = \left(S_yI_x + I_yS_x\right)\left[\cos^2\left(\frac{b_{IS}t'}{2}\right) + \sin^2\left(\frac{b_{IS}t'}{2}\right)\right]$$
$$= S_yI_x + I_yS_x$$

Which shows the double quantum operator is not affected by the I_zS_z interaction. Hence,

$$\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x} + t'\right) \tag{4.146}$$
$$= -\cos\left(\frac{b_{IS}\tau}{2}\right)(I_z + S_z) + i\sin\left(\frac{b_{IS}\tau}{2}\right)(I^+S^+ - I^-S^-)$$

To convert double quantum back into single quantum, we just have to reverse the process by applying 90_{-x}.

$$\begin{aligned}
&\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x} + t' + t_{-\frac{\pi}{2}x}\right) \\
&= -\cos\left(\frac{b_{IS}\tau}{2}\right)\exp\left(-i\frac{\pi}{2}I_x\right)(I_z + S_z)\exp\left(i\frac{\pi}{2}I_x\right) \\
&+i\sin\left(\frac{b_{IS}\tau}{2}\right)\exp\left(-i\frac{\pi}{2}I_x\right)(I^+S^+ - \ I^-S^-)\exp\left(i\frac{\pi}{2}I_x\right) \\
&= -\cos\left(\frac{b_{IS}\tau}{2}\right)\left(I_y + S_y\right) - 2\sin\left(\frac{b_{IS}\tau}{2}\right)(S_zI_x + I_zS_x)
\end{aligned} \tag{4.147}$$

Then they will evolve again under I_zS_z interaction in time t:

$$\rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x} + t' + t_{-\frac{\pi}{2}x} + t\right)$$

$$= \exp(-ib_{IS}I_zS_zt)\ \rho\left(t_{\frac{\pi}{2}x} + \tau + t_{\frac{\pi}{2}x} + t' + t_{-\frac{\pi}{2}x}\right)\exp(ib_{IS}I_zS_zt))$$

$$= -\cos\left(\frac{b_{IS}\tau}{2}\right)\left\{\left[I_y\cos\left(\frac{b_{IS}t}{2}\right) - 2S_zI_x\sin\left(\frac{b_{IS}t}{2}\right)\right] + \left[S_y\cos\left(\frac{b_{IS}t}{2}\right) - 2I_zS_x\sin\left(\frac{b_{IS}t}{2}\right)\right]\right\}$$

$$-2\sin\left(\frac{b_{IS}\tau}{2}\right)\left\{S_z\left[I_x\cos\left(\frac{b_{IS}t}{2}\right) + 2S_zI_y\sin\left(\frac{b_{IS}t}{2}\right)\right] + I_z\left[S_x\cos\left(\frac{b_{IS}t}{2}\right) + 2I_zS_y\sin\left(\frac{b_{IS}t}{2}\right)\right]\right\}$$

$$= -\cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)\left(I_y + S_y\right) - 2\cos\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)(S_zI_x + I_zS_x)$$

$$-2\sin\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)(S_zI_x + I_zS_x) - 4\sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)(S_z^2I_y + I_z^2S_y)$$

Again we have $I_z^2 = \frac{1}{4}$ for spin ½ nuclei:

$$= -\cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right)\left(I_y + S_y\right) - 4\cos\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)(S_zI_x + I_zS_x)$$

$$-\sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)\left(I_y + S_y\right)$$

$$= -\left(I_y + S_y\right)\left[-\cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right) - \sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)\right]$$

$$-4\cos\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)(S_zI_x + I_zS_x)$$

Among the terms, the last term won't contribute signals since they have trace zero spin z terms involved.

$$= \left(I_y + S_y\right)\left[-\cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right) - \sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right)\right]$$

$$= -\left(I_y + S_y\right)\cos\left(\frac{b_{IS}(\tau - t)}{2}\right)$$

So when $\tau = t$, the signal will reach maximal at the y axis, which is called a Stimulated Echo.

Among the total amplitude, the contribution from the converted double quantum is:

$$-\sin\left(\frac{b_{IS}\tau}{2}\right)\sin\left(\frac{b_{IS}t}{2}\right) = -\sin^2\left(\frac{b_{IS}\tau}{2}\right) = \frac{1}{2}[\cos(b_{IS}\tau) - 1]$$

It reaches maximal when $b_{IS}\tau = \pi,\ \ \tau = \frac{\pi}{b_{IS}}$. At this value, $-\cos\left(\frac{b_{IS}\tau}{2}\right)\cos\left(\frac{b_{IS}t}{2}\right) = -\cos^2\left(\frac{b_{IS}\tau}{2}\right) = \frac{1}{2}[\cos(b_{IS}\tau) + 1] = 0$. So the signal comes entirely from converted double quantum.

Conversely, when $b_{IS}\tau = 2\pi, \tau = \frac{2\pi}{b_{IS}}$, we get zero contribution from double quantum in the stimulated echo, but entirely from the single quantum.

In real experiments, we may have atoms bonded by either dipolar or J coupling, or any kinds coupling in the form of $H_C = b_{IS}I_zS_z$. We can exploit the above demonstrated methods of solid echo to refocus the interaction (decouple), to transfer the coherence from one to the other, and to generate double quantum.

We note in real scenarios; the coupling constant may not be a unique value for all coupled atoms in the system. For example, in dipolar coupled system, the coupling constant is $b_{IS} = \frac{\hbar\gamma_I\gamma_S}{r^3}$ (in cgs unit. If you like SI unit, $b_{IS} = \frac{\mu_0\hbar\gamma_I\gamma_S}{4\pi r^3}$). Therefore, between pairs of spins at different separations, the coupling strength b_{IS} will be different, which means you can't use a single τ to optimize the sequence for all coupled sites. Either you selectively maximize a specific pair, or you make compromise for a majority. Hence, you can use this to differentiate/count a certain pairs in the compounds. In general, the weaker the coupling, the longer τ it takes to build up the signal. If there is additional coupling that can lead to a fast spin spin relaxation, we may need to apply corresponding decoupling sequence to attenuate that relaxation effect.

What about the resonance offset, or spins with non identical chemical shifts?

Recall in normal 2D correlation experiments, the transverse magnetization of single quantum will precess freely in the indirect dimension. Here we have left the double quantum y to precess freely in the indirect dimension(well, we need to increment the indirect dimension if it were actually a 2D experiment). To generalize our discussing, the system evolves in the indirect dimension under multiple quantum operators (with order $p = 1,2,3,\ldots$). Therefore, the density matrix can be represented by the corresponding multiple quantum spin operators.

The effect of non identical chemical shifts $\Delta\omega_i$ or resonance offset ΔH_i, is to have in the rotating frame an additional Hamiltonian in the form of Zeeman interaction:

$$H_{cs} = -\sum_{i=1}^{p} \gamma_i \Delta H_i I_{zi} = -\sum_{i=1}^{p} \Delta\omega_i I_{zi} \tag{4.148}$$

Then the evolution of density operator by this term in the indirect dimension is:

$$\exp\left(-i\sum_{i=1}^{p} \Delta\omega_i I_{zi}\, t\right)\rho \exp\left(i\sum_{i=1}^{p} \Delta\omega_i I_{zi}\, t\right) = \exp(-ip\sum_{i=1}^{p} \Delta\omega_i I_{zi}\, t)\rho \tag{4.149}$$

Where p is the coherence order of the system.

When we inspect the frequency spectra, we have to apply Fourier Transform to the time domain signal:

$$F(\omega) = \int_{-\infty}^{\infty} \rho(t) \exp(-i\omega t)\, dt$$

So with the effect of chemical shifts or resonance offset for a specific coherence order, we have:

$$\begin{aligned} F(\omega) &= \int_{-\infty}^{\infty} \rho(t) \exp(-ip\Delta\omega_i t) \exp(-i\omega t)\, dt \\ &= \int_{-\infty}^{\infty} \rho(t) \exp[-\mathrm{i}(\omega + p\Delta\omega_i)t] dt \end{aligned} \tag{4.150}$$

Which means the corresponding site in frequency spectral shifts the frequency by $p\Delta\omega_i$.

This explains in our normal single quantum spectrum we can differentiate different sites by their chemical shifts $\Delta\omega_i$. In multiple quantum, the indirect dimension evolution will enhance the shifts by the order of the quantum coherence times the corresponding shifts.

Note for our double quantum example, $\Delta\omega = \Delta\omega_I + \Delta\omega_S$, not $2(\Delta\omega_I + \Delta\omega_S)$. This can be shown by write out the explicit form of the double quantum $\rho = I_2^y = \frac{1}{2i}(I^+S^+ - I^-S^-)$. We have:

$$\rho(t) = \exp(-i\Delta\omega_I I_z t) \exp(-i\Delta\omega_S S_z t)\, \rho \exp(i\Delta\omega_I I_z t) \exp(i\Delta\omega_S S_z t)$$

$$= \exp(-i\Delta\omega_I I_z t) \exp(-i\Delta\omega_S S_z t) \frac{1}{2i}(I^+S^+ - I^-S^-) \exp(i\Delta\omega_I I_z t) \exp(i\Delta\omega_S S_z t)$$

$$= \frac{1}{2i}\left[\begin{matrix} \exp(-i\Delta\omega_I I_z t) I^+ \exp(i\Delta\omega_I I_z t) \exp(-i\Delta\omega_S S_z t)\, S^+ \exp(i\Delta\omega_S S_z t) \\ - \exp(-i\Delta\omega_I I_z t) I^- \exp(i\Delta\omega_I I_z t) \exp(-i\Delta\omega_S S_z t)\, S^- \exp(i\Delta\omega_S S_z t) \end{matrix}\right]$$

$$\rho(t) = \frac{1}{2i}\{\exp[-i(\Delta\omega_I + \Delta\omega_S)t] I^+\, S^+ - \exp[i(\Delta\omega_I + \Delta\omega_S)t] I^-\, S^-\} \tag{4.151}$$

So we see the shift of frequency is $\Delta\omega_I + \Delta\omega_S$ for $+2$ quantum, and $-(\Delta\omega_I + \Delta\omega_S)$ for -2 quantum.

In fact, you may already realize that higher quantum terms should comprising structures such as $\prod_{i=1}^{p} I_1^+ I_2^+ \ldots I_i^+ \pm I_1^- I_2^- \ldots I_i^-$. When they evolve under chemical shifts or resonance offset, by density operator for unlike spins, you will get terms like:

$$\rho(t) = \tag{4.152}$$

$$\prod_{i=1}^{p} \exp(-i\Delta\omega_1 I_{z1} t) \ldots \exp(-i\Delta\omega_i I_{zi} t) \left(\prod_{i=1}^{p} I_1^+ I_2^+ \ldots I_i^+ \pm I_1^- I_2^- \ldots I_i^- \right)$$

$$\prod_{i=1}^{p} \exp(i\Delta\omega_1 I_{z1} t) \ldots \exp(i\Delta\omega_i I_{zi} t)$$

You can follow our prior derivation to show that these evolution operators will result in:

$$\rho(t) = \tag{4.153}$$

$$(\prod_{i=1}^{p} \exp\left[-i\left(\sum_{i=1}^{p} \Delta\omega_i\right)t\right] I_1^+ I_2^+ \ldots I_i^+ \pm \exp\left[i\left(\sum_{i=1}^{p} \Delta\omega_i\right)t\right] I_1^- I_2^- \ldots I_i^-)$$

which will give you the sum of all chemical shifts and shifted in positive and negative frequency direction.

The other question is, we need to acquire both x and y direction in the indirection dimension, just like a quadrature detection in the direct detection dimension. This allows us to differentiate positive and negative shift. This is normally achieved by the State method by alternating x and y component for chemical shift labeling in the indirect dimension, for single quantum.

How can we do that if we have multiple quantum in the indirect dimension?

To achieve a 90 degree alternating phase in the indirect dimension, for the single quantum, it is simply to apply a rotation around z direction by 90: $U = exp\left(-i\frac{\pi}{2}I_{z1}\right)$. Hence, for multiple quantum, to achieve the same goal of a 90 degree alternating phase, we have to account for the combined coherence change.

As we showed earlier, if we apply a rotation $U = exp(-i\theta I_{z1})$ to order p multiple quantum, the effective rotation is $exp(-ip\theta)$.

Hence all we need is to satisfy: $p\theta = \frac{\pi}{2}$, and $\theta = \frac{\pi}{2p}$. For example, this means for double quantum, to alternate from the x and y component in the indirect dimension, all we need is to apply a overall phase shift of $\frac{\pi}{4}$ for the excitation sequence, and all the processing steps can use the same processing scripts for single quantum in NMRPipe or whatever software you prefer.

4.12 Cross polarization for signal enhancement of low γ and low abundant nuclei in a static sample

We introduced how to transfer polarization between heteronuclei using the coupling such as INEPT or REDOR/TEDOR sequences. INEPT is used for weak coupling strength with long T_2. It is most commonly applied in liquids samples.

In solid NMR, an equally powerful approach is cross polarization, discovered by Hartmann and Hahn. Their original seminar paper involves very dense statistics, and may be difficult to follow for non-physics major. Here I will try to explain its mechanism following the approach shown by Wu and Zilm (XL. Wu and KW. Zilm, JMR 104, 154-165 (1993), and Malcolm H Levitt JCP 94, 30 (1991).

Cross polarization uses the dipolar interaction to transfer polarizations between two heteronuclei. Hence the system Hamiltonian is:

$$\begin{aligned}\hat{H} &= \\ &-\gamma_I H_0 I_z - \gamma_S H_0 S_z - 2H_{1I}\cos(\omega_{0I}t)\, I_x - 2H_{1S}\cos(\omega_{0S}t)\, S_x + 2b_{IS}I_zS_z \\ &= -\omega_I I_z - \omega_S S_z - 2H_{1I}\cos(\omega_{0I}t)\, I_x - 2H_{1S}\cos(\omega_{0S}t)\, S_x + 2b_{IS}I_zS_z\end{aligned} \tag{4.154}$$

Here ω_{0I} and ω_{0S} are the Larmor frequencies for I and S spins. We intentionally have the chemical shifts ω_I and ω_S of I and S spins not equal to their respective Larmor frequency to include the chemical shift offset effect in this discussion. We can transfer $\hat{H}$ to the rotating frame of reference and remove the Zeeman terms by:

$$\hat{H}_r = \exp(i\omega_I I_z t)\exp(i\omega_S S_z t)\hat{H}\exp(-i\omega_I I_z t)\exp(-i\omega_S S_z t)$$

You can duplicate our work in Chapter 2 and show that after the Hamiltonian in rotating frame becomes:

$$\hat{H}_r = -\Delta\omega_I I_z - \Delta\omega_S S_z - H_{1I}I_x - H_{1S}S_x + b_{IS}I_zS_z \tag{4.155}$$

Where $\Delta\omega_I$ and $\Delta\omega_S$ are the chemical shifts offsets relative to their respective Larmor frequencies:

$$\Delta\omega_I = \omega_I - \omega_{0I};\ \Delta\omega_S = \omega_S - \omega_{0S}$$

Since cross polarization happens during the continuous application of RF pulses, to further facilitate the interpretation, we wish to combine the chemical shift offset and RF field into one offset field so our perspective is more transparent.

Let's apply the second transformation into the tilted frame of reference. This was also shown in Sect. 3.2 earlier, by:

$$\widehat{H_t} = \exp\left(i\, S_y\theta_S\right)\exp\left(i\, I_y\theta_I\right)\widehat{H_r}\exp\left(-i\, I_y\theta_I\right)\exp\left(-i\, S_y\theta_S\right)$$

Where $\tan\theta_i = \frac{\gamma H_{1i}}{\Delta\omega_i}$, $i = I, S$

Follow our work in Chapter 3, you can easily show that for the first four terms in the Hamiltonian, they will become:

$$\exp\left(i\, S_y\theta_S\right)\exp\left(i\, I_y\theta_I\right)[-\Delta\omega_I I_z-\Delta\omega_S S_z-H_{1I}I_x-H_{1S}S_x]\exp\left(-i\, I_y\theta_I\right)\exp\left(-i\, S_y\theta_S\right)$$

$$=-\gamma_I H_{eI}I_z-\gamma_S H_{eS}S_z$$

Where

$H_{ei}=\sqrt{(\frac{\Delta\omega_i}{\gamma_i})^2+(H_{1i})^2}\,,\, i=I,S$

Now we just have to transform the coupling term:

$$\exp\left(i\, S_y\theta_S\right)\exp\left(i\, I_y\theta_I\right)b_{IS}I_zS_z\exp\left(-i\, S_y\theta_S\right)\exp\left(-i\, I_y\theta_I\right)$$

$$=b_{IS}(I_z\cos\theta_I-I_x\sin\theta_I)(S_z\cos\theta_S-S_x\sin\theta_S)$$

$$=b_{IS}I_zS_z\cos\theta_I\cos\theta_S-b_{IS}I_zS_x\cos\theta_I\sin\theta_S-b_{IS}S_zI_x\cos\theta_S\sin\theta_I+b_{IS}I_xS_x\sin\theta_I\sin\theta_S$$

Now, we consider some approximations. With small chemical shift offset, $\Delta\omega_i \ll \gamma_i H_{1i}$. This means that RF is strong compared to chemical shift offset, $\theta_i \sim \frac{\pi}{2}$, so $\cos\theta_i \sim 0$, and $\sin\theta_i \sim 1$. This condition is easily satisfied in our cross polarization experiments by strong spin locking field on two nuclei channels. Then we can drop all the terms containing $\cos\theta_i$:

$$\exp\left(i\, S_y\theta_S\right)\exp\left(i\, I_y\theta_I\right)b_{IS}I_zS_z\exp\left(-i\, S_y\theta_S\right)\exp\left(-i\, I_y\theta_I\right)\cong b_{IS}I_xS_x$$

Hence we have the system Hamiltonian in the tilted rotating frame as:

$$\widehat{H_t}=-\gamma_I H_{eI}I_z-\gamma_S H_{eS}S_z+b_{IS}I_xS_x=-\omega_{eI}I_z-\omega_{eS}S_z+b_{IS}I_xS_x \qquad (4.156)$$

Now we have to recall our fictitious two spin operator sets, since we are dealing with two coupled spins. This allows us to convert our view to the spin 1 and spin 0 space of two coupled nuclear pair:

$I_2^x=\frac{1}{2}(I^+S^+ + I^-S^-)=I_xS_x-I_yS_y;$ $\qquad I_0^x=\frac{1}{2}(I^+S^- + I^-S^+)=I_xS_x+I_yS_y$

$I_2^y=\frac{1}{2i}(I^+S^+ - I^-S^-)=I_xS_y+I_yS_x;$ $\qquad I_0^y=\frac{1}{2i}(I^+S^- - I^-S^+)=I_yS_x-I_xS_y$

$I_2^z=\frac{1}{2}(I_z+S_z);$ $\qquad I_0^z=\frac{1}{2}(I_z-S_z)$

We can decompose the chemical shift offset and the coupling terms in terms of two spin operators:

$$I_xS_x=\frac{1}{2}(I_0^x+I_2^x) \qquad (4.157)$$

Then we can use the formula:

$$AI_z+BS_z=(A+B)I_2^z+(A-B)I_0^z \qquad (4.158)$$

This allow us to convert the chemical shift dependent terms into:

$$-\omega_{eI} I_z - \omega_{eS} S_z = -\Delta I_0^z - \Sigma I_2^z \tag{4.159}$$

Where $\Delta = \omega_{eI} - \omega_{eS}$, and $\Sigma = \omega_{eI} + \omega_{eS}$.

Now, we have the system Hamiltonian as:

$$\widehat{H_t} = -\Delta I_0^z + \frac{b_{IS}}{2} I_0^x - \Sigma I_2^z + \frac{b_{IS}}{2} I_2^x \tag{4.160}$$

We have to realize now the fictitious spin 0 and 2 are living in their own space, and won't interfere with each other without external interference.

You can think this situation as if the spin 0 and spin 2 are two different nuclei. They have completely different resonance frequencies, one resonance at sum of resonance frequency of I and S and one resonance at the difference of the resonance frequencies of I and S.

Now you see why we have to pay so much efforts to change the format of our Hamiltonian. We now turn the system of two coupled spins I and S into two uncoupled fictitious spins I_0 and I_2, in their respective rotating frame.

Since we have prior experience dealing with a single spin's resonance situation in rotating frame, we can first qualitatively analyze the two fictitious spins separately and visualize what will happen for each of them:

Situation A: For the spin 2 space, if we have $\Sigma \gg \frac{b_{IS}}{2}$, this means the magnetization of spin 2 will be locked along its z axis. Thus I_2^z will not change much, and precess around its effective field direction. As long as $\Sigma \gg \frac{b_{IS}}{2}$ is satisfied, we have $I_2^z = \frac{1}{2}(I_z + S_z)$ to be near a constant. Therefore:

$$\rho_z^2(t) = \rho_z^2(t=0) = \frac{1}{2}[\rho_I(t=0) + \rho_S(t=0)] = \frac{1}{2}\rho_I(t=0) = \Sigma \tag{4.161}$$

Let's look at the spin 0 space. Initially all polarization of the system is at $+I_0^z$ direction, Which means for spin 0, its initial spins will be along the positive z axis, and it comes entirely from spin I:

$$\rho_z^0(t=0) = \frac{1}{2}[\rho_I(t=0) - \rho_S(t=0)] = \frac{1}{2}\rho_I(t=0) = \Sigma \tag{4.162}$$

If we also set up the experiment to satisfy:

$$\omega_{eI} = \omega_{eS}$$

$$\Delta = \omega_{eI} - \omega_{eS} = 0,$$

This means

$$\rho^0(t) = \exp\left(-i\frac{b_{IS}}{2}I_0^x\right)I_0^z\exp\left(i\frac{b_{IS}}{2}I_0^x\right) \tag{4.163}$$

$$= [I_0^z\cos(\frac{b_{IS}}{2}t) - I_0^y\sin(\frac{b_{IS}}{2}t)]$$

$\rho_I(0)$ is the density operator of I spin tipped along the x axis in the rotating frame by the initial $\pi/2$ pulse. So we have $\rho_I(0) = I_0^z(0) = \Sigma$, as shown in Eq. 4.162, and $I_0^y(0) = 0$.

Recall in our introduction of density operator Eq. 4.57,

$$\rho_I(0) = \exp(-i\frac{\pi}{2}I_y)\frac{I_z\exp\left(-\frac{E_z}{kT}\right)}{Z_I}\exp(-i\frac{\pi}{2}I_y) = \frac{N_I\gamma_I H_0}{kT(2I+1)^{N_I}}I_x$$

The polarization of spin 0 will be rotating around its x axis. After a π rotation, all polarization will be inverted:

$$\rho_z^0(t=\pi) = \frac{1}{2}[\rho_I(t=\pi) - \rho_S(t=\pi)] \tag{4.164}$$

$$= -\rho_z^0(t=0) = -\frac{1}{2}[\rho_I(t=0) - \rho_S(t=0)] = -\Sigma$$

However, at this moment, due to the dominating $\Sigma \gg \frac{b_{IS}}{2}$, M_z^2 remains a constant:

$$\rho_z^2 = \frac{1}{2}[\rho_I(t=\pi) + \rho_S(t=\pi)] = \Sigma \tag{4.165}$$

We see that this means $\rho_S(t=\pi) = \rho_I(t=0) = 2\Sigma$, it achieved 100% positive transfer. Recall that the I_z and S_z in the tilted reference frame is actually the I_x and S_x operators in the rotating frame, hence we have:

$$\rho_S = \frac{\gamma_S N_S H_0}{kT_S(2S+1)^{N_S}}S_x = \rho_I = \frac{\gamma_I N_I H_0}{kT_I(2I+1)^{N_I}}I_x$$

So we have:

$$T_S = \frac{\gamma_S N_S(2S+1)^{N_S}}{\gamma_I N_I(2I+1)^{N_I}}T_I\frac{S_x}{I_x} \tag{4.166}$$

This means the spin temperature of S is lowered in this process, as the rest are physical constants that do not vary with experiments. We can insert this into the polarization expression Eq. 1.12 in Chapter 1, and assume their spins are identical:

$$M_S = \frac{N_S\gamma_S^2\hbar^2 S(S+1)}{3kT_S}H_0 = \frac{\gamma_I N_I(2I+1)^{N_I}}{\gamma_S N_S(2S+1)^{N_S}T_I}M_{S0} \tag{4.167}$$

The magnetization of S spin is thus enhanced by the ratio of $\frac{\gamma_I N_I(2I+1)^{N_I}}{\gamma_S N_S(2S+1)^{N_S}}$, as the temperature of S spin becomes equivalent to that of I spin. Furthermore, according to Eq. 4.167, if I is low abundant in the system, cross polarization can lead to additional enhancement proportional to the concentration ratio of I and S.

By more rigorous treatment, we have to take into account spin diffusion effect when I and S are in contact to approach a common temperature. You can read C. P. Slichter's book for a nice discussion about spin temperature.

More generally, if $\Delta = \omega_{eI} - \omega_{eS} \neq 0$ but $\Delta \ll \frac{b_{IS}}{2}$, after a π rotation, the magnetization $M_z^0(t = \pi)$ will be at 2θ angle with respective to the –z axis in spin 0 space, where:

$$\theta_0 = \tan^{-1}\frac{b_{IS}}{2\Delta} \tag{4.168}$$

From this we can show that $\sin\theta_0 = \frac{b_{IS}}{\sqrt{4\Delta^2 + b_{IS}^2}}$; $\cos\theta_0 = \frac{\Delta}{\sqrt{4\Delta^2 + b_{IS}^2}}$.

Hence we can follow a pictorial derivation. For simplicity, let's ignore the precess around the z axis in spin 0 space, since $\Delta \ll \frac{b_{IS}}{2}$: initially the polarization in the spin 0 space is at its z axis. It will precess around the effective field axis in spin 0 space, making a constant angle θ_0 with respect to the effective field direction. After a π rotation:

$$\rho_z^0(t = \pi) = \frac{1}{2}[-\rho_I(t = \pi) + \rho_S(t = \pi)] = \rho_z^0(t = 0)\cos(\pi - 2\theta) \tag{4.169}$$

$$= \Sigma\cos(\pi - 2\theta) = \Sigma(\sin^2\theta_0 - \cos^2\theta_0) = \Sigma\left(\frac{\frac{b_{IS}^2}{4}}{\Delta^2 + \frac{b_{IS}^2}{4}} - \frac{\Delta^2}{\Delta^2 + \frac{b_{IS}^2}{4}}\right)$$

On top of this, we know ρ_z^0 is precessing around the effective field so $\rho_z^0 = \exp(i\Delta t)\rho_z^0\exp(-i\Delta t)$

Recall the sum of magnetization is still conserved:

$$\rho_z^2 = \frac{1}{2}[\rho_I(t = \pi) + \rho_S(t = \pi)] = \Sigma$$

$$\rho_S(t = \pi) = \Sigma\left(1 + \frac{\frac{b_{IS}^2}{4} - \Delta^2}{\Delta^2 + \frac{b_{IS}^2}{4}}\right) = \Sigma\frac{\frac{b_{IS}^2}{2}}{\Delta^2 + \frac{b_{IS}^2}{4}}$$

The efficiency of transfer is

$$\frac{\rho_S(t = \pi)}{\rho_I(t = 0)} = \frac{\frac{b_{IS}^2}{4}}{\Delta^2 + \frac{b_{IS}^2}{4}}$$

Hence if $\Delta \ll \frac{b_{IS}}{2}$, we will get ~ 100% efficiency. We note in this process, it is the zero quantum terms $I^+S^-/\,I^-S^+$ that induce the cross polarization.

In a more rigorous treatment, to see how the spins move in the spin 0 space, we can apply a transformation into the tilted frame in spin 0 space. Before the transformation, we have:

$$\widehat{H^0} = -\Delta I_0^z + \frac{b_{IS}}{2} I_0^x \tag{4.170}$$

$$\widehat{H}_t^0 = \exp\left(i\theta_0 I_0^y\right) \widehat{H^0} \exp\left(-i\theta_0 I_0^y\right) = -\Delta(I_0^z \cos\theta_0 + I_0^x \sin\theta_0) + \frac{b_{IS}}{2}(I_0^x \cos\theta_0 - I_0^z \sin\theta_0)$$

$$= -I_0^z\left(\Delta\cos\theta_0 + \frac{b_{IS}}{2}\sin\theta_0\right) + I_0^x\left(\frac{b_{IS}}{2}\cos\theta_0 - \Delta\sin\theta_0\right)$$

Since

$$\theta_0 = \tan^{-1}\frac{b_{IS}}{2\Delta}$$

$$\sin\theta_0 = \frac{\frac{b_{IS}}{2}}{\sqrt{\Delta^2 + (\frac{b_{IS}}{2})^2}}; \cos\theta_0 = \frac{\Delta}{\sqrt{\Delta^2 + (\frac{b_{IS}}{2})^2}}$$

$$\widehat{H}_t^0 = -I_0^z\left(\frac{\Delta^2 + \left(\frac{b_{IS}}{2}\right)^2}{\sqrt{\Delta^2 + \left(\frac{b_{IS}}{2}\right)^2}}\right)$$

$$+I_0^x\left(\frac{\frac{b_{IS}}{2}\Delta - \Delta\frac{b_{IS}}{2}}{\sqrt{\Delta^2 + \left(\frac{b_{IS}}{2}\right)^2}}\right)$$

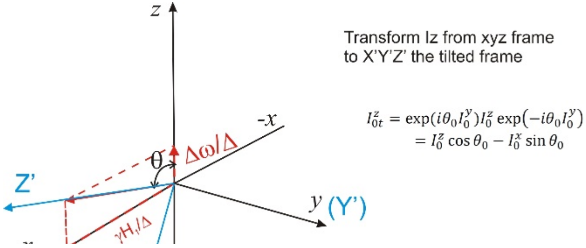


Figure 4.8. Transformation of observation references in fictitious spin 0 space.

$$\widehat{H}_t^0 = -I_0^z\sqrt{\Delta^2 + \left(\frac{b_{IS}}{2}\right)^2} = -\omega_0^e I_0^z \tag{4.171}$$

Similarly, we can transform the spin 2 space Hamiltonian into its tilted frame by:

$$\widehat{H}_t^2 = \exp\left(i\theta_2 I_2^y\right) \widehat{H^2} \exp\left(-i\theta_2 I_2^y\right)$$

$$\widehat{H^2} = -\Sigma I_2^z + \frac{b_{IS}}{2} I_2^x$$

$$\theta_2 = \tan^{-1}\frac{b_{IS}}{2\Sigma}$$

$$\hat{H}_t^2 = -I_2^z\sqrt{\Sigma^2 + \left(\frac{b_{IS}}{2}\right)^2} = -\omega_2^e I_2^z \tag{4.172}$$

In this tilted frame, the evolution of density operator of spin along z in space 0 will be:

$$\rho_0^t(t) = I_{0t}^z = \exp(i\theta_0 I_0^y) I_0^z \exp\left(-i\theta_0 I_0^y\right) = I_0^z \cos\theta_0 - I_0^x \sin\theta_0 \tag{4.173}$$

It will evolve under the $\hat{H}_t^2$ *by*:

$$\begin{gathered}\rho_0^t(t) = \exp\left(-i\hat{H}_t^0 t\right)\rho_0(t)\exp\left(i\hat{H}_t^0 t\right) \\ = \exp(i\omega_0^e I_0^z t)\,\rho_0(t)\exp(-i\omega_0^e I_0^z t) \\ = I_0^z\cos\theta_0 - \sin\theta_0\left(I_0^x\cos\omega_0^e t + I_0^y\sin\omega_0^e t\right)\end{gathered} \tag{4.174}$$

Now we transform back into the normal spin 0 space:

$$\begin{gathered}\rho_0(t) = \exp\left(-i\theta_0 I_0^y\right)\rho_0^t(t)\exp\left(i\theta_0 I_0^y\right) \\ = I_0^z\cos^2\theta_0 + I_0^x\sin\theta_0\cos\theta_0 - \sin\theta_0\cos\omega_0^e t\left(I_0^x\cos\theta_0 - I_0^z\sin\theta_0\right) - I_0^y\sin\theta_0\sin\omega_0^e t\end{gathered} \tag{4.175}$$

Therefore, we can evaluate:

$$\langle I_0^z\rangle = Tr\{I_0^z\rho_0(t)\} = Tr\{(I_0^z)^2\}[\cos^2\theta_0 + \sin^2\theta_0\cos\omega_0^e t] \tag{4.176}$$

While the trace of cross terms $I_0^x I_0^z$ and $I_0^y I_0^z$ will vanish since they are traceless. Recall $I_0^z(0) = I_z, S_z = 0, Tr\{(I_0^z)^2\} = Tr\{I_z^2\} = \frac{1}{4}$. Hence we have:

$$\langle I_0^z\rangle = \frac{1}{4}[\cos^2\theta_0 + \sin^2\theta_0\cos\omega_0^e t] \tag{4.177}$$

Similarly we can get:

$$\langle I_2^z\rangle = \frac{1}{4}[\cos^2\theta_2 + \sin^2\theta_2\cos\omega_2^e t] \tag{4.178}$$

The polarization on S is:

$$\begin{gathered}\langle S_z(t)\rangle = \langle I_2^z\rangle - \langle I_0^z\rangle \\ = \frac{1}{4}(\cos^2\theta_2 - \cos^2\theta_0 + \sin^2\theta_2\cos\omega_2^e t - \sin^2\theta_0\cos\omega_0^e t)\end{gathered} \tag{4.179}$$

PS: you can use the above transformation to show the resonance offset effect we derived in Chapter 2 in classical picture using geometry. It will be more straight forward.

Here

$\omega_2^e = \sqrt{\Sigma^2 + \left(\frac{b_{IS}}{2}\right)^2}, \omega_0^e = \sqrt{\Delta^2 + \left(\frac{b_{IS}}{2}\right)^2}, \theta_0 = \tan^{-1}\frac{b_{IS}}{2\Delta}, \theta_2 = \tan^{-1}\frac{b_{IS}}{2\Sigma}$

$$\sin\theta_0 = \frac{\frac{b_{IS}}{2}}{\sqrt{\Delta^2 + (\frac{b_{IS}}{2})^2}}; \cos\theta_0 = \frac{\Delta}{\sqrt{\Delta^2 + (\frac{b_{IS}}{2})^2}}$$

$$\sin\theta_2 = \frac{\frac{b_{IS}}{2}}{\sqrt{\Sigma^2 + (\frac{b_{IS}}{2})^2}}; \cos\theta_2 = \frac{\Sigma}{\sqrt{\Sigma^2 + (\frac{b_{IS}}{2})^2}}$$

If we apply the approximation $\Sigma \gg \frac{b_{IS}}{2}$, $\sin\theta_2 = 0, \cos\theta_2 = 1$, we have:

$$\langle S_z(t)\rangle = \langle I_2^z\rangle - \langle I_0^z\rangle \tag{4.180}$$

$$= \frac{1}{4}(1 - \cos^2\theta_0 - \sin^2\theta_0 \cos\omega_0^e t) = \frac{1}{4}\sin^2\theta_0\,(1 - \cos\omega_0^e t) = \frac{1}{2}\sin^2\theta_0 \sin^2\frac{\omega_0^e t}{2}$$

$$= \frac{1}{2}\frac{(\frac{b_{IS}}{2})^2}{\Delta^2 + (\frac{b_{IS}}{2})^2}\sin^2\frac{\sqrt{\Delta^2 + \left(\frac{b_{IS}}{2}\right)^2}\,t}{2}$$

To sum it up, to achieve the cross polarization in situation A, we need to satisfy the following conditions:

1. $\omega_{eI} = \omega_{eS} = \sqrt{(\Delta\omega_I)^2 + (\gamma_I H_{1I})^2} = \sqrt{(\Delta\omega_S)^2 + (\gamma_S H_{1S})^2}$, or for on resonance, $\gamma_I H_{1I} = \gamma_S H_{1S}$
2. $\omega_{eI} + \omega_{eS} = \sqrt{(\Delta\omega_I)^2 + (\gamma_I H_{1I})^2} + \sqrt{(\Delta\omega_S)^2 + (\gamma_S H_{1S})^2} \gg \frac{b_{IS}}{2}$, in physics it means spin locking field is much stronger that internal coupling between IS
3. Prepare the *I* spin by tip its magnetization onto x axis, but leave the *S* spin at z direction.
4. The transfer process has to be short compared to the spin lattice relaxation under spin locking (called $T_{1\rho}$), so the initial spin polarization on *I* can be converted to positive S by $I^+S^-/\ I^-S^+$ before it decays. The transfer time τ is $\frac{b_{IS}}{2}\tau = \pi$, or $\tau = \frac{2\pi}{b_{IS}}$.

Situation B: For the spin 0 space, if we have $\Delta \gg \frac{b_{IS}}{2}$, we have the $\rho_z^0 = \rho_z^0(t=0) = \frac{1}{2}[\rho(t=0) - \rho_S(t=0)] = \frac{1}{2}\rho_I(t=0) = \Delta$

For the spin 2 space, if we have $\Sigma \ll \frac{b_{IS}}{2}$, we will have similar situation like situation A. This cannot be satisfied at the same time for a static sample, but can be satisfied for rotating sample:

$$|\Delta - n\omega_r| \gg \frac{b_{IS}}{2} \tag{4.181}$$
$$|\Sigma - n\omega_r| \ll \frac{b_{IS}}{2}$$

The M_z^2 will process around the effective field by $\frac{b_{IS}}{2}$ and $|\Sigma - n\omega_r|$, with a precessing angle $\theta = \tan^{-1}\frac{b_{IS}}{2|\Sigma - n\omega_r|}$,

If we follow through the same pictorial derivation, we will see:

$$\frac{\rho_S(t=\pi)}{\rho_I(t=0)} = \frac{\frac{b_{IS}^2}{4}}{|\Sigma - n\omega_r|^2 + \frac{b_{IS}^2}{4}} \tag{4.182}$$

Hence if $|\Sigma - n\omega_r| \ll \frac{b_{IS}}{2}$, we will get ~ 100% efficiency. We note in this process, it is the double quantum terms $I^+S^+/\ I^-S^-$that induce the cross polarization. The polarization transferred to S will be negative, however.

If you apply the same density matrix treatment in the spin 0 and 2 space, you can get:

$$\begin{aligned} \langle S_z(t)\rangle &= \langle I_2^z\rangle - \langle I_0^z\rangle \\ &= \frac{1}{4}(\cos^2\theta_2 - \cos^2\theta_0 + \sin^2\theta_2\cos\omega_2^e t - \sin^2\theta_0\cos\omega_0^e t) \end{aligned} \tag{4.183}$$

But this time, the approximation is :

$$|\Delta - n\omega_r| \gg \frac{b_{IS}}{2} \tag{4.184}$$

So $\sin\theta_0 = 0, \cos\theta_0 = 1$, we have:

$$\begin{aligned} \langle S_z(t)\rangle &= \frac{1}{4}(\cos^2\theta_2 - 1 - \sin^2\theta_2\cos\omega_2^e t) = -\frac{1}{4}\sin^2\theta_2\,(1-\cos\omega_2^e t) \\ &= -\frac{1}{2}\sin^2\theta_2\sin^2\frac{\omega_2^e t}{2} \\ &= -\frac{1}{2}\frac{(\frac{b_{IS}}{2})^2}{|\Sigma - n\omega_r|^2 + (\frac{b_{IS}}{2})^2}\sin^2\frac{\sqrt{|\Sigma - n\omega_r|^2 + \left(\frac{b_{IS}}{2}\right)^2}\,t}{2} \end{aligned} \tag{4.185}$$

To sum it up, to achieve the cross polarization in situation B, we need to satisfy the following conditions:

1. $|\omega_{eI} + \omega_{eS} - n\omega_r| = \left|\sqrt{(\Delta\omega_I)^2 + (\gamma_I H_{1I})^2} + \sqrt{(\Delta\omega_S)^2 + (\gamma_S H_{1S})^2} - n\omega_r\right|$, or for on resonance, $\gamma_I H_{1I} + \gamma_S H_{1S} = n\omega_r$

2. $|\omega_{eI} - \omega_{eS} - n\omega_r| = \left|\sqrt{(\Delta\omega_I)^2 + (\gamma_I H_{1I})^2} - \sqrt{(\Delta\omega_S)^2 + (\gamma_S H_{1S})^2} - n\omega_r\right| \gg \frac{b_{IS}}{2}$, in physics it means spin locking field is much stronger that internal coupling between IS
3. Prepare the I spin by tip its magnetization onto x axis, but leave the S spin at z direction.
4. The transfer process has to be shorter compared to the spin lattice relaxation under spin locking (called $T_{1\rho}$), so the initial spin polarization on I can be converted to negative S by $I^+S^+/\ I^-S^-$ before it decays. The transfer time τ is $\frac{b_{IS}}{2}\tau = \pi$, or $\tau = \frac{2\pi}{b_{IS}}$.

4.13 Cogwheel phase cycling selection of coherence pathway

We have learned so far how to excite multiquantums, how to select their x and y component for indirect dimension observation, and how to convert the multiquantum back into observable -1 single quantum. In a system of N spins, in theory we could excite up to N quantum. However, we normally need to select a specific pathway in a pulse sequence. This is so called coherence pathway selection. It exploits the different responses of of different coherence orders to phase rotation as shown in Eq. 4.151 and 4.152: $R_z(\theta)\rho R_z^{-1}(\theta)$, $\exp(-i\phi I_z)\,\rho\,\exp(i\phi I_z) = \exp(-ip\phi)\rho$. This mechanism not only can be applied for coherence selection, but also helps relieve the pulse imperfection (tip angle, unbalanced amplification of two channels in quadrature detection, etc). However, with multiple pulses in our sequences, possible pathways get more and more complicated, and it can be puzzling to figure out what would be the most efficient phase cycling strategy to select a desired pathway. A concise scheme called Cogwheel phase cycling laid out by Malcolm H. Levitt in JMR 155, 300 (2002). I will follow his paper to explain briefly how it works.

There are a few unchanged melodies in coherence pathway selection in any pulse sequences:

1. All pathways start from coherence order 0 in 0th segment along the pathway. This is because we always start from equilibrium magnetization along external magnetic field direction z.
2. All pathways end at coherence order -1. Let's assume the pulse sequence ends with the Nth segment in the pathway. We explained earlier that only -1 coherence can be detected in our conventional quadrature detection setup.
3. Coherence order remains unchanged between pulses, but are changed by each pulse block.
4. Applying a phase shift ϕ_i on the ith RF pulse block will induce a phase factor $\exp[-i(p_i - p_{i-1})\phi_i]$, where p_i and p_{i-1} are the coherence order after and before the pulse block. Or we can say $\Delta P_i = p_i - p_{i-1}$ is the change of coherence order activated by this specific pulse block.

Rule 1-3 are pretty self-explanatory. Let's see why 4 is true.

Let's assume the ith RF block changes the signal component with coherence order P_{i-1} to P_i. It is achieved by the Hamiltonian H_i associated from ith RF pulse block in the pulse duration t_i. Then according to evolution of density matrix, this is expressed as:

$$\rho_i^{P_i} = U_i \rho_{i-1}^{P_{i-1}} U_i^{-1} = \exp(-iH_i t_i)\rho_{i-1}^{P_{i-1}}\exp(iH_i t_i) \qquad (4.186)$$

If we apply a phase shift ϕ_i on ith RF pulse block, by density matrix it means:

$$U'_i = \exp(-i\phi_i I_z)\exp(-iH_i t_i)\exp(i\phi_i I_z) \tag{4.187}$$

So $U_i'^{-1}$ =[$\exp(-i\phi_i I_z)\exp(-iH_i t_i)\exp(i\phi_i I_z)]^{-1}$

Using the matrix operation rule, if A, B, C and D are matrices:

$$D = ABC, D^{-1} = (ABC)^{-1} = C^{-1}B^{-1}A^{-1} \tag{4.188}$$

Therefore, we have:

$$U'^{-1}_i = \exp(-i\phi_i I_z)\exp(iH_i t_i)\exp(i\phi_i I_z)$$

Plug back into Eq. 4.186:

$$\begin{aligned}
\rho'^{P_i}_i &= U'_i \rho^{P_{i-1}}_{i-1} U'^{-1}_i \\
&= \exp(-i\phi_i I_z)\exp(-iH_i t_i)\exp(i\phi_i I_z)\,\rho^{P_{i-1}}_{i-1}\exp(-i\phi_i I_z)\exp(iH_i t_i)\exp(i\phi_i I_z) \\
&= \exp(-i\phi_i I_z)\left\{\exp(-iH_i t_i)\left[\exp(i\phi_i I_z)\,\rho^{P_{i-1}}_{i-1}\exp(-i\phi_i I_z)\right]\exp(iH_i t_i)\right\}\exp(i\phi_i I_z) \\
&= \exp(-i\phi_i I_z)\left\{\exp(-iH_i t_i)\left[\exp(i\phi_i P_{i-1})\,\rho^{P_{i-1}}_{i-1}\right]\exp(iH_i t_i)\right\}\exp(i\phi_i I_z) \\
&= \exp(i\phi_i P_{i-1})\exp(-i\phi_i I_z)\left\{\exp(-iH_i t_i)\,\rho^{P_{i-1}}_{i-1}\exp(iH_i t_i)\right\}\exp(i\phi_i I_z) \\
&= \exp(i\phi_i P_{i-1})\exp(-i\phi_i I_z)\left\{\rho^{P_i}_i\right\}\exp(i\phi_i I_z) = \exp(i\phi_i P_{i-1})\exp(-i\phi_i P_i)\,\rho^{P_i}_i
\end{aligned}$$

$$\rho'^{P_i}_i = \exp[-i(P_i - P_{i-1})\phi_i]\rho^{P_i}_i \tag{4.189}$$

Hence if we have N block, we repeat the experiment M times, each time we apply $\phi_i^{m_i}$ to ith RF pulse block, the final signal by adding up the signal from all m acquisition through a coherence pathway will be:

$$\begin{aligned}
S &= \frac{1}{M}\sum_{m_i=1}^{M}\sum_{i=1}^{N}\exp\left[-i(P_i - P_{i-1})\phi_i^{m_i}\right]\rho^{P_i}_i \\
&= \frac{1}{M}\sum_{m=1}^{M}\sum_{i=1}^{N}\exp\left[-i\Delta P_i\phi_i^{m_i}\right]\rho^{P_i}_i \\
&= \begin{cases} 1, for\ chosen\ pathway \\ 0, for\ all\ others \end{cases}
\end{aligned} \tag{4.170}$$

$$M = \prod_{i=1}^{N} m_i$$

This expression is called the cogwheel phase cycling. A small computer program will be needed to select out the most effection phase cycling with minimum value of M.

Chapter 5 Tensor and NMR with magic angle spinning

Our introduction of density matrix and operator formalism will be nearly sufficient to understand most NMR pulse sequences. In this chapter, we will introduce a new concept called the tensor, which will greatly simply the analyses of spin dynamics in many more complicated scenarios. We will skim over the Wigner-Eckart theory, which provides a generalized format to transform tensors under rotation operations. The Wigner-Eckart theory has many more advanced applications that can make your heads (and mine) spin. But please don't be scared by it. We will show you that it is nothing more than a tool. We will demonstrate how to use this tool by deriving the effect of Magic Angle Spinning (MAS). This derivation will make the analyses of the evolution of spin dynamics under both MAS and RF irradiation easy to understand. This chapter will be the foundation for our discussion of some popular recoupling effects in Chapter 6.

5.1 Rotation of a vector operator around an arbitrary axis

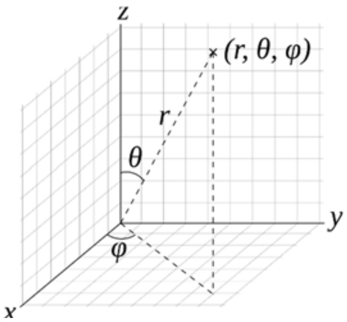


Figure 5.1. Azimuth angle φ and polar angle θ to represent a vector n in 3D space.

By now we know how to deal with vectors (including operator vectors in the Hilbert space) and the impact of rotation, either in geometric space or spin space. We have applied such manipulations in the transformation of reference frames (rotating frame and tilted frame) for both classical and quantum mechanical picture.

We note that the transformation we applied is straightforward for single spin operators. However, when we apply a rotation of an angle β about an arbitrary axis $\boldsymbol{n}$, with its direction designated in terms of polar and azimuth angle (θ, φ), the result is not so obvious:

$$U[R(\beta, \boldsymbol{n})] = \exp(-i\frac{\beta}{\hbar}\boldsymbol{n}\cdot\boldsymbol{J}) \tag{5.1}$$

$$U(R)^{\dagger}V_i U(R) = \sum_j R_{ij}V_j\,, i, j = x, y, z\ component\ of\ vector\ V$$

We can expand this expression in terms of the directional vector of the rotation axis $\boldsymbol{n}$:

$$[R(\theta, \boldsymbol{n})] = \exp\left(-i\frac{\beta}{\hbar}\boldsymbol{n}\cdot\boldsymbol{J}\right) \tag{5.2}$$

$$U = \exp\left[-i\beta\left(I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta\right)\right]$$

$$= \exp(-i\beta\{\exp(-i\varphi I_z)\left[\exp(-i\theta I_y)\, I_z \exp(i\theta I_y)\right]\exp(i\varphi I_z)\})$$

Here we absorbed $\hbar$ by recording angular momentum in units of $\hbar$, which is a common practice in quantum mechanics. This generic rotation operator may remind you of the treatment we applied to analyze the cross polarization in the double quantum/zero quantum space.

We all know by now how to treat rotation of a single spin operator around I_x, I_y, I_z:

$$\exp(-i\theta I_y)\, I_z \exp(i\theta I_y) = I_z\cos\theta + I_x\sin\theta \tag{5.3}$$

$$\exp(-i\theta I_x)\, I_z \exp(i\theta I_x) = I_z \cos\theta - I_y \sin\theta$$
$$\exp\left(-i\theta I_y\right) I_x \exp\left(i\theta I_y\right) = I_x \cos\theta - I_z \sin\theta$$
$$\exp(-i\theta I_z)\, I_x \exp(i\theta I_z) = I_x \cos\theta + I_y \sin\theta$$
$$\exp(-i\theta I_z)\, I_y \exp(i\theta I_z) = I_y \cos\theta - I_x \sin\theta$$
$$\exp(-i\theta I_x)\, I_y \exp(i\theta I_x) = I_y \cos\theta + I_z \sin\theta$$

But normally for exponential operators, we have:

$$\exp(A + B) \neq e^A e^B$$

So it is not obvious how a single spin operator responds to a rotation around a generic axis defined in Eq. 5.2.

We can take a different approach, by applying a rotation transformation to rotate to a new reference frame where its z' axis aligns with $\boldsymbol{n}$. Then the rotation operation around axis n, will be a rotation around the new axis z'. In this new reference frame, we just have to compute what is the expression of our current single spin operator:

$$I_z = I_z' \cos\theta - I_y' \sin\theta \tag{5.4}$$

So in this new reference frame, the rotation around $\boldsymbol{n}$ becomes:

$$\begin{aligned} &\exp(-i\beta n \cdot J)\, I_z \exp(i\beta n \cdot J) \\ &= \exp(-i\beta I_z')(I_z' \cos\theta - I_y' \sin\theta)\exp(i\beta I_z') \\ &= I_z' \cos\theta - I_y' \sin\theta \cos\beta + I_x' \sin\theta \sin\beta \end{aligned} \tag{5.5}$$

Now we have to transform the computed result in x'y'z' frame back to xyz frame. For I_z' and I_y', their expressions can easily be shown by drawing a picture with the two references frame overlaid:

$$\begin{aligned} I_z' &= I_x \sin\theta \cos\varphi + I_y \sin\theta \sin\varphi + I_z \cos\theta \\ I_y' &= -I_z \sin\theta + I_x \cos\theta \cos\varphi + I_y \cos\theta \sin\varphi \end{aligned} \tag{5.6}$$

To show the expression of I_x':

$$\begin{aligned} I_x' = I_y' \times I_z' &= \left(-I_z \sin\theta + I_x \cos\theta \cos\varphi + I_y \cos\theta \sin\varphi\right) \\ &\times \left(I_x \sin\theta \cos\varphi + I_y \sin\theta \sin\varphi + I_z \cos\theta\right) \end{aligned} \tag{5.7}$$

$$= -I_y \sin^2\theta \cos\varphi + I_x \sin^2\theta \sin\varphi - I_y \cos^2\theta \cos\varphi + I_z \sin\theta \cos\theta \sin\varphi \cos\varphi$$

$$-I_z \sin\theta \cos\theta \sin\varphi \cos\varphi + I_x \cos^2\theta \sin\varphi$$

$$I_x' = I_x \sin\varphi - I_y \cos\varphi$$

So we have:

$$\mathrm{Exp}(-i\beta n \cdot J)\, I_z \exp(i\beta n \cdot J) = \left(I_x \sin\theta \cos\varphi + I_y \sin\theta \sin\varphi + I_z \cos\theta\right) \cos\theta$$

$$-\left(-I_z \sin\theta + I_x \cos\theta \cos\varphi + I_y \cos\theta \sin\varphi\right) \sin\theta \cos\beta$$

$$+\left(I_x \sin\varphi - I_y \cos\varphi\right)\sin\theta\sin\beta$$

$$= I_x(\sin\theta\cos\theta\cos\varphi - \sin\theta\cos\theta\cos\varphi\cos\beta + \sin\theta\sin\varphi\sin\beta)$$

$$+I_y(\sin\theta\cos\theta\sin\varphi - \sin\theta\cos\theta\sin\varphi\cos\beta - \sin\theta\cos\varphi\sin\beta) + I_z(\cos^2\theta + \sin^2\theta\cos\beta)$$

$$\begin{gathered}
\mathrm{Exp}(-i\beta n\cdot J)\, I_z \exp(i\beta n\cdot J) \\
= I_x \sin\theta\cos\theta\cos\varphi\,(1-\cos\beta) + I_x \sin\theta\sin\varphi\sin\beta \\
+ I_y \sin\theta\cos\theta\sin\varphi\,(1-\cos\beta) \\
-I_y \sin\theta\cos\varphi\sin\beta + I_z(\cos^2\theta + \sin^2\theta\cos\beta)
\end{gathered} \tag{5.8}$$

Hence we immediately recognize if we apply this formula to our cross polarization treatment in spin 2 and spin 0 space, by combing Eq. 4.174 and 4.179, we can just plug Eq. 5.7 to:

$$\begin{gathered}
\langle s_x(t)\rangle = \frac{1}{2} Tr\{I_z^2 \exp(-i\beta^2 n^2\cdot I_z^2)\, I_z^2 \exp(-i\beta^2 n^2\cdot I_z^2)\} \\
-\frac{1}{2} Tr\{I_z^0 \exp(-i\beta^0 n^0\cdot I_z^0)\, I_z^0 \exp(-i\beta^0 n^0\cdot I_z^0)\}
\end{gathered} \tag{5.9}$$

Alternatively, here is an easy way to compute the rotation around $\boldsymbol{n}$:

$$\begin{aligned}
U &= \exp(-i\beta n\cdot J) \\
&= \exp\left[-i\beta\left(I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta\right)\right] \\
&= \exp(-i\varphi I_z)\,[\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\exp\left(i\theta I_y\right)]\exp(i\varphi I_z)
\end{aligned} \tag{5.10}$$

This conversion turns the general rotation around an axis $\boldsymbol{n}$ with angle (θ, φ) as a mixture of rotation about x, y and z axis into a SEQUENTIAL rotation around y and z axis. The sequential rotation is easy to compute as the standard rotation of single operators. Equivalently, we can show that:

$$U = \exp(-i\beta n\cdot J) = \exp\left[-i\beta\left(I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta\right)\right]$$

$$= \exp[-i(\varphi + \frac{\pi}{2})I_z]\,[\exp(-i\theta I_x)\exp(-i\beta I_z)\exp(i\theta I_x)]\exp\exp[i(\varphi + \frac{\pi}{2})I_z]$$

Which will make application of the general rotation around an axis $\boldsymbol{n}$ with angle (θ, φ) to the x, y and z axis into combination of SEQUENTIAL rotation around x and z axis.

We will stick with the conversion of rotation as the sequential rotation about y and z axis. The reverse of the rotation is simply:

$$\begin{aligned}
U^{-1} &= \exp(i\beta n\cdot J) = \exp\left[i\beta\left(I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta\right)\right] \\
&= \exp(-i\varphi I_z)\,[\exp\left(-i\theta I_y\right)\exp(i\beta I_z)\exp\left(i\theta I_y\right)]\exp(i\varphi I_z)
\end{aligned} \tag{5.11}$$

Here we used Eq. 4.188:

$$D = ABC, D^{-1} = (ABC)^{-1} = C^{-1}B^{-1}A^{-1}$$

Please note after the inversion, we still $\exp(-i\varphi I_z)$ and $\exp\left(-i\theta I_y\right)$ ahead of $\exp(i\beta I_z)$. Essentially it means we have the same sequential rotations applied, but applied to $\exp(i\beta I_z)$, not $\exp(-i\beta I_z)$. Hence:

$$\begin{gathered}\exp(-i\beta n\cdot J)\, I_z \exp(i\beta n\cdot J) \\ = \left\{\exp(-i\varphi I_z)\left[\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\exp\left(i\theta I_y\right)\right]\exp(i\varphi I_z)\right\} I_z \\ \left\{\exp(-i\varphi I_z)\left[\exp\left(-i\theta I_y\right)\exp(i\beta I_z)\exp\left(i\theta I_y\right)\right]\exp(i\varphi I_z)\right\}\end{gathered} \tag{5.12}$$

Which after re-combination, we can show this helps convert the computation into a series of standard single operator rotations, which can easily be computed step by step:

$$= \exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\exp\left(i\theta I_y\right)\left[\exp(i\varphi I_z)\, I_z \exp(-i\varphi I_z)\right]$$

$$\exp\left(-i\theta I_y\right)\exp(i\beta I_z)\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= \exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\exp\left(i\theta I_y\right) I_z \exp\left(-i\theta I_y\right)\exp(i\beta I_z)\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= \exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\left[\exp\left(i\theta I_y\right) I_z \exp\left(-i\theta I_y\right)\right]\exp(i\beta I_z)\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= \exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\left[I_z\cos\theta - I_x\sin\theta\right]\exp(i\beta I_z)\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= \cos\theta\exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\left[I_z\right]\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$-\sin\theta\exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\left[I_x\right]\exp(i\beta I_z)\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= \cos\theta\exp(-i\varphi I_z)\left[I_z\cos\theta + I_x\sin\theta\right]\exp(i\varphi I_z)$$

$$-\sin\theta\exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\left[I_x\cos\beta + I_y\sin\beta\right]\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= I_z\cos^2\theta + \sin\theta\cos\theta\exp(-i\varphi I_z)\left[I_x\right]\exp(i\varphi I_z)$$

$$-\sin\theta\cos\beta\exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\left[I_x\right]\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$-\sin\theta\sin\beta\exp(-i\varphi I_z)\exp\left(-i\theta I_y\right)\left[I_y\right]\exp\left(i\theta I_y\right)\exp(i\varphi I_z)$$

$$= I_z\cos^2\theta + \sin\theta\cos\theta\cos\varphi\, I_x + \sin\theta\cos\theta\sin\varphi\, I_y$$

$$-\sin\theta\cos\beta\exp(-i\varphi I_z)\left[I_x\cos\theta - I_z\sin\theta\right]\exp(i\varphi I_z)$$

$$-\sin\theta\sin\beta\exp(-i\varphi I_z)\left[I_y\right]\exp(i\varphi I_z)$$

$$= I_z\cos^2\theta + \sin\theta\cos\theta\cos\varphi\, I_x + \sin\theta\cos\theta\sin\varphi\, I_y - \sin\theta\cos\theta\cos\beta\cos\varphi\, I_x$$

$$-\sin\theta\cos\theta\cos\beta\sin\varphi\, I_y + I_z\sin^2\theta\cos\beta - \sin\theta\sin\beta\cos\varphi\, I_y + \sin\theta\sin\beta\sin\varphi\, I_x$$

$$= I_z(\cos^2\theta + \sin^2\theta\cos\beta) + I_x(\sin\theta\cos\theta\cos\varphi - \sin\theta\cos\theta\cos\beta\cos\varphi + \sin\theta\sin\beta\sin\varphi)$$

$$+I_y(\sin\theta\cos\theta\sin\varphi - \sin\theta\cos\theta\cos\beta\sin\varphi - \sin\theta\sin\beta\cos\varphi)$$

As you can see, this is the same as Eq. 5.7, the result obtained by the first approach by transformation into tilted frame of reference.

Either way, the computation is rather messy.

In general, a rotation around any arbitrary axis can be replaced by a sequential rotation of angle α about the original z axis, then rotation of angle β about the current y' axis (or sometimes called the node axis), and a third rotation of angle γ about the final axis z":

$$R(\alpha\beta\gamma) = R_{z''}(\gamma)R_{y'}(\beta)R_z(\alpha) \tag{5.13}$$

Any rotation about the x axis can be replaced by a rotation about y, followed by a negative $\frac{\pi}{2}$ phase shift around z:

$$R_x(\beta) = \exp(-i\beta I_x) = \exp(i\frac{\pi}{2}I_z)\exp\left(-i\beta I_y\right)\exp(-i\frac{\pi}{2}I_z) \tag{5.14}$$

Or equivalently, rotation about x axis can be replaced by the same angle of phase shift about z, followed by a positive $\frac{\pi}{2}$ rotation about y:

$$R_x(\beta) = \exp(-i\beta I_x) = \exp(-i\frac{\pi}{2}I_y)\exp(-i\beta I_z)\exp(i\frac{\pi}{2}I_y) \tag{5.15}$$

However, when there are two operators involved, things become very messy. For example:

$$\begin{aligned} e^{-i\theta I_z}I_xI_ye^{+i\theta I_z} &= e^{-i\theta I_z}I_xe^{i\theta I_z}e^{-i\theta I_z}I_ye^{+i\theta I_z} = \left(I_x\cos\theta + I_y\sin\theta\right)\left(I_y\cos\theta - I_x\sin\theta\right) \\ &= I_xI_y\cos^2\theta - I_yI_x\sin^2\theta + (I_y^2 - I_x^2)\sin\theta\cos\theta \end{aligned}$$

Is there a more generic rule of transformation we can exploit for transformation involving two or more spin operators?

Yes! The combinations of vectors are in fact tensors. More accurately, tensors are not just simple combinations of vectors, but any combinations of vectors can be expressed in terms of tensors. The rotation transformation of tensors is described by the Wigner-Eckart theorem.

5.2 What are tensors?

So what exactly are tensors?

Tensors are objects obeying fixed rules about rotation in the multidimension space. Tensors are categorized by its rank k (can be fraction and integer numbers, but we will limit this discussion to integers). Under rotation, a tensor will merely turn into linear combinations of the $2k + 1$ tensors of the same rank k.

For example, a zero rank tensor is a scalar (number), which does not change (invariant) by rotation. A rank 1 tensor is a vector, and it transforms by rotation operators as defined in Eq. 5.3. We can think scalars and vectors as objects in the three dimensional space, where scalar is a point in space that is not affected by rotation, and vectors are the spatially straight lines with nonzero magnitude and directions. Rotation only changes the direction but not length of vectors. Naturally, there are three independent basis in the 3D space, and all vectors in this space can be expressed as linear combination of these bases.

In physics/maths, we have higher dimensional spaces and objects in higher dimensional spaces also carries similar properties like vectors in 3D space: they have length (or magnitude, or norm) that is not affected by rotation, and they exhibit properties dependent on directions just like vectors in 3D space. They are called higher rank tensors. Example in physics include stress (tensile and shear stress), magnetic permeability, and chemical shielding (shift) tensor. Thus when these objects are rotated, or viewers change their perspectives by rotation, expressions of these directional dependent properties will change. However, physics measurable (Hamiltonian, for example) of the system should not be affected by rotation, as we showed in Chapter 4 that the observables are just the trace of the density matrix expression, independent from rotation.

In general, there is always a one-2-one correspondence of conservation of physics principle/laws and symmetry (Noether's theorem), or so called invariance of transformation. For example, the conservation of energy corresponds to the time invariance. Conservation of linear momentum corresponds to translation invariance. Conservation of angular momentum corresponds to rotation invariance. For each symmetry, there is a generator of transformation. For rotation, this generator is angular momentum (and spin angular momentum in our NMR).

So how do we construct and express physics properties (or more generally, mathematical objects in high dimensional space) with direction dependence, especially those with rank higher than 1?

In general, a tensor is represented by symbol T_p^k or T_{kp}, where k is its rank, p is the component index. Within each rank, there are $p = -k, -(k-1), \ldots (k-1), k,$ altogether $2k+1$ linear independent component T_{kp} (Doesn't this remind you angular momentum space?). When a T_{kp} is rotated, it turns into a new tensor of the same rank T_{kp}, which can be represented by the linear combinations of these $2k+1$ tensors. The coefficient of the combination due to rotation, is defined by Wigner-Eckart theorem, which we will show you soon.

There are various ways to define/construct tensors. We can define tensors in terms of vectors $V = \left(V_x V_y V_z\right)$ and $W = \left(W_x W_y W_z\right)$, or in terms of an array D. However, we need to note that not all array/matrices are tensors, as tensor components have to obey certain symmetry relation regarding rotating. We will introduce both methods to construct tensors, since we will encounter tensors defined in both ways in different occasions.

Assume we have a conventional array(matrix) D. Without the loss of generality, D can be expressed as:

$$D = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \tag{5.16}$$

A rank 0 tensor is just scalar T_0, which does not change by rotation.

If we have two vectors of arbitrary dimension, the relationship between the two vectors that remain invariant under rotation is their dot product (or inner product), so we can define the rank 0 tensor in terms of two vectors as:

$$T_0 = \frac{1}{3} V \cdot W \tag{5.17}$$

Alternatively, we can define it in terms of the array(matrix) D. Because the trace of an array remains invariant under rotation, we can also define a rank 0 tensor as:

$$T_0 = \frac{1}{3} Tr\{D_{ij}\} = \frac{1}{3} \sum_i D_{ii} \tag{5.18}$$

Some definition of a rank 0 tensor will have a different normalization factor as:

$$T_0 = -\frac{1}{\sqrt{3}} Tr\{D_{ij}\} = -\frac{1}{\sqrt{3}} \sum_i D_{ii} \tag{5.19}$$

For example, the isotropic chemical shift δ_{iso} is a rank 0 tensor. δ_{iso} is defined as the ratio of the difference between the Larmor frequency of a nucleus in a specific chemical environment and the Larmor frequency of the same nucleus in a chemical compound as the chosen reference, divided by the Larmor frequency of the reference in ppm unit:

$$\delta_{iso} = \frac{\omega_{obs} - \omega_{ref}}{\omega_{ref}} \times 10^6 (ppm) \tag{5.20}$$

δ_{iso} is the scalar part(rank 0 tensor) of the chemical shielding tensor σ_{csa} (which you can think is a 3x3 matrix for the moment).

The chemical shielding arises from the local magnetic field due to the orbital motion of valence electrons in a external magnetic field. It depends on the orientation of the electron distribution (orbits), thus requires a second rank tensor to describe. However, since δ_{iso} is the scalar part of the tensor, isotropic chemical shifts does not change its value when a molecule reorients in either solution or solid NMR.

Tensors of rank 1 are vectors. Naturally, they can be defined as the cross product of two vectors in the same space, with 3 independent and antisymmetric components:

$$T_{1p} = \frac{1}{2}(V \times W)_p = \frac{1}{2}\begin{vmatrix} \boldsymbol{e_x} & \boldsymbol{e_y} & \boldsymbol{e_z} \\ V_x & V_y & V_z \\ W_x & W_y & W_z \end{vmatrix} \tag{5.21}$$

$$= \frac{1}{2}[(V_yW_z - V_zW_y)\boldsymbol{e_x} - (V_xW_z - V_zW_x)\boldsymbol{e_y} + (V_xW_y - V_yW_x)\boldsymbol{e_z}]$$

In terms of a matrix, the components of the rank 1 tensors can be defined as:

$$T_{1p} = \frac{1}{2}(D_{ij} - D_{ji}) \tag{5.22}$$

You can see that the rank 1 tensors are asymmetric part of a matrix. They behave just like any vectors, with three components represent x, y and z direction projections.

Any vector operators are in fact rank 1 tensors. For example, our spin operators I has the three components I_x, I_y, I_z. When we rotate any single component of spin operator, we always get the result as a combination of the components. Although we know the formula of transformation of vector operator by rotation, we will show that they are in fact following a more general transformation defined by the Wigner-rotation matrix. This a general expression that works even for higher rank tensors.

Now we move to something unfamiliar. Tenors of rank 2 can be formed by the outer products of vectors:

$$T_{2p} = V \otimes W - \frac{1}{3}V \cdot W - \frac{1}{2}(V \times W) \tag{5.23}$$

We briefly introduced the outer product of two vectors in Chapter 4 when introducing the density matrix, in Eq. 4.39. Similarly, here the outer product of vectors V and W is a matrix as well, and here is the general expression:

$$V \otimes W = \begin{pmatrix} V_xW_x & V_xW_y & V_xW_z \\ V_yW_x & V_yW_y & V_yW_z \\ V_zW_x & V_zW_y & V_zW_z \end{pmatrix} \tag{5.24}$$

Or in terms of matrix the components of a rank 2 tensor can be expressed as:

$$T_{2p} = \frac{1}{2}(D_{ij} + D_{ji}) - \frac{1}{3}Tr\{D_{ij}\} \tag{5.25}$$

Therefore, rank 2 tensors have 5 independent and symmetric components. They can be written in a matrix format with the xyz Cartesian components of vectors or a matrix. Please note these rank

2 tensors are traceless. Examples in NMR are the Hamiltonians of dipolar interaction or quadrupolar interaction. They are in fact traceless rank 2 tensors.

We can also construct higher rank tensors. Rank 3 tensors will have 2*3+1=7 independent components. You can find the delineation in various papers, for example, in Malcoln Levitt's JCP 122, 244510 (2005) paper, where he shows rank 3 tensor components constructed by three spin operators.

We want to emphasize again: a tensor is not equivalent to an array/Matrix, but arrays can be decomposed into tensors of various rank according to their behavior under rotations (rotational symmetry).

Now, we show a generic format of how all tensors transform under rotation. To do so, we need to change the coordinate system of representation, from Cartesian coordinate, into spherical coordinate. Thus, we will turn tensors in the Cartesian coordinate to spherical tensors. This is because the rotational symmetry is conserved naturally in the spherical coordinate system.

Just like the tensors in the Cartesian coordinate, spherical tensors still have the same categorization in terms of rank: within each rank k, they have $2k+1$ linearly independent components, called irreducible spherical tensors T_{kp}. These irreducible spherical tensors can be expressed in terms of Cartesian tensors of the same rank.

Assume T_{kp} is formed by the second order dyadic (outer product) $T = I \otimes S$. I and S are vectors (or vector operators), and can be casted into the spherical basis

$$T_0 = -\frac{1}{\sqrt{3}} I \cdot S = -\frac{1}{\sqrt{3}}(I_x S_x + I_y S_y + I_z S_z) \tag{5.26}$$

Here we exploit the fact that the inner product of two vectors is a scalar.

$$T_{1,\pm p} = \frac{1}{i\sqrt{2}}(I \times S)_q, q = 0, \pm 1, or\ explicitly: \tag{5.27}$$

$$T_{10} = -\frac{i}{\sqrt{2}}(I_x S_y - I_y S_x), \text{ or } T_{10} = I_z$$

$$T_{1,\pm 1} = -\frac{1}{2}[I_z S_x - I_x S_z \pm i(I_z S_y - I_y S_z)], or\ T_{1,\pm 1} = \mp \frac{1}{\sqrt{2}}(I_x \pm i I_y)$$

Here we exploit the fact that the cross product of two vectors is another vector, with its direction aligned to the norm of the plain defined by these two vectors.

The second rank tensors can be defined as:

$$T_{2,\pm 2} = I^{\pm} S^{\pm} = \frac{1}{2}[I_x S_x - I_y S_y \pm i(I_x S_y + I_y S_x)] \tag{5.28}$$

$$T_{2,\pm 1} = \frac{1}{\sqrt{2}}(I^{\pm} S_z + S^{\pm} I_z) = \mp \frac{1}{2}[I_x S_Z + I_z S_x \pm i(I_y S_z + I_z S_y)]$$

$$T_{20} = \frac{1}{\sqrt{6}}[3 I_z S_z - I \cdot S]$$

$$= \frac{1}{\sqrt{6}}\left[3I_zS_z - \left(I_xS_x + I_yS_y + I_zS_z\right)\right] = \frac{1}{\sqrt{6}}\left[2I_zS_z - \frac{1}{2}(I^+S^- + I^-S^+)\right]$$

We note the irreducible spherical tensors of rank k has $2k+1$ components. The pth component T_{kp} and $-pth$ component $T_{k,-p}$ are related by:

$$T_{kp} = (-1)(T_{k,-p})^* \tag{5.29}$$

We can also appreciate that tensors can be a good way to represent interactions/couplings between multiple nuclei. For example, double quantum or multiple quantum M are just one or two component in rank 2 or corresponding rank M tensor. The coupling/interactions of multiple M nuclei ½ spins will produce tensor components up to rank M tensor.

5.3 How to use the Wigner-Eckart theorem to describe tensor rotation?

We showed in Eq. 5.13 that any rotation can be written as a sequential rotation of angle α about the original z axis, then rotation of angle β about the nodal axis, and a third rotation of angle γ about the final axis z":

$$R(\alpha\beta\gamma) = R_{z''}(\gamma)R_{y'}(\beta)R_z(\alpha)$$

Equivalently, the same rotation can be accomplished by a sequential rotation about the z and y axis of the original axis system as:

$$R(\alpha\beta\gamma) = R_{z''}(\gamma)R_{y'}(\beta)R_z(\alpha) = R_z(\alpha)R_y(\beta)R_z(\gamma) \tag{5.30}$$

Note the order rotation of $\alpha, \beta,$ and γ is reversed.

The Wigner-Eckart theorem describes what happens if we rotate an irreducible spherical tensor T_{kp}:

$$T'_{km} = R(\alpha\beta\gamma)T_{km}R^{-1}(\alpha\beta\gamma) = \sum_{p=-k}^{k} T_{kp}\, D^k_{pm}(\alpha\beta\gamma) \tag{5.31}$$

In plain words, it declares: if we apply a rotation defined by $R(\alpha\beta\gamma)$ to an irreducible spherical tensors T_{km} in some specific reference frame, the result will be a linear combination of the tensors of same rank in the same reference frame T_{km}, or alternatively, the exact same tensor T'_{km} in a new frame of reference obtained by the same rotation $R(\alpha\beta\gamma)$ applied to the original reference frame.

Hence this theory is used to describe two different kinds rotations:

(1) T'_{km} is a tensor in reference frame B, it can be expressed as a linear combination of tensors of the same rank T_{kp} in reference frame A. Reference frame B is obtained by a z-y-z rotation $R(\alpha\beta\gamma)$ from of reference frame A. The coefficient of combination is defined by $D^k_{pm}(\alpha\beta\gamma)$. This interpretation is used to derive the expression of MAS. It helps to relate spatial part of different

interactions in their principal axis frame to a common rotor frame of reference, and to the laboratory frame of reference.

(2) We stay in the same reference frame A, but rotate a tensor T_{km}, by z-y-convention $R(\alpha\beta\gamma)$. The result is to turn T_{km} into a linear combination of tensors of the same rank T_{kp}, with the coefficient defined by $D^k_{pm}(\alpha\beta\gamma)$. This interpretation is used to describe the effect of RF pulses to the spin parts of Hamiltonians.

Now let's see the detailed expression of Wigner rotation matrix $D^k_{pm}(\alpha\beta\gamma)$. In NMR, we normally choose the eigenstates of Zeeman interaction as our basis of discussion. They are just the eigenstates of spin I_z angular momentum. So these basis functions can be recorded in the Dirac notation as $\{|Jm\rangle\}$, where J is the major angular momentum quantum number, and m is its spin I_z quantum number.

As the Wigner rotation describes the effect of rotation generated by $R(\alpha\beta\gamma)$, hence it naturally connects different eigenstates of $\{|Jm\rangle\}$:

$$\begin{aligned} D^J_{mn}(\alpha\beta\gamma) &= \langle Jm| \exp(-\mathrm{i}\alpha J_z) \exp\left(-i\beta J_y\right) \exp(-\mathrm{i}\gamma J_z) \, |Jn\rangle \\ &= \exp(-im\alpha) \, \langle Jm| \exp\left(-i\beta J_y\right) |Jn\rangle \exp(-in\gamma) = e^{-im\alpha} d^J_{mn}(\beta) e^{-in\gamma} \end{aligned} \quad (5.32)$$

Where $d^J_{mn}(\beta)$ is the reduced Wigner rotation matrix. It rotates the eigenstate $|Jn\rangle$ into $|Jm\rangle$, and enjoys the following properties:

$$d^J_{mn}(\beta) = d^J_{nm}(-\beta) = (-1)^{m-n} d^J_{nm}(\beta) = d^J_{\bar{n}\bar{m}}(\beta) \; or \; d^J_{-n,-m}(\beta) \quad (5.33)$$

Quote from M.E. Rose, Elementary Theory of Angular Momentum, John Wiley and Sons, 1957, the explicit format of $d^J_{mn}(\beta)$ is:

$$\begin{aligned} &d^J_{mn}(\beta) \\ &= \sum_s \frac{(-1)^s [(J+n)!\,(J-n)!\,(J+m)!\,(J-m)!]}{s!\,(J-s-m)!\,(J+n-s)!\,(m+s-n)!} (\cos\frac{\beta}{2})^{2J+n-m-2s} (-\sin\frac{\beta}{2})^{m-n+2s} \end{aligned} \quad (5.34)$$

Here m and n are the component index of the tensor, and J is the angular momentum quantum number, corresponding to the rank of the tensor. The summation is over all values of integers for the factorial arguments equal or greater than zero.

For our normal NMR applications, we probably only need the reduced Wigner rotation matrices for rank 1 and 2 tensors:

$d^1_{m'm}(\beta)$			
m'\m	1	0	-1
1	$\frac{1}{2}(1+\cos\beta)$	$-\frac{1}{\sqrt{2}}\sin\beta$	$\frac{1}{2}(1-\cos\beta)$

0	$\frac{1}{\sqrt{2}}\sin\beta$	$\cos\beta$	$-\frac{1}{\sqrt{2}}\sin\beta$
-1	$\frac{1}{2}(1-\cos\beta)$	$\frac{1}{\sqrt{2}}\sin\beta$	$\frac{1}{2}(1+\cos\beta)$

$d^2_{m'm}(\beta)$					
m’\m	2	1	0	-1	-2
2	$\frac{1}{4}(1+\cos\beta)^2$	$-\frac{1}{2}\sin\beta\,(1+\cos\beta)$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$-\frac{1}{2}\sin\beta\,(1-\cos\beta)$	$\frac{1}{4}(1-\cos\beta)^2$
1	$\frac{1}{2}\sin\beta\,(1+\cos\beta)$	$\frac{1}{2}(2\cos^2\beta+\cos\beta-1)$	$-\sqrt{\frac{3}{8}}\sin 2\beta$	$-\frac{1}{2}(2\cos^2\beta-\cos\beta-1)$	$-\frac{1}{2}\sin\beta\,(1-\cos\beta)$
0	$\sqrt{\frac{3}{8}}\sin^2\beta$	$\sqrt{\frac{3}{8}}\sin 2\beta$	$\frac{1}{2}(3\cos^2\beta-1)$	$-\sqrt{\frac{3}{8}}\sin 2\beta$	$\sqrt{\frac{3}{8}}\sin^2\beta$
-1	$\frac{1}{2}\sin\beta\,(1-\cos\beta)$	$-\frac{1}{2}(2\cos^2\beta-\cos\beta-1)$	$\sqrt{\frac{3}{8}}\sin 2\beta$	$\frac{1}{2}(2\cos^2\beta+\cos\beta-1)$	$-\frac{1}{2}\sin\beta\,(1+\cos\beta)$
-2	$\frac{1}{4}(1-\cos\beta)^2$	$\frac{1}{2}\sin\beta\,(1-\cos\beta)$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$\frac{1}{2}\sin\beta\,(1+\cos\beta)$	$\frac{1}{4}(1+\cos\beta)^2$

Note Mattias Eden’s Computer Simulations in ssNMR I spin dynamics theory had the sign mistaken.

Note. I intentionally adopted m and m' as the index. Sometimes Wigner Eckart theorem is written as:

$$T'_{kq} = R(\alpha\beta\gamma)T_{kq}R^{-1}(\alpha\beta\gamma) = \sum_{p=-k}^{k} T_{kp}\, D^k_{pq}(\alpha\beta\gamma) \tag{5.35}$$

I find p and q as index are kind of confusing, as they can be mistakened as each other.

We see rotation of any irreducible spherical tensor will always be turned into combination of its peer tensors of the same rank, with the coefficient of combination designated by Wigner rotation matrix.

Therefore, we can view the Wigner rotation matrix of rank k as the coefficient of the linear combination for various components of the same rank k tensors to represent a rotated component of that rank. A reduced Wigner rotation matrix is the rotation action around y axis in the basis of angular momentum operator k.

Here are some additional properties of Wigner rotation matrix. They are rarely encountered in our normal NMR computation, but it is good to be aware of them:

The Wigner rotation matrix are orthogonal and unitary:

$$\sum_{p=-k}^{k} D^{k}_{pq}(\alpha\beta\gamma)\,[D^{k}_{p'q}(\alpha\beta\gamma)]^{\star} = \delta_{pp'} \tag{5.36}$$

$$\sum_{p=-k}^{k} D^{k}_{pq'}(\alpha\beta\gamma)\,[D^{k}_{pq'}(\alpha\beta\gamma)]^{\star} = \delta_{qq'}$$

Also they satisfy the symmetry relation:

$$\begin{gathered}[D^{k}_{pm}(\alpha\beta\gamma)]^{\star} = \\ [D^{k}_{pm}(R)]^{\star} = (-1)^{p-m} D^{k}_{-p,-q}(\alpha\beta\gamma)\ or\ (-1)^{p-m} D^{k}_{\bar{p}\bar{m}}(\alpha\beta\gamma) \\ = D^{k}_{pm}(R^{-1}) = D^{k}_{pm}[(\pi-\gamma)\beta(\pi-\alpha)] \\ = D^{k}_{pm}[(-\gamma)(-\beta)(-\alpha)]\end{gathered} \tag{5.36}$$

With integer k, and $m = 0$,

$$D^{k}_{p0}(\alpha\beta\gamma) = \sqrt{\frac{4\pi}{2k+1}}\, Y^{*}_{kp}(\beta\gamma) = C^{*}_{kp}(\beta\gamma) \tag{5.37}$$

Where $Y^{*}_{kp}(\beta\gamma)$ is the complex conjugate of spherical harmonics $Y_{kp}(\beta\gamma)$, with

$$\begin{gathered}Y^{*}_{kp}(\beta\gamma) = (-1)^{p} Y_{k,-p}(\beta\gamma)\ or\ (-1)^{p} Y_{k\bar{p}}(\beta\gamma) \\ Y_{kp}(\beta\gamma) = (-1)^{p}\sqrt{\frac{2k+1}{4\pi}\frac{(k-p)!}{(k+p)!}}\, P_{kp}(\cos\beta)\exp(im\gamma) \\ C_{k0}(\beta\gamma) = P_{k}(\cos\beta)\end{gathered} \tag{5.38}$$

Where $P_{k}(\cos\beta)$ is the Legendre polynomial of degree k, and $C_{k0}(0\gamma) = 1$

The product of two Wigner matrices of different ranks can be expressed in terms of the Clebsch-Gordon series:

$$\begin{gathered}D^{k_1}_{p_1q_1}(\alpha\beta\gamma)D^{k_2}_{p_2q_2}(\alpha\beta\gamma) \\ = \sum_{k,p,q} c(k_1\,k_2k;p_1p_2p)c(k_1k_2k;q_1q_2q)D^{k}_{pq}(\alpha\beta\gamma)\end{gathered} \tag{5.39}$$

Where $c(k_1k_2k;q_1q_2q) = c(k_1k_2k;q_1q_2)$ denote the Clebsch-Gordon coefficients with $q = q_1+q_2$.

The Wigner matrices are also orthogonal:

$$\frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} D^{k_1}_{p_1q_1}(\alpha\beta\gamma)D^{k_2}_{p_2q_2}(\alpha\beta\gamma)\,d\alpha\sin\beta\,d\beta d\gamma = \frac{1}{2k_1+1}\delta_{p_1p_2}\delta_{q_1q_2}\delta_{k_1k_2} \tag{5.40}$$

The Wigner matrices also have the summation rule:

$$\sum_n D^k_{mn}(\alpha_1\beta_1\gamma_1)D^k_{nm\prime}(\alpha_2\beta_2\gamma_2) = D^k_{mm\prime}(\alpha\beta\gamma) \tag{5.41}$$

Where the Euler angles $(\alpha\beta\gamma)$ are the resultant of two successive rotations by $(\alpha_1\beta_1\gamma_1)$ followed by $(\alpha_2\beta_2\gamma_2)$

What does this theorem and irreducible spherical tensors do, besides the generic format of rotation for all tensors?

If it only provides a universal format of registry, physicists wouldn't be so much in love with irreducible spherical tensors. It is because once we convert objects (operators, vectors, and their combinations) into irreducible spherical tensors, we can track how polarization spread over different mode of couplings (one nuclear spin as 3 rank 1 tensors, two coupled nuclear spins as 5 rank 2 tensors, etc).

In molecular physics, the interaction selection rules become apparent if represented by spherical tensors, which eliminates immediately many integrations as they are not allowed by the selection rules. Thirdly, we also can separate the parameters of interactions into geometric space and spin space, and describe rotations applied to each space respectively. For example, what MAS does is the physical rotation, which only affects the parameters in geometric space, while RF pulse sequences activates the rotation to the parameters in spin space only. Combined, these rotations can interfere with each other. Irreducible spherical tensor representation makes the analyses more transparent in the sense of physical picture.

Now let's apply the Wigner rotation matrix for some simple test.

Could you try to prove:

$$e^{-i\theta I_z}I_x e^{+i\theta I_z} = I_x\cos\theta + I_y\sin\theta$$

First, we need to express the Cartesian operator I_x as irreducible spherical tensors and convert the rotation into z-y-z format if they are not.
Recall Eq. 5.27 we have:

$$T_{1,\pm1} = \mp\frac{1}{\sqrt{2}}(I_x \pm iI_y)$$

Hence:

$$I_x = \frac{1}{\sqrt{2}}(T_{1,-1} - T_{1,1})$$

$$e^{-i\theta I_z} I_x e^{+i\theta I_z} = R(\alpha = \theta, \beta = 0, \gamma = 0)\frac{1}{\sqrt{2}}\left(T_{1,-1} - T_{1,1}\right)R^{-1}$$

$$= \frac{1}{\sqrt{2}}\sum_{m=-1}^{1}\left[T_{1,m}\, D^1_{m-1}(\alpha = \theta, \beta = 0, \gamma = 0) - T_{1,m} D^1_{m+1}(\alpha = \theta, \beta = 0, \gamma = 0)\right]$$

$$= \frac{1}{\sqrt{2}}[T_{1,1}D^1_{1-1}(\theta,0,0) + T_{1,0}D^1_{0-1}(\theta,0,0) + T_{1,-1}D^1_{-1-1}(\theta,0,0)$$

$$-T_{1,1}D^1_{11}(\theta,0,0) - T_{1,0}D^1_{01}(\theta,0,0) - T_{1,-1}D^1_{-11}(\theta,0,0)]$$

$$= \frac{1}{\sqrt{2}}[T_{1,1}\frac{1}{2}(1 - \cos 0)e^{-i1\times\theta} + T_{1,0}\left(-\frac{1}{\sqrt{2}}\sin 0\right)e^{-i0\times\theta} + T_{1,-1}\frac{1}{2}(1 + \cos 0)e^{-i(-1)\times\theta}$$

$$-T_{1,1}\frac{1}{2}(1 + \cos 0)e^{-i1\times\theta} - T_{1,0}\left(\frac{1}{\sqrt{2}}\sin 0\right)e^{-i0\times\theta} - T_{1,-1}\frac{1}{2}(1 - \cos 0)e^{-i(-1)\times\theta}]$$

$$= \frac{1}{\sqrt{2}}\left[T_{1,-1}e^{i\theta} - T_{1,1}e^{-i\theta}\right] = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(I_x - iI_y)e^{i\theta} - \frac{1}{\sqrt{2}}(-I_x - iI_y)e^{-i\theta}\right]$$

$$= \frac{1}{2}\left[I_x\left(e^{i\theta} + e^{-i\theta}\right) - iI_y\left(e^{i\theta} - e^{-i\theta}\right)\right] = I_x\cos\theta - iI_y(i\sin\theta) = I_x\cos\theta + I_y\sin\theta$$

It seems that this makes the rotation computation more complicated.

However, when using computer coding, the uniform format will be an advantage to code the transformation. In addition, when applying rotation to higher rank tensor, it will be much easier.

Could you use Wigner-Eckart theorem to prove the transformation of I_z by a general rotation

$$U = \exp(-i\beta n \cdot J)?$$

$$Hint\ convert\ \exp(-i\beta n \cdot J) = \exp(-i\varphi I_z)\left[\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\exp\left(i\theta I_y\right)\right]\exp(i\varphi I_z)$$

5.4 Transformation of Hamiltonian of common solid state NMR interactions in their irreducible spherical tensor representation and effect of Magic Angle Spinning.

This part of tutorial greatly benefits from the following work:

Mattias Eden, Computer Simulations in Solid-State NMR I Spin Dynamics Theory, Concepts in Magnetic Resonance Part (A) 34(35) (2003).

P. Hodgkinson, L. Emsley, Numerical simulation of solid-state NMR experiments, Progress in Nuclear Magnetic Resonance Spectroscopy 36, 201-239 (2000).

C. P. Jaroniec, Heteronuclear Decoupling and Recoupling, ssNMR Winterschool lecture note (2008).

Mehring M, Principles of high-resolution NMR in solids

M. Matti Maricq and J. S. Waugh, NMR in rotating solids, JCP 70, 3300-3315 (1979)

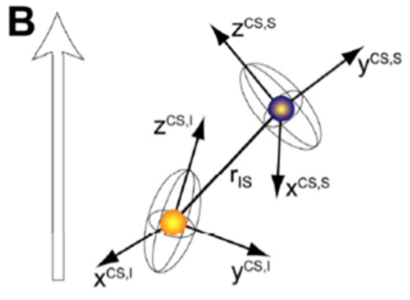


Figure 5.2. Chemical shielding around two different sites in the molecule. Adapted from C. P. Jaroniec's 2008 Winterschool lecture note.

The common interactions in NMR include chemical shielding, hetero and homonuclear dipolar and J coupling interactions, and first-order quadrupolar interactions. To conveniently describe their behaviors under the physical rotation by MAS and spin rotation by RF pulses, we can convert them into irreducible spherical tensor format.

Let's look at the Hamiltonian for chemical shielding first. Chemical shielding effect is the auxiliary magnetic field due to the orbital motion of valence electrons in external magnetic field. Previously, we always present the nuclei with spin I to interact with external magnetic field by:

$$H_0 = -\gamma I \cdot B_0 = -\omega_0 I_z$$

Due to the chemical shielding effect:

$$H_0 = -\gamma I \cdot B_0 = -\gamma I \cdot (1-\sigma) \cdot B \tag{5.42}$$

Where the chemical shielding effect produces a small shift of orientation dependent magnetic field experienced by the nucleus:

$$H_{cs} = \gamma I \cdot \sigma \cdot B = \gamma \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \tag{5.43}$$

We could have use Eq. 5.21 to 5.25 to decompose σ into the scalar δ_{iso}, three rank 1 antisymmetric tensors, and five symmetric rank 2 tensors.

However, to make our analysis of NMR pulse sequence more convenient, we would separate spatial R_m^l and spin part T_m^l of Hamiltonians into respective tensors, so we absorb the magnetic field part with the chemical shielding tensor first, which turns into:

$$H_{cs} = \gamma \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \begin{pmatrix} \sigma_{xz} B_0 \\ \sigma_{yz} B_0 \\ \sigma_{zz} B_0 \end{pmatrix} = \sum_l \sum_{m=-l}^{l} (-1)^m R_m^l T_m^l \tag{5.44}$$

$$= \frac{1}{3} Tr\{\sigma H_0\} I_z + (-1)^1 \times \frac{1}{2} [(R_1^1 + R_{-1}^1) + (-R_1^2 + R_{-1}^2)] \times [-\frac{1}{\sqrt{2}} (T_{-1}^1 + T_{+1}^1)]$$

$$+ \frac{1}{2i} [(-R_1^1 + R_{-1}^1) - (R_1^2 + R_{-1}^2)] \times [\frac{1}{i\sqrt{2}} (T_{-1}^1 - T_{+1}^1)] + (\sqrt{\frac{2}{3}} \sigma_{zz} H_0 - \frac{1}{3} Tr\{\sigma H_0\}) \sqrt{\frac{2}{3}} I_z$$

The first term is the isotropic chemical shift. It arises from $\sigma_{zz}H_0$, associated with the trace of the shielding tensor.

The second term arises from the antisymmetric $R^1_{\pm1}$ and symmetric $R^2_{\pm1}$, comprising the mixture of $\sigma_{xz}H_0$ and $\sigma_{yz}H_0$. Then we also have the third term, R^2_0 associated with $\sigma_{zz}H_0$.

We can prove by perturbation theory that the rank 1 terms is higher order terms compared to the scalar and R^2_0 term. This can be proved by applying the Magnus expansion, which is normally applied to systems with time dependent Hamiltonian $H(t)$ with its period $T = \frac{2\pi}{\omega}$. Assume we evaluate its different orders of approximation over the period T:

$$H^0 = \frac{\omega}{2\pi}\int_0^{t=\frac{2\pi}{\omega}} H(t)dt \tag{5.45}$$

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega}} dt_2 \int_0^{t_2} [H(t_2), H(t_1)]dt_1$$

$$H^2 = \frac{1}{6t\hbar^2}\int_0^{t=\frac{2\pi}{\omega}} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \{[H(t_3), [H(t_2), H(t_1)]] + [H(t_1), [H(t_2), H(t_3)]]\}$$

Please note the order integration of t_2, t_1, and the order of commutator is $[H(t_2), H(t_1)]dt_1$. This is the same as in C. P. Slichter's book Principles of Magnetic Resonance, Appendixes K, P.623 or M. Mehring's High Resonultion NMR Spectroscopy in Solids, or the original paper for Magnus expansion by W. Magnus, Commun. Pure. Appl. Math. 7,649 (1954), or more recently application of the method by S. Blanes, F. Casas, J.A. Oteo, and J. Ros's The Magnus expansion and some of its applications in 2008. However, please be aware that the order of the commutator in some publication was mistaken, for example, Eq. 5 in JCP 128, 052321 (2008).

For convenience of evaluating the average Hamiltonian using Magnus expansion, we will use the standard format:

$$H_{cs} = \gamma(\sigma_{xz}B_0I_x + \sigma_{yz}B_0I_y + \sigma_{zz}B_0I_z) = \omega_0(\sigma_{xz}I_x + \sigma_{yz}I_y + \sigma_{zz}I_z) \tag{5.46}$$

We need to transform into the rotating frame to eliminate the Zeeman interaction:

$$\begin{aligned} \widetilde{H_{cs}} &= \exp(iH_0t)\, H_{cs} \exp(-iH_0t) \\ &= \exp(-i\omega_0I_zt)\, \omega_0\left(\sigma_{xz}I_x + \sigma_{yz}I_y + \sigma_{zz}I_z\right) \exp(i\omega_0I_zt) \\ &= \omega_0(\sigma_{xz}e^{-i\omega_0I_zt}I_xe^{i\omega_0I_zt} + \sigma_{yz}e^{-i\omega_0I_zt}I_ye^{i\omega_0I_zt} + \sigma_{zz}I_z) \end{aligned} \tag{5.47}$$

This transformation into interaction frame works the same way as our previous transformation into rotating frame, or tilted reference frame.

Now we can evaluate the zeroth order approximation by integrating over the period corresponding to Larmor frequency:

$$H^0 = \frac{\omega_0}{2\pi}\int_0^{t=\frac{2\pi}{\omega_0}} H(t)dt \tag{5.48}$$

$$= \frac{\omega_0}{2\pi}\int_0^{t=\frac{2\pi}{\omega_0}} \omega_0(\sigma_{xz}e^{-i\omega_0 I_z t}I_x e^{i\omega_0 I_z t} + \sigma_{yz}e^{-i\omega_0 I_z t}I_y e^{i\omega_0 I_z t} + \sigma_{zz}I_z)dt$$

It is easy to see all terms with the same modulating frequency ω_0 will give zero contribution:

$$H^0 = \omega_0\sigma_{zz}I_z \tag{5.49}$$

Now, we compute the first order term:

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega_0}} dt_2 \int_0^{t_2} dt_1 \tag{5.50}$$

$$[\omega_0\left(\sigma_{xz}e^{-i\omega_0 I_z t_2}I_x e^{i\omega_0 I_z t_2} + \sigma_{yz}e^{-i\omega_0 I_z t_2}I_y e^{i\omega_0 I_z t_2} + \sigma_{zz}I_z\right),$$
$$\omega_0\left(\sigma_{xz}e^{-i\omega_0 I_z t_1}I_x e^{i\omega_0 I_z t_1} + \sigma_{yz}e^{-i\omega_0 I_z t_1}I_y e^{i\omega_0 I_z t_1} + \sigma_{zz}I_z\right)]$$

$$= -\frac{i\omega_0^2}{2t}\int_0^{t=\frac{2\pi}{\omega_0}} dt_2 \int_0^{t_2} dt_1\, [\left(\sigma_{xz}e^{-i\omega_0 I_z t_2}I_x e^{i\omega_0 I_z t_2} + \sigma_{yz}e^{-i\omega_0 I_z t_2}I_y e^{i\omega_0 I_z t_2} + \sigma_{zz}I_z\right),$$

$$\left(\sigma_{xz}e^{-i\omega_0 I_z t_1}I_x e^{i\omega_0 I_z t_1} + \sigma_{yz}e^{-i\omega_0 I_z t_1}I_y e^{i\omega_0 I_z t_1} + \sigma_{zz}I_z\right)]$$

we can compute the inside commutator first:

$$A = [\left(\sigma_{xz}e^{-i\omega_0 I_z t_2}I_x e^{i\omega_0 I_z t_2} + \sigma_{yz}e^{-i\omega_0 I_z t_2}I_y e^{i\omega_0 I_z t_2} + \sigma_{zz}I_z\right),$$

$$\left(\sigma_{xz}e^{-i\omega_0 I_z t_1}I_x e^{i\omega_0 I_z t_1} + \sigma_{yz}e^{-i\omega_0 I_z t_1}I_y e^{i\omega_0 I_z t_1} + \sigma_{zz}I_z\right)]$$

$$= [\sigma_{xz}(I_x\cos\omega_0 t_2 + I_y\sin\omega_0 t_2) + \sigma_{yz}(I_y\cos\omega_0 t_2 - I_x\sin\omega_0 t_2)$$

$$+\sigma_{zz}I_z, \sigma_{xz}(I_x\cos\omega_0 t_1 + I_y\sin\omega_0 t_1) + \sigma_{yz}(I_y\cos\omega_0 t_1 - I_x\sin\omega_0 t_1) + \sigma_{zz}I_z]$$

$$= [I_x\left(\sigma_{xz}\cos\omega_0 t_2 - \sigma_{yz}\sin\omega_0 t_2\right) + I_y\left(\sigma_{yz}\cos\omega_0 t_2 + \sigma_{xz}\sin\omega_0 t_2\right)$$

$$+\sigma_{zz}I_z, I_x\left(\sigma_{xz}\cos\omega_0 t_1 - \sigma_{yz}\sin\omega_0 t_1\right) + I_y\left(\sigma_{yz}\cos\omega_0 t_1 + \sigma_{xz}\sin\omega_0 t_1\right) + \sigma_{zz}I_z]$$

$$= \left(\sigma_{xz}\cos\omega_0 t_2 - \sigma_{yz}\sin\omega_0 t_2\right)\left(\sigma_{yz}\cos\omega_0 t_1 + \sigma_{xz}\sin\omega_0 t_1\right)[I_x, I_y]$$

$$+\left(\sigma_{yz}\cos\omega_0 t_2 + \sigma_{xz}\sin\omega_0 t_2\right)\left(\sigma_{xz}\cos\omega_0 t_1 - \sigma_{yz}\sin\omega_0 t_1\right)[I_y, I_x]$$

$$+\left(\sigma_{xz}\cos\omega_0 t_2 - \sigma_{yz}\sin\omega_0 t_2\right)\sigma_{zz}[I_x, I_z] + \left(\sigma_{yz}\cos\omega_0 t_2 + \sigma_{xz}\sin\omega_0 t_2\right)\sigma_{zz}[I_y, I_z]$$

$$+\sigma_{zz}\left(\sigma_{xz}\cos\omega_0 t_1 - \sigma_{yz}\sin\omega_0 t_1\right)[I_z, I_x] + \sigma_{zz}\left(\sigma_{yz}\cos\omega_0 t_1 + \sigma_{xz}\sin\omega_0 t_1\right)[I_z, I_y]$$

Before we move further, we need to realize the energy shift of various order is to be computed by $\langle n|H^i|n\rangle$, where $|n\rangle$ is the eigenstates of Zeeman interaction, also the eigenstates of I_z. Therefore, any commutator to produce I_x or I_y will be zero in the zeroth order shift. So we just need to keep those commutators to produce I_z, which are the first two terms in the equation above:

$$A = (\sigma_{xz}\cos\omega_0 t_2 - \sigma_{yz}\sin\omega_0 t_2)(\sigma_{yz}\cos\omega_0 t_1 + \sigma_{xz}\sin\omega_0 t_1)[I_x, I_y]$$

$$+(\sigma_{yz}\cos\omega_0 t_2 + \sigma_{xz}\sin\omega_0 t_2)(\sigma_{xz}\cos\omega_0 t_1 - \sigma_{yz}\sin\omega_0 t_1)[I_y, I_x]$$

$$= iI_z(\sigma_{xz}\cos\omega_0 t_2 - \sigma_{yz}\sin\omega_0 t_2)(\sigma_{yz}\cos\omega_0 t_1 + \sigma_{xz}\sin\omega_0 t_1)$$

$$-iI_z(\sigma_{yz}\cos\omega_0 t_2 + \sigma_{xz}\sin\omega_0 t_2)(\sigma_{xz}\cos\omega_0 t_1 - \sigma_{yz}\sin\omega_0 t_1)$$

$$= iI_z[(\sigma_{xz}\cos\omega_0 t_2 - \sigma_{yz}\sin\omega_0 t_2)(\sigma_{yz}\cos\omega_0 t_1 + \sigma_{xz}\sin\omega_0 t_1)$$
$$- (\sigma_{yz}\cos\omega_0 t_2 + \sigma_{xz}\sin\omega_0 t_2)(\sigma_{xz}\cos\omega_0 t_1 - \sigma_{yz}\sin\omega_0 t_1)]$$

$$= iI_z[\sigma_{xz}\sigma_{yz}\cos\omega_0 t_2\cos\omega_0 t_1 - \sigma_{yz}^2\sin\omega_0 t_2\cos\omega_0 t_1 - \sigma_{xz}\sigma_{yz}\sin\omega_0 t_2\sin\omega_0 t_2$$

$$+\sigma_{xz}^2\cos\omega_0 t_2\sin\omega_0 t_1 - \sigma_{xz}\sigma_{yz}\cos\omega_0 t_2\cos\omega_0 t_1 + \sigma_{yz}^2\cos\omega_0 t_2\sin\omega_0 t_1$$

$$-\sigma_{xz}^2\sin\omega_0 t_2\cos\omega_0 t_1 + \sigma_{xz}\sigma_{yz}\sin\omega_0 t_2\sin\omega_0 t_2$$

$$= iI_z\sigma_{xz}^2(\cos\omega_0 t_2\sin\omega_0 t_1 - \sin\omega_0 t_2\cos\omega_0 t_1)$$

$$+iI_z\sigma_{yz}^2(\cos\omega_0 t_2\sin\omega_0 t_1 - \sin\omega_0 t_2\cos\omega_0 t_1)$$

$$= iI_z(\sigma_{xz}^2 + \sigma_{yz}^2)\sin\omega_0(t_1 - t_2)$$

Hence the first order term is:

$$H^1 = -\frac{i\omega_0^2}{2t}\int_0^{t=\frac{2\pi}{\omega_0}} dt_2 \int_0^{t_2} iI_z(\sigma_{xz}^2 + \sigma_{yz}^2)\sin\omega_0(t_1 - t_2)dt_1$$

$$= \frac{\omega_0^2 I_z(\sigma_{xz}^2 + \sigma_{yz}^2)}{2t}\int_0^{t=\frac{2\pi}{\omega_0}} dt_2 \int_0^{t_2} \sin\omega_0(t_1 - t_2)dt_1$$

$$= \frac{\omega_0^2 I_z(\sigma_{xz}^2 + \sigma_{yz}^2)}{2t}\int_0^{t=\frac{2\pi}{\omega_0}} dt_2\{-\frac{1}{\omega_0}[\cos\omega_0(t_2 - t_2) - \cos\omega_0(0 - t_2)]\}$$

$$= \frac{\omega_0^2 I_z(\sigma_{xz}^2 + \sigma_{yz}^2)}{2t}\left[\frac{-1}{\omega_0}t\right]$$

$$H^1 = -\frac{\omega_0}{2}(\sigma_{xz}^2 + \sigma_{yz}^2)I_z \qquad (5.51)$$

Normally σ_{xz}, σ_{yz}, and σ_{zz} are about the same order of magnitude, 10^{-4} to 10^{-5}. So we can see H^1/H^0 is also 10^{-4} to 10^{-5}.

Therefore, we normally have the Hamiltonian of chemical shielding as the scalar part and R_0^2 terms:

$$H_{cs} = \frac{1}{3}\gamma Tr\{\sigma H_0\}I_z + \gamma(\sqrt{\frac{2}{3}}\sigma_{zz}H_0 - \frac{1}{3}Tr\{\sigma H_0\})\sqrt{\frac{2}{3}}I_z \tag{5.52}$$

If we have:

$$\omega_{iso} = \omega_0\delta_{iso} = \frac{1}{3}Tr\{\sigma H_0\} \tag{5.53}$$

Which is the first term in the H_{cs}, we turn the first term into the $R_0^0T_0^0$ term in terms of the tensor format. The spatial part of the second term, is R_{20}. It will turn into combinations of other second rank tensors once rotation is applied, as in the case of MAS.

As we introduced, any reorientation can be achieved by the z-y-z style sequential rotation $R(\alpha,\beta,\gamma)$. Here we introduce two different frame of references. The first one is the laboratory reference frame, with its z axis aligned along the external magnetic field direction and x and y axis following the right hand rule. The second reference frame is rotor fixed reference frame, where its z axis is aligned with the rotation axis of the NMR rotor. So a tensor in the lab frame is expressed as a linear combination of tensors of the same rank in the rotor fixed frame by a rotation transformation: $R^{LR}(\alpha_{LP} = \omega_r t, \beta_{LP} = \theta_M, \gamma_{LP} = 0)$ in the z-y-z convention.

However, for interactions expressed by second rank irreducible spherical tensors, this is not the end of the transformation. The tensor format expression will vary depending on the orientation of the molecule in the sample. To get a consistent reference frame for molecules at all orientations in solid samples, we introduce the principal axis reference frame. In this reference frame, the expression of the second rank tensor is diagonalized. Let's take H_{cs} as an example, after we have taken out the trace part of the H_{cs}, now in the diagnolized frame, its second rank tensor part is traceless, just like other interactions such as dipolar and quadrupolar interactions.

According to the Haeberlen convention, in diagonalized principal axis frame, the second rank tensor part of chemical shielding/shift is:

$$\omega_{aniso} = \omega_0\delta_{aniso} \tag{5.54}$$

$$\delta_{aniso} = \delta_{zz}^P - \delta_{iso} \text{ (reduced anisotropy)}$$

$$\Delta\delta = \delta_{zz}^P - \frac{\left(\delta_{xx}^P + \delta_{yy}^P\right)}{2} = \frac{3}{2}\delta_{aniso} \text{ (anisotropy)}$$

$$\eta = \frac{\delta_{yy}^P - \delta_{xx}^P}{\delta_{zz}^P - \delta_{iso}} \ (asymmetry)$$

Then:

$$R_{22}^P = R_{2-2}^P = -\frac{1}{2}\eta\omega_{aniso}; R_{20}^P = \sqrt{\frac{3}{2}}\omega_{aniso};\ R_{21}^P = R_{2-1}^P = 0$$

Here the subscript P means in the principal axis frame. I also shifted the rank label down as the leading subscript.

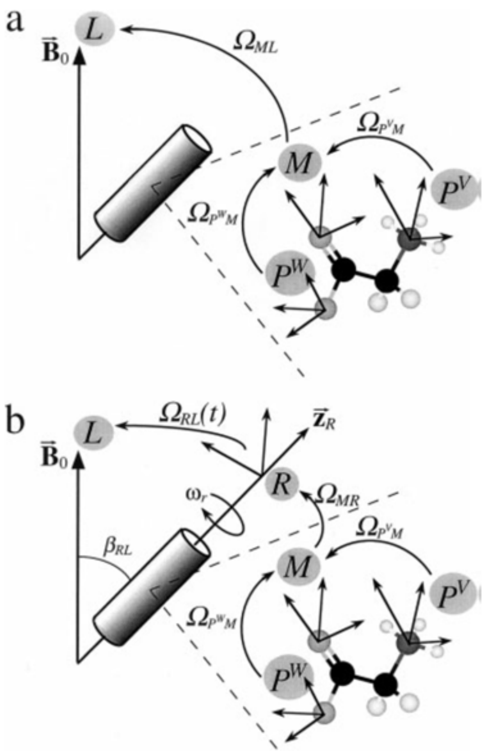


Figure 5.3. Transformation of reference frame in solid-state NMR experiments. Adapted from Mattias Eden' Computer simulations in ssNMR I spin dynamics theory, Concepts in Magnetic Resonance Part (A) 34(35) (2003).

Thus the chemical shielding tensor in this reference frame is unique for the same sites in all molecules. Their values are entirely determined by the electron distribution, with the most extended direction of electron orbits along the z direction. Then molecules in different orientation can be related to this frame by rotations defined by their respective Euler angle.

Therefore, we can correlate the molecule in rotor fixed frame to this principal axis frame by another set of Euler z-y-z rotation $R^{RP}(\alpha_{RP}, \beta_{RP}, \gamma_{RP})$, where $\alpha_{RP}, \beta_{RP}, \gamma_{RP}$ depends on the molecular orientation in the rotor. In simulation, we will average the angles $\alpha_{RP}, \beta_{RP}, \gamma_{RP}$ to represent the powder distribution in solids. We also can see the rotation angle γ_{RP} in the transformation from the principal axis frame to the rotor fixed frame has the same effect in the final combined transformation as the α_{LP} for the subsequent transformation from the rotor fixed frame to the Lab frame. By these two transformations principal axis frame-> rotor fixed frame-> lab frame, we can represent all molecules in powder manipulated by MAS. As the chemical shielding‘s expression of second rank tensor part in the lab frame only has the R^L_{20} component, we can represent the spatial part of Hamiltonians in the lab frame with the principal values in the principal axis frame by Wigner-Eckart theorem, joining two rotation transformations:

$$\begin{aligned} R^L_{20} &= \sum_{m=-2}^{2} R^R_{2m}\, D^2_{m0}(\omega_r t, \theta_M, 0) \\ &= \sum_{m=-2}^{2} \sum_{m=-2}^{2} R^P_{2m'}\, D^2_{m'm}(\alpha, \beta, \gamma) D^2_{m0}(\omega_r t, \theta_M, 0) \end{aligned} \tag{5.55}$$

Since in principal axis frame we have $R^P_{21} = R^P_{2-1} = 0$, this double transformation of reference frames leaves us only three double summation terms:

$$\begin{aligned} &R^L_{20} \\ &= \sum_{m=-2}^{2} R^P_{22} D^2_{2m}(\alpha, \beta, \gamma) D^2_{m0}(\omega_r t, \theta_M, 0) \\ &+ \sum_{m=-2}^{2} R^P_{2,-2} D^2_{-2,m}(\alpha, \beta, \gamma) D^2_{m0}(\omega_r t, \theta_M, 0) \end{aligned} \tag{5.56}$$

$$+\sum_{m=-2}^{2} R^P_{20} D^2_{0m}(\alpha,\beta,\gamma) D^2_{m0}(\omega_r t,\theta_M,0)$$

Let’s do them one by one:

$$\sum_{m=-2}^{2} R^P_{22} D^2_{2m}(\alpha,\beta,\gamma) D^2_{m0}(\omega_r t,\theta_M,0)$$

$$= R^P_{22}[e^{-i(2\alpha+2\gamma)} d^2_{22}(\beta) d^2_{20}(\theta_M) e^{-i2\omega_r t} + e^{-i(2\alpha+\gamma)} d^2_{21}(\beta) d^2_{10}(\theta_M) e^{-i\omega_r t}$$

$$+e^{-i(2\alpha)} d^2_{20}(\beta) d^2_{00}(\theta_M)$$

$$+e^{-i(2\alpha-\gamma)} d^2_{2,-1}(\beta) d^2_{-1,0}(\theta_M) e^{i\omega_r t} + e^{-i(2\alpha-2\gamma)} d^2_{2,-2}(\beta) d^2_{-2,0}(\theta_M) e^{i2\omega_r t}]$$

$$\sum_{m=-2}^{2} R^P_{2,-2} D^2_{-2,m}(\alpha,\beta,\gamma) D^2_{m0}(\omega_r t,\theta_M,0)$$

$$= R^P_{2,-2}[e^{-i(-2\alpha+2\gamma)} d^2_{-2,2}(\beta) d^2_{20}(\theta_M) e^{-i2\omega_r t} + e^{-i(-2\alpha+\gamma)} d^2_{-2,1}(\beta) d^2_{10}(\theta_M) e^{-i\omega_r t}$$

$$+e^{i(2\alpha)} d^2_{-2,0}(\beta) d^2_{00}(\theta_M) + e^{-i(-2\alpha-\gamma)} d^2_{-2,-1}(\beta) d^2_{-1,0}(\theta_M) e^{i\omega_r t}$$

$$+e^{-i(-2\alpha-2\gamma)} d^2_{-2,-2}(\beta) d^2_{-2,0}(\theta_M) e^{i2\omega_r t}]$$

$$\sum_{m=-2}^{2} R^P_{20} D^2_{0m}(\alpha,\beta,\gamma) D^2_{m0}(\omega_r t,\theta_M,0)$$

$$= R^P_{20}[e^{-i(2\gamma)} d^2_{02}(\beta) d^2_{20}(\theta_M) e^{-i2\omega_r t} + e^{-i(\gamma)} d^2_{01}(\beta) d^2_{10}(\theta_M) e^{-i\omega_r t} + d^2_{00}(\beta) d^2_{00}(\theta_M)$$

$$+e^{i(\gamma)} d^2_{0,-1}(\beta) d^2_{-1,0}(\theta_M) e^{i\omega_r t} + e^{i(2\gamma)} d^2_{0,-2}(\beta) d^2_{-2,0}(\theta_M) e^{i2\omega_r t}]$$

Note that $d^2_{-2,-2}(\beta) = d^2_{22}(\beta) = \frac{1}{4}(1+\cos\beta)^2,$ $d^2_{20}(\theta_M) = d^2_{-2,0}(\theta_M) = \sqrt{\frac{3}{8}}\sin^2\theta_M$, $d^2_{2,-2}(\beta) = d^2_{-22}(\beta) = \frac{1}{4}(1-\cos\beta)^2$; Hence we have:

$$d^2_{22}(\beta) d^2_{20}(\theta_M) = d^2_{-2,-2}(\beta) d^2_{-2,0}(\theta_M) = \frac{1}{4}\sqrt{\frac{3}{8}}(1+\cos\beta)^2 \sin^2\theta_M\,;$$

$$d^2_{2,-2}(\beta) d^2_{-2,0}(\theta_M) = d^2_{-22}(\beta) d^2_{20}(\theta_M) = \frac{1}{4}\sqrt{\frac{3}{8}}(1-\cos\beta)^2 \sin^2\theta_M\,;$$

$$d^2_{2,-1}(\beta) = -d^2_{-21}(\beta) = -\frac{1}{2}\sin\beta\,(1-\cos\beta)$$

$$d^2_{-1,0}(\theta_M) = -d^2_{10}(\theta_M) = \sqrt{\frac{3}{8}}\sin 2\theta_M$$

$$d^2_{2,1}(\beta) = -d^2_{-2-1}(\beta) = -\frac{1}{2}\sin\beta\,(1+\cos\beta)$$

Hence we have:

$$d^2_{21}(\beta)d^2_{10}(\theta_M) = d^2_{-2,-1}(\beta)d^2_{-1,0}(\theta_M) = -\tfrac{1}{2}\sin\beta\,(1+\cos\beta)\left(-\sqrt{\tfrac{3}{8}}\sin 2\theta_M\right)$$

$$= \frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1+\cos\beta)\sin 2\theta_M$$

$$d^2_{-2,1}(\beta)d^2_{10}(\theta_M) = d^2_{2,-1}(\beta)d^2_{-1,0}(\theta_M) = -\frac{1}{2}(1-\cos\beta)\sin\beta\sqrt{\frac{3}{8}}\sin 2\theta_M$$

$$= -\frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1-\cos\beta)\sin 2\theta_M$$

$$d^2_{01}(\beta)d^2_{10}(\theta_M) = d^2_{0,-1}(\beta)d^2_{-1,0}(\theta_M) = \sqrt{\frac{3}{8}}\sin 2\beta\left(-\sqrt{\frac{3}{8}}\sin 2\theta_M\right) = -\frac{3}{8}\sin 2\beta\sin 2\theta_M$$

$$d^2_{02}(\beta) = d^2_{0,-2}(\beta) = \sqrt{\frac{3}{8}}\sin^2\beta$$

Hence we have:

$$d^2_{02}(\beta)d^2_{20}(\theta_M) = d^2_{0,-2}(\beta)d^2_{-2,0}(\theta_M) = \sqrt{\frac{3}{8}}\sin^2\beta\sqrt{\frac{3}{8}}\sin^2\theta_M = \frac{3}{8}\sin^2\beta\sin^2\theta_M$$

$$d^2_{20}(\beta)d^2_{00}(\theta_M) = d^2_{-2,0}(\beta)d^2_{00}(\theta_M) = \frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\beta\,(3\cos^2\theta_M - 1)$$

$$d^2_{00}(\beta)d^2_{00}(\theta_M) = \frac{1}{4}(3\cos^2\beta - 1)(3\cos^2\theta_M - 1)$$

So we can rewrite the three terms as, recall $R^P_{22} = R^P_{2-2}$:

$$\sum_{m=-2}^{2} R^{P}_{22} D^{2}_{2m}(\alpha,\beta,\gamma) D^{2}_{m0}(\omega_r t,\theta_M,0) =$$

$$R^{P}_{22}[e^{-i(2\alpha+2\gamma)} e^{-i2\omega_r t} \frac{1}{4}\sqrt{\frac{3}{8}}(1+\cos\beta)^2 \sin^2\theta_M$$

$$+e^{-i(2\alpha+\gamma)} e^{-i\omega_r t} \frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1+\cos\beta)\sin 2\theta_M$$

$$+e^{-i(2\alpha)} \frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\beta\,(3\cos^2\theta_M-1) - e^{-i(2\alpha-\gamma)} e^{i\omega_r t} \frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1-\cos\beta)\sin 2\theta_M$$

$$+e^{-i(2\alpha-2\gamma)} e^{i2\omega_r t} \frac{1}{4}\sqrt{\frac{3}{8}}(1-\cos\beta)^2 \sin^2\theta_M]$$

$$\sum_{m=-2}^{2} R^{P}_{2,-2} D^{2}_{-2,m}(\alpha,\beta,\gamma) D^{2}_{m0}(\omega_r t,\theta_M,0) =$$

$$R^{P}_{2,2}[e^{-i(-2\alpha+2\gamma)} e^{-i2\omega_r t} \frac{1}{4}\sqrt{\frac{3}{8}}(1-\cos\beta)^2 \sin^2\theta_M$$

$$-e^{-i(-2\alpha+\gamma)} e^{-i\omega_r t} \frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1-\cos\beta)\sin 2\theta_M$$

$$+e^{i(2\alpha)} \frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\beta\,(3\cos^2\theta_M-1) + e^{-i(-2\alpha-\gamma)} e^{i\omega_r t} \frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1+\cos\beta)\sin 2\theta_M$$

$$+e^{-i(-2\alpha-2\gamma)} e^{i2\omega_r t} \frac{1}{4}\sqrt{\frac{3}{8}}(1+\cos\beta)^2 \sin^2\theta_M]$$

$$\sum_{m=-2}^{2} R^{P}_{20} D^{2}_{0m}(\alpha,\beta,\gamma) D^{2}_{m0}(\omega_r t,\theta_M,0)$$

$$= R^{P}_{20}[e^{-i(2\gamma)} e^{-i2\omega_r t} \frac{3}{8}\sin^2\beta \sin^2\theta_M - e^{-i(\gamma)} e^{-i\omega_r t} \frac{3}{8}\sin 2\beta \sin 2\theta_M$$

$$+\frac{1}{4}(3\cos^2\beta-1)(3\cos^2\theta_M-1) - e^{i(\gamma)} e^{i\omega_r t} \frac{3}{8}\sin 2\beta \sin 2\theta_M$$

$$+e^{i(2\gamma)}e^{i2\omega_r t}\frac{3}{8}\sin^2\beta\sin^2\theta_M]$$

Combine together we have:

$$R_{20}^{L} \tag{5.57}$$

$$=\left\{R_{20}^{P}\frac{1}{4}(3\cos^2\beta-1)+R_{22}^{P}\left[e^{-i(2\alpha)}\frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\beta+e^{i(2\alpha)}\frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\beta\right]\right\}(3\cos^2\theta_M-1)$$

$$+R_{22}^{P}[e^{-i2\omega_r t}e^{-i(2\alpha+2\gamma)}+e^{-i(-2\alpha-2\gamma)}e^{i2\omega_r t}]\frac{1}{4}\sqrt{\frac{3}{8}}(1+\cos\beta)^2\sin^2\theta_M$$

$$+R_{22}^{P}[\,e^{-i(2\alpha-2\gamma)}e^{i2\omega_r t}+e^{-i(-2\alpha+2\gamma)}e^{-i2\omega_r t}]\,\frac{1}{4}\sqrt{\frac{3}{8}}(1-\cos\beta)^2\sin^2\theta_M$$

$$+R_{20}^{P}\left[e^{i(2\gamma)}e^{i2\omega_r t}+e^{-i(2\gamma)}e^{-i2\omega_r t}\right]\frac{3}{8}\sin^2\beta\sin^2\theta_M$$

$$-R_{20}^{P}\left[e^{-i(\gamma)}e^{-i\omega_r t}+e^{i(\gamma)}e^{i\omega_r t}\right]\frac{3}{8}\sin 2\beta\sin 2\theta_M$$

$$+R_{22}^{P}\left[e^{-i(2\alpha+\gamma)}e^{-i\omega_r t}+e^{-i(-2\alpha-\gamma)}e^{i\omega_r t}\right]\frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1+\cos\beta)\sin 2\theta_M$$

$$-R_{22}^{P}[e^{-i(2\alpha-\gamma)}e^{i\omega_r t}+e^{-i(-2\alpha+\gamma)}e^{-i\omega_r t}]\frac{1}{2}\sqrt{\frac{3}{8}}\sin\beta\,(1-\cos\beta)\sin 2\theta_M$$

Notice the pattern of the exponential factors in the brackets, we can first compute this formula:

$$e^{-i\alpha}e^{-i\beta}+e^{i\alpha}e^{i\beta}=(\cos\alpha-i\sin\alpha)(\cos\beta-i\sin\beta)+(\cos\alpha+i\sin\alpha)(\cos\beta+i\sin\beta)$$

$$=\cos\alpha\cos\beta-\sin\alpha\sin\beta-i(\cos\alpha\sin\beta+\sin\alpha\cos\beta)+\cos\alpha\cos\beta-\sin\alpha\sin\beta$$

$$+i(\cos\alpha\sin\beta+\sin\alpha\cos\beta)=2(\cos\alpha\cos\beta-\sin\alpha\sin\beta)=2\cos(\alpha+\beta)$$

Apply this to the above derivation:

$$R_{20}^{L}=\left[\frac{1}{4}R_{20}^{P}(3\cos^2\beta-1)+R_{22}^{P}\cos 2\alpha\sqrt{\frac{3}{8}}\sin^2\beta\right](3\cos^2\theta_M-1)$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}(1+\cos\beta)^2\sin^2\theta_M\cos 2(\omega_r t+\alpha+\gamma)\,R_{22}^{P}$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}(1-\cos\beta)^2\sin^2\theta_M\cos 2(\omega_r t-\alpha+\gamma)\,R_{22}^P+\frac{3}{4}\sin^2\beta\sin^2\theta_M\cos 2(\omega_r t+\gamma)\,R_{20}^P$$

$$-\frac{3}{4}\sin 2\beta\sin 2\theta_M\cos(\omega_r t+\gamma)\,R_{20}^P-\sqrt{\frac{3}{8}}\sin\beta\,(1+\cos\beta)\sin 2\theta_M\cos(\omega_r t+2\alpha+\gamma)\,R_{22}^P$$

$$-\sqrt{\frac{3}{8}}\sin\beta\,(1-\cos\beta)\sin 2\theta_M\cos(\omega_r t-2\alpha+\gamma)\,R_{22}^P$$

Recall $R_{22}^P=-\frac{1}{2}\eta\omega_{aniso}$, $R_{20}^P=\sqrt{\frac{3}{2}}\omega_{aniso}$, the time independent term is:

$$=[\frac{1}{4}\sqrt{\frac{3}{2}}(3\cos^2\beta-1)-\frac{1}{4}\eta\cos 2\alpha\sqrt{\frac{3}{2}}\sin^2\beta](3\cos^2\theta_M-1)\omega_{aniso} \tag{5.58}$$

$$=\sqrt{\frac{3}{2}}\omega_{aniso}\frac{(3\cos^2\theta_M-1)}{2}[\frac{(3\cos^2\beta-1)}{2}-\frac{\eta}{2}\cos 2\alpha\sin^2\beta]$$

Now we need to combine terms with the same time dependent frequency on ω_r.

First let's rearrange terms with $2\omega_r t$ dependence:

$$R_{20}^L(2\omega_r t)$$

$$=\frac{1}{2}\sqrt{\frac{3}{8}}(1+\cos\beta)^2\sin^2\theta_M\cos 2(\omega_r t+\alpha+\gamma)\,R_{22}^P$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}(1-\cos\beta)^2\sin^2\theta_M\cos 2(\omega_r t-\alpha+\gamma)\,R_{22}^P+\frac{3}{4}\sin^2\beta\sin^2\theta_M\cos 2(\omega_r t+\gamma)\,R_{20}^P$$

$$=\frac{1}{2}\sqrt{\frac{3}{8}}(1+\cos\beta)^2\sin^2\theta_M\,R_{22}^P[\cos 2\omega_r t\cos 2(\alpha+\gamma)-\sin 2\omega_r t\sin 2(\alpha+\gamma)]$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}(1-\cos\beta)^2\sin^2\theta_M\,R_{22}^P[\cos 2\omega_r t\cos 2(\alpha-\gamma)+\sin 2\omega_r t\sin 2(\alpha-\gamma)]$$

$$+\frac{3}{4}\sin^2\beta\sin^2\theta_M\,R_{20}^P[\cos 2\omega_r t\cos 2\gamma-\sin 2\omega_r t\sin 2\gamma]$$

$$= \frac{1}{2}\sqrt{\frac{3}{8}}(1+\cos\beta)^2 \sin^2\theta_M \, R^P_{22} \times$$

$$\left[\begin{matrix}\cos 2\omega_r t\,(\cos 2\alpha \cos 2\gamma - \sin 2\alpha \sin 2\gamma) - \sin 2\omega_r t\,(\sin 2\alpha \cos 2\gamma \\ + \sin 2\gamma \cos 2\alpha)\end{matrix}\right]$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}(1-\cos\beta)^2 \sin^2\theta_M \, R^P_{22} \times$$

$$\left[\begin{matrix}\cos 2\omega_r t\,(\cos 2\alpha \cos 2\gamma + \sin 2\alpha \sin 2\gamma) + \sin 2\omega_r t\,(\sin 2\alpha \cos 2\gamma \\ - \sin 2\gamma \cos 2\alpha)\end{matrix}\right]$$

$$+\frac{3}{4}\sin^2\beta \sin^2\theta_M \, R^P_{20}[\cos 2\omega_r t \cos 2\gamma - \sin 2\omega_r t \sin 2\gamma]$$

$$= \frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\theta_M \, R^P_{22} \cos 2\omega_r t\,[(1+\cos\beta)^2(\cos 2\alpha \cos 2\gamma - \sin 2\alpha \sin 2\gamma)$$

$$+(1-\cos\beta)^2(\cos 2\alpha \cos 2\gamma + \sin 2\alpha \sin 2\gamma)] + \frac{3}{4}\sin^2\beta \sin^2\theta_M \, R^P_{20} \cos 2\gamma \cos 2\omega_r t$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\theta_M \, R^P_{22} \sin 2\omega_r t\,[-(1+\cos\beta)^2(\sin 2\alpha \cos 2\gamma + \sin 2\gamma \cos 2\alpha)$$

$$+(1-\cos\beta)^2(\sin 2\alpha \cos 2\gamma - \sin 2\gamma \cos 2\alpha)] - \frac{3}{4}\sin^2\beta \sin^2\theta_M \, R^P_{20} \sin 2\gamma \sin 2\omega_r t$$

$$= \frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\theta_M \, R^P_{22} \cos 2\omega_r t \left[\begin{matrix}(1+2\cos\beta+\cos^2\beta)(\cos 2\alpha \cos 2\gamma - \sin 2\alpha \sin 2\gamma) \\ +(1-2\cos\beta+\cos^2\beta)(\cos 2\alpha \cos 2\gamma + \sin 2\alpha \sin 2\gamma)\end{matrix}\right]$$

$$+\frac{3}{4}\sin^2\beta \sin^2\theta_M \, R^P_{20} \cos 2\gamma \cos 2\omega_r t$$

$$+\frac{1}{2}\sqrt{\frac{3}{8}}\sin^2\theta_M \, R^P_{22} \sin 2\omega_r t \left[\begin{matrix}-(1+2\cos\beta+\cos^2\beta)(\sin 2\alpha \cos 2\gamma + \sin 2\gamma \cos 2\alpha) \\ +(1-2\cos\beta+\cos^2\beta)(\sin 2\alpha \cos 2\gamma - \sin 2\gamma \cos 2\alpha)\end{matrix}\right]$$

$$-\frac{3}{4}\sin^2\beta \sin^2\theta_M \, R^P_{20} \sin 2\gamma \sin 2\omega_r t$$

$$= \sqrt{\frac{3}{2}}\sin^2\theta_M \frac{R^P_{22}}{2}[\cos 2\alpha \cos 2\gamma\,(1+\cos^2\beta) - 2\sin 2\alpha \sin 2\gamma \cos\beta] \cos 2\omega_r t$$

$$+\frac{3}{4}\sin^2\beta \sin^2\theta_M \, R^P_{20} \cos 2\gamma \cos 2\omega_r t$$

$$+\sqrt{\frac{3}{2}}\sin^2\theta_M\,\frac{R_{22}^P}{2}\sin 2\omega_r t\,[-\sin 2\gamma\cos 2\alpha\,(1+\cos^2\beta)-2\sin 2\alpha\cos 2\gamma\cos\beta]$$

$$-\frac{3}{4}\sin^2\beta\,\sin^2\theta_M\,R_{20}^P\sin 2\gamma\sin 2\omega_r t$$

Recall $R_{22}^P=-\frac{1}{2}\eta\omega_{aniso}$, $R_{20}^P=\sqrt{\frac{3}{2}}\omega_{aniso}$

$$R_{20}^L(2\omega_r t) \tag{5.59}$$

$$=\sqrt{\frac{3}{2}}\sin^2\theta_M\,\omega_{aniso}\{\eta\left[\begin{array}{l}-\frac{1}{4}\cos 2\alpha\cos 2\gamma\,(1+\cos^2\beta)\\ \qquad+\frac{1}{2}\sin 2\alpha\sin 2\gamma\cos\beta\end{array}\right]$$

$$+\frac{3}{4}\sin^2\beta\cos 2\gamma\}\cos 2\omega_r t$$

$$+\sqrt{\frac{3}{2}}\sin^2\theta_M\,\omega_{aniso}\{\,\eta\left[\frac{1}{4}\sin 2\gamma\cos 2\alpha\,(1+\cos^2\beta)+\frac{1}{2}\sin 2\alpha\cos 2\gamma\cos\beta\right]$$

$$-\frac{3}{4}\sin^2\beta\sin 2\gamma\}\sin 2\omega_r t$$

If we represent the coefficient with $\mathcal{C}_2$ and $\mathcal{S}_2$ for the $\cos 2\omega_r t$ and $\sin 2\omega_r t$ terms, respectively:

$$R_{20}^L(2\omega_r t)$$

$$=\sqrt{\frac{3}{2}}\omega_{aniso}(\mathcal{C}_2\cos 2\omega_r t+\mathcal{S}_2\sin 2\omega_r t)$$

Where

$$\mathcal{C}_2=\frac{\sin^2\theta_M}{2}\{\eta\left[-\frac{1}{2}\cos 2\alpha\cos 2\gamma\,(1+\cos^2\beta)+\sin 2\alpha\sin 2\gamma\cos\beta\right]+\frac{3}{2}\sin^2\beta\cos 2\gamma\};$$

$$\mathcal{S}_2=\frac{\sin^2\theta_M}{2}\{\eta\left[\frac{1}{2}\sin 2\gamma\cos 2\alpha\,(1+\cos^2\beta)+\sin 2\alpha\cos 2\gamma\cos\beta\right]-\frac{3}{2}\sin^2\beta\sin 2\gamma\};$$

Now, let's rearrange the $\omega_r t$ dependent terms:

$$R_{20}^L(\omega_r t)=$$

$$-\frac{3}{4}\sin 2\beta\sin 2\theta_M\cos(\omega_r t+\gamma)\,R_{20}^P+\sqrt{\frac{3}{8}}\sin\beta\,(1+\cos\beta)\sin 2\theta_M\cos(\omega_r t+2\alpha+\gamma)\,R_{22}^P$$

$$-\sqrt{\frac{3}{8}}\sin\beta\,(1-\cos\beta)\sin 2\theta_M\cos(\omega_r t-2\alpha+\gamma)\,R_{22}^P$$

$$=-\frac{3}{4}\sin 2\beta\sin 2\theta_M\cos(\omega_r t+\gamma)\,R_{20}^P+\sqrt{\frac{3}{8}}\sin\beta\sin 2\theta_M\,R_{22}^P[\cos(\omega_r t+2\alpha+\gamma)\,(1+\cos\beta)$$

$$-\cos(\omega_r t-2\alpha+\gamma)\,(1-\cos\beta)]$$

$$=-\frac{3}{4}\sin 2\beta\sin 2\theta_M\cos(\omega_r t+\gamma)\,R_{20}^P$$

$$+\sqrt{\frac{3}{8}}\sin\beta\sin 2\theta_M\,R_{22}^P[\cos(\omega_r t+2\alpha+\gamma)-\cos(\omega_r t-2\alpha+\gamma)]$$

$$+\sqrt{\frac{3}{8}}\sin\beta\cos\beta\sin 2\theta_M\,R_{22}^P[\cos(\omega_r t+2\alpha+\gamma)+\cos(\omega_r t-2\alpha+\gamma)]$$

$$=-\frac{3}{4}\sin 2\beta\sin 2\theta_M\cos(\omega_r t+\gamma)\,R_{20}^P-2\sqrt{\frac{3}{8}}\sin\beta\sin 2\theta_M\,R_{22}^P[\sin(\omega_r t+\gamma)\sin 2\alpha]$$

$$+2\sqrt{\frac{3}{8}}\sin\beta\cos\beta\sin 2\theta_M\,R_{22}^P[\cos(\omega_r t+\gamma)\cos 2\alpha]$$

$$-\frac{3}{4}\sin 2\beta\sin 2\theta_M\,R_{20}^P(\cos\omega_r t\cos\gamma-\sin\omega_r t\sin\gamma)$$

$$-2\sqrt{\frac{3}{8}}\sin\beta\sin 2\theta_M\,R_{22}^P[\sin\omega_r t\sin 2\alpha\cos\gamma+\cos\omega_r t\sin 2\alpha\sin\gamma]$$

$$+2\sqrt{\frac{3}{8}}\sin\beta\cos\beta\sin 2\theta_M\,R_{22}^P[\cos\omega_r t\cos 2\alpha\cos\gamma-\sin\omega_r t\cos 2\alpha\sin\gamma]$$

Recall $R_{22}^P=-\frac{1}{2}\eta\omega_{aniso}$, $R_{20}^P=\sqrt{\frac{3}{2}}\omega_{aniso}$

$$R_{20}^L(\omega_r t)$$

$$=-\frac{3}{4}\sin 2\beta\sin 2\theta_M\sqrt{\frac{3}{2}}\omega_{aniso}(\cos\omega_r t\cos\gamma-\sin\omega_r t\sin\gamma)$$

$$+\frac{1}{2}\sqrt{\frac{3}{2}}\sin\beta\sin 2\theta_M\,\eta\omega_{aniso}[\sin\omega_r t\sin 2\alpha\cos\gamma+\cos\omega_r t\sin 2\alpha\sin\gamma]$$

$$-\frac{1}{2}\sqrt{\frac{3}{2}}\sin\beta\cos\beta\sin 2\theta_M\,\eta\omega_{aniso}[\cos\omega_r t\cos 2\alpha\cos\gamma-\sin\omega_r t\cos 2\alpha\sin\gamma]$$

$$=\sqrt{\frac{3}{2}}\sin\beta\sin 2\theta_M\,\omega_{aniso}\left[\frac{\eta}{2}(\sin 2\alpha\sin\gamma-\cos\beta\cos 2\alpha\cos\gamma)-\frac{3}{2}\cos\beta\cos\gamma\right]\cos\omega_r t$$

$$+\sqrt{\frac{3}{2}}\sin\beta\sin 2\theta_M\,\omega_{aniso}[\frac{3}{2}\cos\beta\sin\gamma+\frac{\eta}{2}(\sin 2\alpha\cos\gamma+\cos\beta\cos 2\alpha\sin\gamma)]\sin\omega_r t$$

If we represent the coefficient with $\mathcal{C}_1$ and $\mathcal{S}_1$ for the $\cos\omega_r t$ and $\sin\omega_r t$ terms, respectively:

$$R_{20}^{L}(\omega_r t)$$

$$=\sqrt{\frac{3}{2}}\omega_{aniso}(\mathcal{C}_1\cos\omega_r t+\mathcal{S}_1\sin\omega_r t)$$

$\mathcal{C}_1=\frac{1}{2}\sin\beta\sin 2\theta_M\,[\eta(\sin 2\alpha\sin\gamma-\cos\beta\cos 2\alpha\cos\gamma)-3\cos\beta\cos\gamma];$

$$\mathcal{S}_1=\frac{1}{2}\sin\beta\sin 2\theta_M\,[3\cos\beta\sin\gamma+\eta(\sin 2\alpha\cos\gamma+\cos\beta\cos 2\alpha\sin\gamma)];$$

Note my expression has the position of α and γ exchanged, compared to the expression given by M. Matti Maricq and J. S. Waugh in their seminar paper NMR in rotating solids (JCP 70, 3300-3315, 1979). There is also a reverse of sign for any term involving η, due to the definition of η with the sign difference in our convention. It could either be my mistake of interpreting the Wigner rotation matrix, or Maricq and Waugh. If you know for sure, please let me know.

Therefore, let's rewrite the final form of chemical shielding Hamiltonian under rotation:

$$H_{cs}=\omega_0\left\{\delta_{iso}+\sqrt{\frac{3}{2}}\delta_{aniso}\frac{(3\cos^2\theta_M-1)}{2}\left[\frac{(3\cos^2\beta-1)}{2}-\frac{\eta}{2}\cos 2\alpha\sin^2\beta\right]\right\}I_z+\sqrt{\frac{3}{2}}\omega_0\delta_{aniso}(\mathcal{C}_1\cos\omega_r t+\mathcal{S}_1\sin\omega_r t+\mathcal{C}_2\cos 2\omega_r t+\mathcal{S}_2\sin 2\omega_r t)I_z \tag{5.60}$$

Where we have:

$$\mathcal{C}_1 = \frac{1}{2}\sin\beta \sin 2\theta_M \left[\eta(\sin 2\alpha \sin\gamma - \cos\beta \cos 2\alpha \cos\gamma) - 3\cos\beta\cos\gamma\right]$$

$$\mathcal{S}_1 = \frac{1}{2}\sin\beta \sin 2\theta_M \left[3\cos\beta\sin\gamma + \eta(\sin 2\alpha \cos\gamma + \cos\beta \cos 2\alpha \sin\gamma)\right]$$

$$\mathcal{C}_2 = \frac{\sin^2\theta_M}{2}\left\{\eta\left[-\frac{1}{2}\cos 2\alpha \cos 2\gamma\,(1+\cos^2\beta) + \sin 2\alpha \sin 2\gamma \cos\beta\right] + \frac{3}{2}\sin^2\beta \cos 2\gamma\right\}$$

$$\mathcal{S}_2 = \frac{\sin^2\theta_M}{2}\left\{\eta\left[\frac{1}{2}\sin 2\gamma \cos 2\alpha\,(1+\cos^2\beta) + \sin 2\alpha \cos 2\gamma \cos\beta\right] - \frac{3}{2}\sin^2\beta \sin 2\gamma\right\}$$

This is a generalized expression, and Hamiltonians in various situations can be derived by plugging respective parameters. For MAS experiments, we can replace $\sin^2\theta_M = \frac{2}{3}$; $\cos^2\theta_M = \frac{1}{3}$, $\sin 2\theta_M = \frac{2}{3}\sqrt{2}$;

$$H_{cs} = \omega_0\delta_{iso}I_z + \sqrt{\frac{3}{2}}\,\omega_0\delta_{aniso}(\mathcal{C}_1\cos\omega_r t + \mathcal{S}_1\sin\omega_r t + \mathcal{C}_2\cos 2\omega_r t + \mathcal{S}_2\sin 2\omega_r t)I_z$$

$$= \omega_0\delta_{iso}I_z$$

$$+ \sqrt{\frac{3}{2}}\,\omega_0\delta_{aniso}\left[\begin{array}{c}\frac{\mathcal{S}_1}{2i}\left(e^{i\omega_r t} - e^{-i\omega_r t}\right) + \frac{\mathcal{C}_1}{2}\left(e^{i\omega_r t} + e^{-i\omega_r t}\right) + \frac{\mathcal{S}_2}{2i}\left(e^{i2\omega_r t} - e^{-i2\omega_r t}\right) \\ + \frac{\mathcal{C}_2}{2}\left(e^{i2\omega_r t} + e^{-i2\omega_r t}\right)\end{array}\right]I_z$$

$$H_{cs} = \omega_0\delta_{iso}I_z + \frac{1}{2}\sqrt{\frac{3}{2}}\,\omega_0\delta_{aniso}(\mathcal{C}_1 - i\mathcal{S}_1)e^{i\omega_r t} \tag{5.61}$$

$$+ \frac{1}{2}\sqrt{\frac{3}{2}}\,\omega_0\delta_{aniso}(\mathcal{C}_1 + i\mathcal{S}_1)e^{-i\omega_r t}$$

$$+ \frac{1}{2}\sqrt{\frac{3}{2}}\,\omega_0\delta_{aniso}(\mathcal{C}_2 - i\mathcal{S}_2)e^{i2\omega_r t} + \frac{1}{2}\sqrt{\frac{3}{2}}\,\omega_0\delta_{aniso}(\mathcal{C}_2 + i\mathcal{S}_2)e^{-i2\omega_r t}$$

Plug in the expression and replace $\sin^2\theta_M = \frac{2}{3}$; $\cos^2\theta_M = \frac{1}{3}$, $\sin 2\theta_M = \frac{2}{3}\sqrt{2}$, we can write H_{cs} in a format commonly seen in literature:

$$H_{cs} = \omega_{cs}(t)I_z \tag{5.62}$$

$$\omega_{cs}(t) = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{cs}\,exp(im\omega_r t)$$

$$\omega_{20}^{cs} = \omega_0 \delta_{iso}$$

$$\omega_{2,\pm1}^{cs} = \frac{1}{2}\sqrt{\frac{3}{2}}\omega_0 \delta_{aniso} \frac{1}{2} \sin\beta \sin 2\theta_M \,[\eta(\mp i \sin 2\alpha - \cos\beta \cos 2\alpha) - 3\cos\beta] e^{\pm i\gamma}$$
$$= \frac{\sqrt{3}}{6}\omega_0 \delta_{aniso} \sin\beta \,[\eta(\mp i \sin 2\alpha - \cos\beta \cos 2\alpha) - 3\cos\beta] e^{\pm i\gamma}$$

$$\omega_{2,\pm2}^{cs} = \frac{1}{2}\sqrt{\frac{3}{2}}\omega_0 \delta_{aniso} \frac{\sin^2\theta_M}{2} e^{\pm i2\gamma} [\eta[-\frac{1}{2}\cos 2\alpha\,(1+\cos^2\beta) \mp i \sin 2\alpha \cos\beta] + \frac{3}{2}\sin^2\beta]$$
$$= \frac{\sqrt{6}}{12}\omega_0 \delta_{aniso} \left[\eta[-\frac{1}{2}\cos 2\alpha\,(1+\cos^2\beta) \mp i \sin 2\alpha \cos\beta] + \frac{3}{2}\sin^2\beta\right] e^{\pm i2\gamma}$$

Homework:

1. If you set $\theta_M = 0$, $\omega_r = 0$, you will obtain the static powder distribution of H_{cs}:

$$H_{cs}(\alpha,\beta) = \omega_0 \left\{ \delta_{iso} + \sqrt{\frac{3}{2}}\delta_{aniso} \left[\frac{(3\cos^2\beta - 1)}{2} - \frac{\eta}{2}\cos 2\alpha \sin^2\beta \right] \right\} I_z \tag{5.63}$$

2. Could you apply the same workflow to dipolar interaction? It is much simpler, as dipolar interaction is already diagonalized in lab frame, with constant

$$b_{IS} = -\frac{\mu_0}{4\pi}\frac{\gamma_I \gamma_S}{r_{IS}^3}\ (rad/s)$$

Spin part tensor for heteronucleus dipolar interaction as:

$$T_{20} = \frac{1}{\sqrt{6}}(2I_z S_z)$$

Spin part tensor for homonucleus dipolar interaction as:

$$T_{20} = \frac{1}{\sqrt{6}}(3I_{1z}I_{2z} - I_1 \cdot I_2) = \frac{1}{\sqrt{6}}\left(2I_{1z}I_{2z} - I_{1x}I_{2x} - I_{1y}I_{2y}\right)$$

The derivation is much simpler compared to that for the chemical shielding Hamiltonian, as it has only one term:

$$\sum_{\substack{m=-2\\ \boldsymbol{m\neq 0}}}^{2} R_{20}^{P} D_{0m}^{2}(\alpha,\beta,\gamma) D_{m0}^{2}(\omega_r t,\theta_M,0)$$

$$= R_{20}^{P}[e^{-i(2\gamma)} d_{02}^{2}(\beta) d_{20}^{2}(\theta_M) e^{-i2\omega_r t} + e^{-i(\gamma)} d_{01}^{2}(\beta) d_{10}^{2}(\theta_M) e^{-i\omega_r t} + d_{00}^{2}(\beta) d_{00}^{2}(\theta_M)$$

$$+e^{i(\gamma)} d_{0,-1}^{2}(\beta) d_{-1,0}^{2}(\theta_M) e^{i\omega_r t} + e^{i(2\gamma)} d_{0,-2}^{2}(\beta) d_{-2,0}^{2}(\theta_M) e^{i2\omega_r t}]$$

Recall that $R_{20}^{P} = \sqrt{6} b_{IS}$, the factor of $\sqrt{6}$ comes from the spin part of original H_D is $2I_zS_z\ or\ 3I_{1z}I_{2z} - I_1 \cdot I_2, which\ is\ \sqrt{6}T_{20}$. We have:

$$H_D = \omega_D(t)\sqrt{6}T_{20} \tag{5.64}$$

$$\omega_D(t) = \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2,m}^{D}\, exp(im\omega_r t)$$

$$\omega_{20}^{D} = b_{IS}\frac{(3\cos^2\beta - 1)}{2}\frac{(3\cos^2\theta_M - 1)}{2} = 0$$

$$\omega_{2,\pm1}^{D} = -\frac{b_{IS}}{2\sqrt{2}}\sin 2\beta\, exp(\pm i\gamma)$$

$$\omega_{2,\pm2}^{D} = \frac{b_{IS}}{4}\sin^2\beta\, exp(\pm i2\gamma)$$

Note replace $\sin^2\theta_M = \frac{2}{3}; \cos^2\theta_M = \frac{1}{3}$ were used in the above derivation to replace $d_{20}^{2}(\theta_M) = \sqrt{\frac{3}{8}}\sin^2\theta_M$; $and\ d_{10}^{2}(\theta_M) = -\sqrt{\frac{3}{8}}\sin 2\theta_M$. I will leave this as the last step derivation for you to complete.

In Fig. 5.4, we can see the distinct powder patterns for chemical shielding and dipolar interactions.

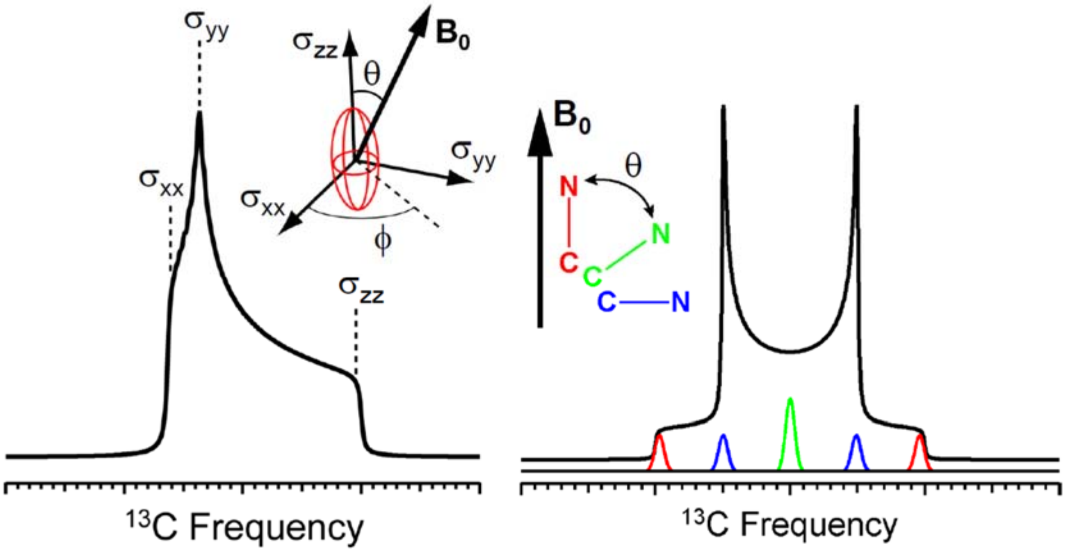


Figure 5.4. Powder distribution of 13C spectra due to the presence of anisotropic chemical shielding and dipolar interaction. Adapted from C. P. Jaroniec's 2008 Winterschool lecturenote.

Another category of interactions that is not very commonly considered in ssNMR with MAS, but have to be accounted for are homonulcear and heteronuclear J coupling. Their spin parts of Hamiltonian share the same expression as that for homonuclear and heteronuclear dipolar interactions, respectively, but their spatial parts are not. In the principal axis frame, for homonuclear J coupling we have:

$$R_{22}^{P} = -\frac{1}{2}\eta J_{aniso}^{II};\ R_{20}^{P} = 2\pi\sqrt{\frac{3}{2}}J_{aniso}^{II}$$

$$T_{20} = \frac{1}{\sqrt{6}}(3I_{1z}I_{2z} - I_1 \cdot I_2) = \frac{1}{\sqrt{6}}\left(2I_{1z}I_{2z} - I_{1x}I_{2x} - I_{1y}I_{2y}\right)$$

And for heteronuclear J coupling we have:

$$R_{22}^{P} = -\frac{1}{2}\eta J_{aniso}^{IS};\ R_{20}^{P} = 2\pi\sqrt{\frac{3}{2}}J_{aniso}^{IS}$$

$$T_{20} = \frac{1}{\sqrt{6}}(2I_zS_z)$$

So the physical parts of their Hamiltonians in the presence of MAS shares the same format with chemical shielding interactions, but spin tensor parts are the same as dipolar interactions. We can obtain their Hamiltonians by replacing previously derived:

$$H_{cs} = \omega_{cs}(t)I_z$$

with corresponding parts:

$$H_J^{II} = -2\pi\sqrt{3}J_{iso}^{II}\frac{1}{\sqrt{3}}I_i \cdot I_j - \omega_J(t)\frac{1}{\sqrt{6}}(3I_{1z}I_{2z} - I_1 \cdot I_2) \tag{5.65}$$

$$H_J^{IS} = -2\pi\sqrt{3}J_{iso}^{IS}\frac{1}{\sqrt{3}}(I_zS_z) - \omega_J(t)\frac{1}{\sqrt{6}}(2I_zS_z) \tag{5.66}$$

With their time dependent oscillation by MAS defined as:

$$\omega_J(t) = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{J}\, exp(im\omega_r t) \tag{5.67}$$

$$\omega_{20}^{cs} = 2\pi J_{iso}$$

$$\omega_{2,\pm1}^{J} = \pi\sqrt{\frac{3}{2}}J_{aniso}\frac{1}{2}\sin\beta\sin 2\theta_M\left[\eta(\mp i\sin 2\alpha - \cos\beta\cos 2\alpha) - 3\cos\beta\right]e^{\pm i\gamma}$$

$$= \frac{\sqrt{6}}{4}\pi J_{aniso}\sin\beta\left[\eta(\mp i\sin 2\alpha - \cos\beta\cos 2\alpha) - 3\cos\beta\right]e^{\pm i\gamma}$$

$$\omega_{2,\pm2}^{J} = \sqrt{\frac{3}{2}}\pi J_{aniso}\frac{\sin^2\theta_M}{2}\left[\eta[-\frac{1}{2}\cos 2\alpha\,(1+\cos^2\beta) \mp i\sin 2\alpha\cos\beta] + \frac{3}{2}\sin^2\beta\right]e^{\pm i2\gamma}$$

$$= \frac{\sqrt{6}}{6}\pi J_{aniso}\left[\eta[-\frac{1}{2}\cos 2\alpha\,(1+\cos^2\beta) \mp i\sin 2\alpha\cos\beta] + \frac{3}{2}\sin^2\beta\right]e^{\pm i2\gamma}$$

However, normally we treat J coupling as isotropic interaction, and neglect its anisotropic parts in protein NMR.

We still have two rounds of reference frame transformation for dipolar interactions, which are already diagonalized in the lab frame. This is to use an intermediate frame (often called molecular frame) as a common frame of reference to have all different interactions in the same rotor fixed reference frame, before we apply the same magic angle transformation between the tilted rotor frame fixed on the rotor and the lab frame.

5.5 General format of Hamiltonians in presence of RF irradiation while spun at Magic Angle

In summary, at this point, with the help of the irreducible spherical tensor representation, we reformulated all interactions in NMR into the same format:

$$H_\Lambda = \sum_{l}\sum_{m=-l}^{l}(-1)^m A_{l,-m}^{\Lambda}T_{l,m}^{\Lambda} \tag{5.68}$$

Where $A_{l,-m}^{\Lambda}$ is the $-mth$ component of rank l tensor representing the spatial part of the Hamiltonian for interaction Λ, and $T_{l,m}^{\Lambda}$ is the mth component of rank l tensor that represent the spin part of the Hamiltonian for interaction Λ.

We also proved all interactions in presence of MAS, can be reformulated into this expression:

$$H = \sum_{\Lambda} H_\Lambda = \omega_0\delta_{\text{iso}}I_z + \sum_{\Lambda}T_{\lambda 0}^{\Lambda}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega_{2m}^{\Lambda}\exp(im\omega_r t) \tag{5.69}$$

$$\omega_{2\text{m}}^{\Lambda} = \sum_{\substack{m=-2\\ m\neq 0}}^{2} R_{2,m'}^{\Lambda}\, D_{m',m}^{2}(\alpha\beta\gamma)d_{m0}^{2}(\theta_M)$$

Here $R_{2,m'}^{\Lambda}$ is the second rank tensor representing the spatial part of interaction Λ in the its principal axis frame. $D_{m',m}^{2}(\alpha\beta\gamma)$ is the Wigner rotation matrix to rotate the principal axis frame of interaction Λ to the Molecular Frame fixed on the tilted rotor, where the Euler angles $\alpha\beta\gamma$ define the molecular orientation in the solid powder distribution. $d_{m0}^{2}(\theta_M)$ is the reduced Wigner rotation matrix to rotate the spatial part of interaction Λ from the rotor fixed frame to the lab frame. The associated spinning in the Wigner rotation matrix is registered separately by $\exp(im\omega_r t)$. $T_{\lambda 0}^{\Lambda}$ is the spin part of Hamiltonian. For chemical shielding, we have it as T_{10}^{cs}, and for dipolar interaction, it is T_{20}^{D}.

The advantage of the unification of all Hamiltonians will manifest when analyzing pulse sequences in the presence of both spatial rotation by MAS and spin rotation by RF pulses. We will be able to address the effect of each rotation respectively, and visualize their combined interference. This separate analysis will be especially convenient to select the desired coherence pathway.

A generic rule of thumb for this, is to transform into the interaction frame of reference of the RF irradiation. This transformation will only affect the spin part of Hamiltonian $T_{\lambda 0}^{\Lambda}$, which equates to an Euler rotation $R(\alpha_T \beta_T \gamma_T)$ applied to the spin part of Hamiltonian $T_{\lambda 0}^{\Lambda}$ in time τ, while the sample is spun at ω_r. In general, the Hamiltonian for a RF pulse can be represented by:

$$\widehat{H}_1 = \omega_1(t)[I_x \cos\phi(t) + I_y \sin\phi(t)] \tag{5.70}$$

Where $\omega_1(t)$ is the pulse amplitude, and ϕ is the phase. It can be rewritten as:

$$\widehat{H}_1 = \omega_1(t) e^{-i\phi(t) I_z} I_x e^{i\phi(t) I_z} = \omega_1(t) e^{-i[\phi(t)-\frac{\pi}{2}] I_z} I_y e^{i[\phi(t)-\frac{\pi}{2}] I_z} \tag{5.71}$$

Here we used the relation Eq. 5.14:

$$I_x = e^{i(\frac{\pi}{2}) I_z} I_y e^{-i(\frac{\pi}{2}) I_z}$$

Therefore, we can apply Wigner rotation matrix to the spin part to effect the spin rotation by the RF pulse we have:

$$e^{i\widehat{H}_1 \tau} T_{\lambda 0}^{\Lambda} e^{-i\widehat{H}_1 \tau} \tag{5.72}$$

$$= \exp\left(i \int_0^\tau dt \omega_1(t) e^{-i\left[\phi(t)-\frac{\pi}{2}\right] I_z} I_y e^{i\left[\phi(t)-\frac{\pi}{2}\right] I_z}\right) T_{\lambda 0}^{\Lambda} \exp\left(-i \int_0^\tau dt \omega_1(t) e^{-i\left[\phi(t)-\frac{\pi}{2}\right] I_z} I_y e^{i\left[\phi(t)-\frac{\pi}{2}\right] I_z}\right)$$

Here we can use the formula $Ae^B A^{-1} = e^{ABA^{-1}}$ to rearrange:

$$\exp\left(i \int_0^\tau dt \omega_1(t) e^{-i\left[\phi(t)-\frac{\pi}{2}\right] I_z} I_y e^{i\left[\phi(t)-\frac{\pi}{2}\right] I_z}\right) = e^{-i \int_0^\tau dt\left[\phi(t)-\frac{\pi}{2}\right] I_z} e^{i \int_0^\tau \omega_1(t) dt I_y} e^{i \int_0^\tau dt\left[\phi(t)-\frac{\pi}{2}\right] I_z}$$

Hence in the format of Wigner-rotation matrix:

$$e^{i\widehat{H}_1 \tau} T_{\lambda 0}^{\Lambda} e^{-i\widehat{H}_1 \tau} \tag{5.73}$$

$$= R(\alpha_T \beta_T \gamma_T) T_{\lambda 0}^{\Lambda} R^{-1}(\alpha_T \beta_T \gamma_T) = \sum_{\mu=-\lambda}^{\lambda} T_{\lambda \mu}^{\Lambda}\, e^{-i\mu\alpha(\tau)} d_{\mu 0}^{\lambda}[-\beta(\tau)]$$

Where $\alpha_T(\tau) = \int_0^\tau dt\left[\phi(t) - \frac{\pi}{2}\right]$ is the phase shift, and $\beta(\tau) = \int_0^\tau \omega_1(t)dt$ is the tipping angle of the RF pulse along the y axis.

Note the angle argument in $d_{\mu 0}^{\lambda}$ is negative, this is because the transformation into interaction frame of RF pulse is the reverse of the normal right-handed rotation.

Meanwhile, the MAS will incur an additional rotation to the spatial part $\sum_{m=-2}^{2} \omega_{2m}^{\Lambda}$by $\gamma_R(\tau) = \omega_r\tau$ in the rotor fixed frame, since its two other Euler angles of rotation corresponding to MAS are zero:

$$R(\omega_r\tau, 0,0) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\, R^{-1}(\omega_r\tau, 0,0) \tag{5.74}$$

$$= \sum_{\substack{m=-2 \\ m\neq 0}}^{2} R_{2,m'}^{\Lambda}\, D_{m',m}^{2}(\alpha, -\beta, \gamma + \omega_r\tau) d_{m0}^{2}(\theta_M)$$

Here please note that the rotation by MAS effect has to be applied to the γ angle in the transformation from the principal axis frame to the rotor fixed frame. As we commented earlier, they play the same role in the two consecutive rotations. Therefore we have an additional phase factor $e^{-im\omega_r\tau}$:

$$R(\omega_r\tau, 0,0) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\, R^{-1}(\omega_r\tau, 0,0) = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\, e^{-im\omega_r\tau}$$

Together, the Hamiltonian of interaction Λ under such a RF pulse during MAS becomes:

$$e^{i\hat{H}_1\tau} R(\omega_r\tau, 0,0)\left[T_{\lambda 0}^{\Lambda} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\right] R^{-1}(\omega_r\tau, 0,0) e^{-i\hat{H}_1\tau} \tag{5.75}$$

$$= \sum_{\mu=-\lambda}^{\lambda} T_{\lambda\mu}^{\Lambda}\, e^{-i\mu\alpha(\tau)} d_{\mu 0}^{\lambda}[-\beta(\tau)] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\, e^{-im\omega_r\tau}$$

Normally our pulse sequence may have multiple pulses sequentially applied. Then we will just have the sequential application of transformations to the interaction frame $exp^{i\hat{H}_1\tau}$:

$$R_{RF}(t) = \vec{T}\exp[i\int_0^t \omega_1(t')[I_x \cos\phi(t') + I_y \sin\phi(t')]\, dt'] \tag{5.76}$$

Where $\vec{T}$ is the time ordering operator that represents the expansion of the sequential ordered pulses in the pulse sequence.

To summarize, it shows the pulse sequence effect can be represented in a modular fashion with the irreducible spherical tensor format, which will greatly simplify the derivation of the effect of complicated pulse sequences in such modular arrangements. We will come back to the above derived generic expression in derivation of SPC5 double quantum sequence (belonging to the so called C symmetry pulse sequence, please read the seminal papers by Malcolm H. Levitt and his colleagues: JCP 111, 1511 (1999) and 112, 8539 (2000)).

Let's step back take a closer look at the derived general form of Hamiltonians for various interactions under MAS.

Marciq and Waugh noted there are two kinds of interactions: homogeneous and inhomogeneous. Hamiltonians of the inhomogeneous interactions are those at different time commute with themselves, and includes chemical shift/shielding, J and dipolar interactions between unliked spins, and first order quadrupolar interactions. Hamiltonians of the homogeneous interactions are those do not commute with themselves, and includes the J and homonuclear dipolar interactions between liked spins. This can be shown by the homonuclear dipolar Hamiltonians between nuclear I_i and I_j, and nuclear I_j and I_k:

$$\begin{aligned} &\left[3I_{zi}I_{zj} - I_i \cdot I_j, 3I_{zi}I_{zk} - I_i \cdot I_k\right] \\ &= 4iI_{xi}\left(I_{yj}I_{zk} - I_{zj}I_{yk}\right) + 4iI_{yi}\left(I_{zj}I_{xk} - I_{xj}I_{zk}\right) + iI_{zi}\left(I_{xj}I_{yk} - I_{yj}I_{xk}\right) \\ &= -(I_i^+I_k^- - I_k^+I_i^-)I_{zj} + \left(I_i^+I_j^- - I_j^+I_i^-\right)I_{zk} - \frac{1}{2}\left(I_j^+I_k^- - I_k^+I_j^-\right)I_{zi} \\ &\neq 0 \end{aligned} \tag{5.77}$$

The incommutable Hamiltonian means that the evolution operator for the density matrix of the system cannot be isolated into individual exponent factors with argument by the eigenvalues of the Hamiltonian at that specific time point:

$$U(t) = \vec{T}\exp[-i\int_0^t \sum_{i\neq j} H_{ij}\,dt'] \neq \prod_{i\neq j} \vec{T}\exp[-i\int_0^t \sum_{i\neq j} H_{ij}\,dt']$$

This issue can be traced back to the exponential operator rule that:

$$\begin{aligned} \mathrm{e}^{A+B} &= \mathrm{e}^{A}\mathrm{e}^{B}, \text{if } [\mathrm{A},\mathrm{B}] = 0 \\ \mathrm{e}^{A+B} &\neq \mathrm{e}^{A}\mathrm{e}^{B}, \text{if } [\mathrm{A},\mathrm{B}] \neq 0 \end{aligned} \tag{5.78}$$

It means that we will not be able to obtain an analytical solution of the system Hamiltonian.

In contrast, if the system contains only homogeneous interactions that commute with each other and among themselves at different time points, then we can replace the Hamiltonian in the evolution operator by their respective eigenvalues(usually in the eigenbasis of the Zeeman interaction, e.g. , the eigenstates of I_{zi}). This will convert the system to time-independent Hamiltonian and make evaluation of any observables by density matrix method trivial. It converts the computation into numerical exponential multiplications.

For systems that contain at least one inhomogeneous interaction, the system Hamiltonians do not commute at different points and are time-dependent. We cannot obtain an analytical solution and the computation has to decompose into small time intervals. In each time interval we can apply approximation (such as the Magnus expansion) to convert the time-dependent Hamiltonians into time-independent terms. Then eigenvalues of approximated Hamiltonians will be computed for the density matrix method.

We will show analyses of systems with the inhomogeneous interactions presence in Chapter 7. For now, let's demonstrate the simplest case for system comprising entirely homogeneous interactions:

$$U(t) = \vec{T}\exp\left[-i\int_0^t \sum_{\Lambda} H_{\Lambda}\, dt'\right] = \prod_{\Lambda} \exp[-i\int_0^t H_{\Lambda}\, dt'] \tag{5.79}$$

Then assume if we would like to evaluate the expectation value of observable A, by density matrix expression it should be:

$$\langle A\rangle = Tr\{A\rho(t)\} = Tr\{AU(t)\rho(0)U^{-1}(t)\} \tag{5.80}$$

$$= \sum_{u=1}^{N} \left\langle u\middle| A\prod_{\Lambda}\exp[-i\textstyle\int_0^t H_{\Lambda}\, dt']\rho(0)\prod_{\Lambda}\exp[i\int_0^t H_{\Lambda}\, dt']\middle| u\right\rangle$$

We can insert the identity operator in between each operator:

$$\sum_{u,v,r,s=1}^{N} \langle u|A|v\rangle \langle v|\prod_{\Lambda}\exp[-i\int_0^t H_{\Lambda}\, dt']|r\rangle\langle r|\rho(0)|s\rangle\langle s|\prod_{\Lambda}\exp[i\int_0^t H_{\Lambda}\, dt'|u\rangle \tag{5.81}$$

Now, let's look at the H_{Λ}, as we derived, we can simplify the expression further as:

$$H_{\Lambda} = T_{\lambda 0}^{\Lambda}\sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\exp(im\omega_r t) = T_{\lambda 0}^{\Lambda}\omega(t) \tag{5.82}$$

$$\langle v|\exp(-i\int_0^t H_{\Lambda}\, dt)|r\rangle = \exp\left[-i\langle v|T_{\lambda 0}^{\Lambda}|r\rangle \sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega_{2m}^{\Lambda}\int_0^t \exp(im\omega_r t)\, dt\right]$$

$$= \exp\left[-i\delta_{vr}Z_r \sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega_{2m}^{\Lambda}\int_0^t \exp(im\omega_r t)\, dt\right]$$

$$= \exp\left\{-i\delta_{vr}Z_r \sum_{\substack{m=-2\\m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}}{im\omega_r}[\exp(im\omega_r t)-1]\right\}$$

Where $\delta_{vr} = \begin{cases}1, v = r\\0, v \neq r\end{cases}$, Z_r is the expectation value $\langle v|T_{\lambda 0}^{\Lambda}|r\rangle$ of spin part Hamiltonian at $|r\rangle$ state. Then the above $\langle A\rangle$ expression becomes:

$$\langle A\rangle = \sum_{u,v,r,s=1}^{N} \begin{matrix}\langle u|A|v\rangle \exp\left\{-i\delta_{vr}Z_r \sum_{\substack{m=-2\\m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}(r)}{im\omega_r}[\exp(im\omega_r t)-1]\right\}\\ \langle r|\rho(0)|s\rangle \exp\left\{i\delta_{su}Z_s \sum_{\substack{m=-2\\m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}(s)}{im\omega_r}[\exp(im\omega_r t)-1]\right\}\end{matrix}$$

$$\langle A\rangle = \sum_{r,s=1}^{N} \langle s|A|r\rangle\langle r|\rho(0)|s\rangle \tag{5.83}$$

$$\exp\left\{-i \sum_{\substack{m=-2\\m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}[\exp(im\omega_r t)-1]}{im\omega_r}[Z_r - Z_s]\right\}$$

We can now introduce a term $\Phi(t,0)$ called dynamic phase, as this is a time-dependent factor determined by the dynamic rotation of the sample under MAS:

$$\langle r|\Phi(t,0)|r\rangle = \tag{5.84}$$

$$\langle r|\int_0^t H_\Lambda\, dt)|r\rangle = \frac{Z_r}{i\omega_r}\sum_{\substack{m=-2\\m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}}{m}[\exp(im\omega_r t)-1] = \Phi_r(t,0)$$

Then we have:

$$\langle A\rangle = \sum_{r,s=1}^{N} \langle s|A|r\rangle\langle r|\rho(0)|s\rangle \exp\{-i[\Phi_s(t,0) - \Phi_r(t,0)]\} \tag{5.85}$$

$$= \sum_{r,s=1}^{N} \langle s|A|r\rangle\langle r|\rho(0)|s\rangle \exp\{-i[\Phi_{sr}(t,0)\}$$

$$\exp\{-i[\Phi_{sr}(t,0)\} = \exp\{-\frac{Z_r - Z_s}{\omega_r}\sum_{\substack{m=-2\\m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}}{m}[\exp(im\omega_r t)-1]\}$$

This phase factor can be expanded in the infinite Fourier series as it has periodicity of ω_r, and the spacing between adjacent frequency is ω_r, which in the frequency spectrum is the side band. The example spectrum is shown in Fig. 5.5.

Here we note we didn't include the $m = 0$ term from isotropic chemical shift. The treatment is simpler than what we did above:

$$\langle r|\Phi(t,0)|r\rangle = Z_r \omega_0 \delta_{\mathrm{iso}} \mathrm{t}$$

If it is spin ½ nucleus, $Z_r = \pm\frac{1}{2}$:

$$\exp\{-i[\Phi_{sr}(t,0)\} = \exp(-i\omega_0\delta_{\mathrm{iso}}\mathrm{t})$$

$$\langle A\rangle = \exp(-i\omega_0\delta_{\mathrm{iso}}\mathrm{t}) \exp\{-\frac{Z_r - Z_s}{\omega_r}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\frac{\omega_{2m}^{\Lambda}}{m}[\exp(im\omega_r t) - 1] \tag{5.86}$$

The $\exp(-i\omega_0\delta_{\mathrm{iso}}\mathrm{t})$ will give the central band position at $\omega_0\delta_{\mathrm{iso}}$, which does not oscillate with the MAS frequency ω_r.

If we include multiple inhomogeneous interactions:

$$\langle A\rangle = \exp(-i\omega_0\delta_{\mathrm{iso}}\mathrm{t}) \tag{5.87}$$
$$\prod_{\Lambda}\exp\{-\frac{Z_r - Z_s}{\omega_r}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\frac{\omega_{2m}^{\Lambda}}{m}[\exp(im\omega_r t) - 1]\}$$

More complete discussion following this including the homogeneous interactions can be found in Malcolm Levitt et al. "Theory and simulations of homonuclear spin pair systems in rotating solids" J. Chem. Phys. 92(11), 1, (1990).

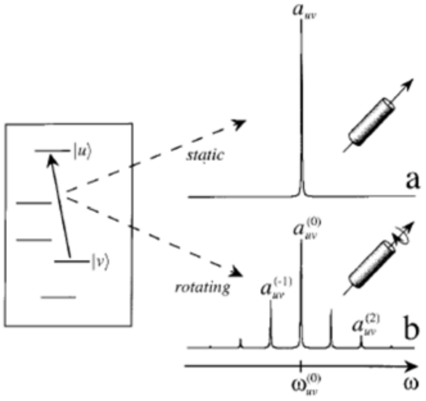


Figure 5.5. Typical spectrum from a single crystal sample in static (top) state and spinning at Magic Angle. Adapted from Mattias Eden' Computer simulations in ssNMR I spin dynamics theory. Concepts in Magnetic Resonance Part (A) 34(35) (2003)

But before we go there and explain why MAS spectra can still exhibit significant linewidth, we need to understand the interference effect due to homogeneous interactions. And before we can dissect this detrimental interference effect, I think it is very beneficial for us to analyze various recoupling effect and tricks. To do that, it will soon be manifested that our lengthy introduction of tensor formalism is worth the efforts.

Chapter 6 Recoupling of interactions under magic under spinning

At this step, we can appreciate how MAS helps to enhance spectral resolution and sensitivity by focusing the spread powder pattern into individual spinning side bands and the central line. In this process, all the anisotropic interactions are uniformly affected/attenuated by MAS.

However, in many applications of ssNMR, we need to selectively resurrect one or more species of these anisotropic interactions.

Why? These interactions when they are alive, can modulate NMR signals as a function of time according to their Hamiltonians. The specific modulation pattern contains corresponding structural information. For example, chemical shielding or dipolar tensor, their magnitude and orientations inform us the dynamics and structural of molecules. Alternatively, recoupled interactions can be used as "rulers" to interrogate dynamics and structural parameters of selected sites of interests. For example, dipolar dephasing can be used to measure the distance between selectively isotope labeled sites, or the exchange rate of the sites. But when we observe the signals, we wish to have spectral resolution, so we know it is the signal at which site is modulated, and assign the structural information to the site at which the modulation pattern is observed. Therefore, we need to control both the timing and locations to turn on/off the anisotropic interactions.

Beyond the recoupling by artificially designed sequences, the recoupling effects exist intrinsically due to the interference effects associated with incommutable homogeneous interactions (mostly due to homonuclear dipolar interactions), which incurs undesirable line broadening despite MAS.

Therefore, we need a better understanding of the nature of spin physics associated with MAS, so that we can suppress the undesirable recoupling by decoupling, or reversely, we can exploit the recoupling as a powerful strategy to probe into the microscopic space for valuable structural and dynamic information.

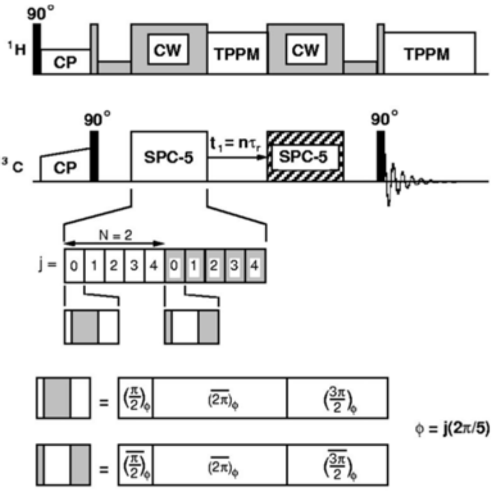


Figure 6.1. SPC5 dipolar recoupling sequence diagram. Adpated from Hohwy. et al., JCP 110, 7983 (1999)

We will review a few popular C symmetry recoupling sequences. Then we will explain various hetero and homonuclear rotary resonance effects, together with the widely used Dipolar-Assisted Rotational Resonance (DARR). Then we will introduce finite pulse RFDR and its advanced combo as PITHIRDS. We will also cover REDOR as the most popolar heteronuclear recoupling sequence.

Let's start from some classical examples in the history of ssNMR, and you will see this is a very exciting journal that you don't want to miss.

6.1 Analysis of SPC5 double quantum recoupling

SPC5 is one of the popular sequences to recouple homonucleus dipolar interaction in the form of double quantum excitation, shown by M. Howy et al., in JCP 110 7983 (1999). It is an improved version of C7/PostC7 sequence of the same concept, and belongs to the so called C symmetry sequence developed by Malcolm Levitt and his colleagues(You can read the original papers: JCP 111, 1511 (1999) and 112, 8539 (2000). This sequence can be used for various purposes, including spectral assignments in crowded single quantum space, polarization transfer, and distance measurements.

As shown in Fig. 6.1, just like the standard C symmetry sequence, SPC5 consists of multiple ($n = 5$) basic C pulse blocks, with each block occupying integers ($N = 2$) of rotor periods. Individual C pulse blocks may comprise a number of pulses (3 in this case), but combined they generate no net rotation. In addition, a $\frac{2\pi}{n}$ phase shift is applied relative to its neighboring blocks, so that the accumulated phase shift at the end of the sequence is 2π, and the system Hamiltonian is returned to the original status.

We can apply Eq. 5.75 and 5.76 to analyze SPC5. The analysis process manifests the advantage of modular design principle and the irreducible spherical tensor representation. As we derived, the generic format of the Hamiltonians in the presence of a continuous RF irradiation and MAS is:

$$H_{\Lambda} = \sum_{\mu=-\lambda}^{\lambda} T^{\Lambda}_{\lambda\mu}\, e^{-i\mu\alpha(\tau)} d^{\lambda}_{\mu 0}[-\beta(\tau)] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\Lambda}_{2m}\, e^{-im\omega_r\tau}$$

We will still use symbol n to represent the number of C blocks, and N to represent the number of rotor periods, as we will show by the Cogwheel cycling selection, we can identify the optimal N and n value to set the parameter of the sequence. Again, the negative sign in front of $\beta(\tau)$ in the reduced Wigner matrix is because the transformation to interaction frame is the reverse of the z-y-z convention with right-handed rotation.

As SPC5 consists of multiple C blocks, each with a fixed spin space phase shift $\frac{2\pi}{n}$, so relative to the first C block, the pth block will have a phase shift of $p\frac{2\pi}{n}$, applied to the spin part of rotation. So it means this spin part of rotation angle $\alpha(\tau)$ in the generic formulas is $p\frac{2\pi}{n}$ for the pth C block. Meanwhile, as all 5 C blocks occupy $N = 2$ rotor periods, it means that each block lasts a fixed spatial space rotation by MAS of $\frac{2\pi}{n}N$. So it means that this spatial part of rotation angle $\omega_r\tau$ in the generic formulas is $p\frac{2\pi}{n}N$ for the pth C block. Remind you the exponential factor caused by phase shift and physical rotation will be amplified by the respective tensor component index μ, and m respectively.

Hence, if the Hamiltonian of interaction Λ for the first C block is H^{Λ}_{c1}, the average Hamiltonian of n combined c blocks is the summation of all n blocks. Each is otherwise identical to the first C block, but with a fixed spatial and spin rotation phase:

$$H^{\Lambda}_{cn} = \frac{1}{n}\sum_{p=0}^{n-1}\sum_{\mu=-\lambda}^{\lambda}\sum_{\substack{m=-l\\ m\neq 0}}^{l} H^{\Lambda}_{c1}\, e^{-i(\mu\alpha(\tau)+m\omega_r\tau)p} \tag{6.1}$$

$$= \frac{1}{n}\sum_{p=0}^{n-1}\sum_{\mu=-\lambda}^{\lambda}\sum_{\substack{m=-l\\m\neq 0}}^{l} H_{c1}^{\Lambda} e^{-i\frac{2\pi}{n}(\mu+mN)p}$$

If in addition, we concatenate two such sequences back to back. Thus they have a constant overall phase shift of Φ. Then if the Hamiltonian of the first n blocks is H_{cn}^{Λ}, the Hamiltonian of the second n blocks will be $H_{cn}^{\Lambda} e^{-i\mu\alpha(\tau)} = H_{cn}^{\Lambda} e^{-i\mu\Phi}$.

The motivation of this concatenation is to help exclude certain μ components, and better average out chemical shift anisotropy effect, as we will show later. We call the sequence obtained by contatenation as a super cycle C sequence, SPCn, and its Hamiltonian is:

$$H_{spcn}^{\Lambda} = \frac{1}{2n}\sum_{p=0}^{n-1}\sum_{\mu=-\lambda}^{\lambda}\sum_{\substack{m=-l\\m\neq 0}}^{l} H_{c1}^{\Lambda} e^{-i\frac{2\pi}{n}(\mu+mN)p}\left(1+e^{-i\mu\Phi}\right) \tag{6.1}$$

Therefore, assume we can compute the Hamiltonian of the first C block, the average Hamiltonian of the combined SPCn sequence is simply the modular format shown above.

We wish to average out chemical shift anisotropy and chemical shift offset effect, both of which contribute to $\mu = \pm 1$ components through their the spin part of Hamiltonian $T_{\lambda\mu}^{\Lambda}$. This can be partially achieved by fixing $\Phi = \pi$, so that $1 + e^{-i\mu\Phi} = 0$ for $\mu = \pm 1$.

To excite pure double quantum, we need to select out $\mu = \pm 2$ terms, as $T_{2,\pm 2}^{H_D} = I^{\pm}S^{\pm}$. According to the Cogwheel cycling principles, only the combinations to make $e^{-i\frac{2\pi}{n}(\mu+mN)p} = 1$ will remain after summation. Other terms will be cancelled out after averaging. It means we need:

$$\mu + mN = nq \tag{6.2}$$

Where q is a integer, and m=0, $\pm 1, \pm 2$, for each μ value.

Now, we want to ensure only one pair of m values are selected to give γ encoding behavior of the sequence. γ encoding means that each selected μ value will only combine with one specific m value.

We can see that by picking $n = 5$, and $N = 2$, only $\mu = -2, m = 1$ and $\mu = 2, m = -1$ will be allowed by the selection rule according to the Cogwheel cycling. Other choices of N and n pair may also work, such as $n = 7$, and $N = 2$ (Which is postC7 sequence). At each pair of these values:

$$e^{-i\frac{2\pi}{n}(\mu+mN)p}\left(1+e^{\pm i\mu\Phi}\right) = e^{-i\frac{2\pi}{n}(0)p}\left(1+e^{\pm i2\pi}\right) = 2 \tag{6.3}$$

Now, we can inspect what kind of pulse combinations we use for each C block. Each C block will not produce any net rotation. To better average out chemical shift anisotropy and chemical shift offset with a spin part T_{10}^{Λ} in their Hamiltonians, each C block comprises 2π positive and 2π

negative rotations around y axis arranged by a 3 pulses train $\frac{\pi}{2} - (-2\pi) - \frac{3\pi}{2}$. This means in the same time when the sample completes $2N\pi$ rounds of physical rotation, it also needs to completes $4n\pi$ spin rotation, so the ratio of rf field strength to MAS is $2\frac{n}{N}$. So it means for SPC5, $\omega_{rf} = 5\omega_r$, while this ratio is escalated to $\omega_{rf} = 7\omega_r$ for postC7, which can be harder to achieve at MAS above 10 kHz. Note that we need simultaneous decoupling field on proton to be at least more than twice the strength of the recoupling irradiation on carbon.

Therefore, the only remaining Hamiltonian is:

$$\begin{aligned} H_{spcn}^{\mathrm{D}} &= \frac{1}{2n}\sum_{p=0}^{n-1}\sum_{\mu=-\lambda}^{\lambda}\sum_{m=-l}^{l} H_{c1}^{\mathrm{D}} e^{-i\frac{2\pi}{n}(\mu+mN)p}\left(1+e^{-i\mu\Phi}\right) \\ &= \frac{1}{10}\sum_{p=0}^{4}\sum_{\mu=-\lambda}^{\lambda}\sum_{m=-l}^{l} 2H_{c1}^{\mathrm{D}} = \sum_{\mu=-\lambda}^{\lambda}\sum_{m=-l}^{l} H_{c1}^{\mathrm{D}} \\ &= [H_{c1}^{\mathrm{D}}(\mu=-2, m=1) + H_{c1}^{\mathrm{D}}(\mu=2, m=-1)] \end{aligned} \tag{6.4}$$

Now we just need to compute the average Hamiltonian of a single C block $H_{c1}^{\mathrm{D}}(\mu=-2, m=1)$ and $H_{c1}^{\mathrm{D}}(\mu=2, m=-1)$.

This is easy to do by applying our generic form of Hamiltonian with RF irradiation during MAS, with known $\mu=-2, m=1$ and $\mu=-2, m=-1$ values and total time duration is $\tau_{c1} = \frac{4\pi}{n\omega_r}$. For each C block, we have three sections of pulses, so we have to further divide the computation into segmental $\widehat{H}_1$ when computing the dipolar interaction in the RF interaction frame of a single C block in SPC5 pulse sequence:

$$\begin{aligned} &\overline{\widetilde{H}_c^{\mathrm{D}}} \\ &= \frac{1}{\tau_{c1}}\int_0^{\tau_{c1}} e^{i\widehat{H}_1\tau}R(\omega_r\tau, 0,0)[\sqrt{6}T_{\lambda 0}^{\mathrm{D}}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\exp(-im\omega_r\tau)]R^{-1}(\omega_r\tau, 0,0)e^{-i\widehat{H}_1\tau} \end{aligned} \tag{6.5}$$

Please note the factor of $\sqrt{6}$ in H_{c1}^{D}. It comes from the normalization $1/\sqrt{6}$ factor in $T_{\lambda 0}^{\mathrm{D}}$.

To do so, let's analyze the segmental $\widehat{H}_1$ one by one:

In $\tau \in \left[0, \frac{1}{8}\tau_{c1}\right]$, $\tau_f = \frac{1}{8}\tau_{c1} = \frac{1}{8}\times\frac{4\pi}{n\omega_r} = \frac{\pi}{2n\omega_r}, \tau_i = 0, \tau_f - \tau_i = \frac{\pi}{2n\omega_r}$. $\omega_{rf} = n\omega_r$. $U = e^{-i\omega_{rf}\tau I_y} = e^{-in\omega_r\tau I_y} = R(0, n\omega_r\tau, 0)$, so:

$$\begin{aligned} &\overline{\widetilde{H}_{c\_1}^{\mathrm{D}}} \\ &= \frac{1}{\tau_f - \tau_i}\int_0^{\tau_f-\tau_i} R^{-1}(0, n\omega_r\tau, 0)\sqrt{6}T_{\lambda 0}^{\mathrm{D}}\, R(0, n\omega_r\tau, 0)\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\exp(-im\omega_r\tau) \end{aligned} \tag{6.6}$$

$$= \frac{1}{\tau_f - \tau_i} \int_0^{\tau_f - \tau_i} \sqrt{6} \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, d_{\mu 0}^{2}(-n\omega_r\tau) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp(-im\omega_r\tau)$$

Note the angle in $d_{\mu 0}^{2}$ is reverse of the angle in $R(0, n\omega_r\tau, 0)$, as the transformation to interaction frame is reverse of the z-y-z rotation in Wigner-Eckart theorem.

$$= \frac{2n\omega_r}{\pi} \int_0^{\frac{\pi}{2n\omega_r}} \sqrt{6} \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, d_{\mu 0}^{2}(-n\omega_r\tau) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp(-im\omega_r\tau)$$

Here we have the rotation due to the pulse applied only to the spin part of Hamiltonian.

In $\tau \in \left[\frac{1}{8}\tau_{c1}, \frac{5}{8}\tau_{c1}\right]$, $\tau_f = \frac{5}{8}\tau_{c1} = \frac{5}{8} \times \frac{4\pi}{n\omega_r} = \frac{5\pi}{2n\omega_r}, \tau_i = \frac{1}{8}\tau_{c1} = \frac{\pi}{2n\omega_r}, \tau_f - \tau_i = \frac{2\pi}{n\omega_r}$. $\omega_{rf} = n\omega_r$.
$U = e^{-i\frac{\pi}{2}I_y} e^{-i[-\omega_{rf}(\tau-\tau_i)]I_y} = e^{-i[\frac{\pi}{2} - n\omega_r\tau(\tau-\tau_i)]I_y} = R\left(0, \frac{\pi}{2} - n\omega_r(\tau - \tau_i), 0\right)$, so:

$$\overline{\widetilde{H}_{c\_4}^{\mathrm{D}}} = \frac{1}{\tau_f - \tau_i} \int_{\tau_i}^{\tau_f} R^{-1}\left(0, \frac{\pi}{2} - n\omega_r(\tau - \tau_i), 0\right) \sqrt{6} T_{\lambda 0}^{\mathrm{D}} \tag{6.7}$$

$$R\left(0, \frac{\pi}{2} - n\omega_r(\tau - \tau_i), 0\right) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp(-im\omega_r\tau)$$

$$= \frac{1}{\tau_f - \tau_i} \int_{\tau_i}^{\tau_f} \sqrt{6} \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, d_{\mu 0}^{2}[-\frac{\pi}{2} + n\omega_r(\tau - \tau_i)] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp[-im\omega_r\tau]$$

Now replace the argument $t = \tau - \tau_i$:

$$= \frac{\exp(-im\omega_r\tau_i)}{\tau_f - \tau_i} \int_0^{\tau_f - \tau_i} \sqrt{6} \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, d_{\mu 0}^{2}[-\frac{\pi}{2} + n\omega_r t] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp[-im\omega_r t]$$

Note that the extra phase factor $\exp(-im\omega_r\tau_i)$ is due to physical rotation by MAS. It signifies the physical rotation always referring back to time 0 of the sequence.

$$= \frac{n\omega_r \exp\left(-i\frac{m\pi}{2n}\right)}{2\pi} \int_0^{\frac{2\pi}{n\omega_r}} \sqrt{6} \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, d_{\mu 0}^{2}[-\frac{\pi}{2} + n\omega_r t] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp[-im\omega_r t]$$

In $\tau \in \left[\frac{5}{8}\tau_{c1}, \tau_{c1}\right]$, $\tau_i = \frac{5}{8}\tau_{c1} = \frac{5}{8} \times \frac{4\pi}{n\omega_r} = \frac{5\pi}{2n\omega_r}, \tau_f = \tau_{c1} = \frac{4\pi}{n\omega_r}, \tau_f - \tau_i = \frac{3\pi}{2n\omega_r}$. $\omega_{rf} = n\omega_r$.
$U = e^{-i\frac{\pi}{2}I_y} e^{-i(-2\pi)I_y} e^{-i\omega_{rf}\,(\tau-\tau_i)I_y} = e^{i[\frac{3\pi}{2} - n\omega_r\tau(\tau-\tau_i)]I_y} = R\left(0, -\frac{3\pi}{2} + n\omega_r(\tau - \tau_i), 0\right)$, so

$$\overline{\widetilde{H}^{\mathrm{D}}_{c\_3}} = \frac{1}{\tau_f - \tau_i}\int_{\tau_i}^{\tau_f} R^{-1}\left(0, -\frac{3\pi}{2} + n\omega_r(\tau - \tau_i), 0\right)\sqrt{6}T^{\mathrm{D}}_{\lambda 0}\, R\left(0, -\frac{3\pi}{2} + n\omega_r(\tau - \tau_i), 0\right)\sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\mathrm{D}}_{2m}\exp(-im\omega_r\tau) \qquad (6.8)$$

Let's replace the argument $t = \tau - \tau_i$:

$$= \frac{\exp(-im\omega_r\tau_i)}{\tau_f - \tau_i}\int_0^{\tau_f - \tau_i}\sqrt{6}\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}[\frac{3\pi}{2} - n\omega_r t]\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp[-im\omega_r t]$$

$$= \frac{2n\omega_r\exp\left(-i\,\frac{5m\pi}{2n}\right)}{3\pi}\int_0^{\frac{3\pi}{2n\omega_r}}\sqrt{6}\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}[\frac{3\pi}{2} - n\omega_r t]\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp[-im\omega_r t]$$

Now, all the physics is done. We just have to complete the math computation. Let's compute a general form first for $\mu = -2, m = 1$. Note $d^2_{-2,0}[\beta(\tau)] = \sqrt{\frac{3}{8}}\sin^2\beta\,(\tau)$:

$$\overline{\widetilde{H}^{\mathrm{D}}_{c_i}}(\mu = -2, m = 1) = \sqrt{6}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{21}\frac{e^{i\omega_r\tau_i}}{\tau_f - \tau_i}\int_0^{\tau_f - \tau_i}\sqrt{\frac{3}{8}}\frac{1 - \cos 2\beta(\tau)}{2}\; e^{-i\omega_r\tau}\,d\tau$$

$$= \sqrt{6}\sqrt{\frac{3}{8}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{21}\frac{e^{i\omega_r\tau_i}}{\tau_f - \tau_i}\int_0^{\tau_f - \tau_i}\frac{1 - \cos 2\beta(\tau)}{2}\; e^{-i\omega_r\tau}\,d\tau$$

$$= \frac{1}{2}\sqrt{6}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{21}\frac{e^{i\omega_r\tau_i}}{\tau_f - \tau_i}\int_0^{\tau_f - \tau_i}\frac{1 - \cos 2n\omega_r\tau}{2}\; e^{-i\omega_r\tau}\,d\tau$$

$$= \frac{\sqrt{6}}{4}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{21}\frac{e^{i\omega_r\tau_i}}{\tau_f - \tau_i}\int_0^{\tau_f - \tau_i}(1 - \cos 2n\omega_r\tau)e^{-i\omega_r\tau}\,d\tau$$

$$= \frac{1}{4}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{21}\frac{e^{i\omega_r\tau_i}}{\tau_f - \tau_i}\int_0^{\tau_f - \tau_i}\left[e^{-i\omega_r\tau} - \frac{1}{2}e^{-i\omega_r\tau}\left(e^{-i2n\omega_r\tau} + e^{i2n\omega_r\tau}\right)\right]d\tau$$

$$= \frac{\sqrt{6}1}{4}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{e^{i\omega_r\tau_i}}{\tau_f-\tau_i}\int_0^{\tau_f-\tau_i}\left(e^{-i\omega_r\tau}-\frac{1}{2}e^{-i(2n+1)\omega_r\tau}-\frac{1}{2}e^{i(2n-1)\omega_r\tau}\right)d\tau$$

$$= \frac{\sqrt{6}}{4}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{e^{i\omega_r\tau_i}}{\tau_f-\tau_i}[-\frac{1}{i\omega_r}\left(e^{-i\omega_r(\tau_f-\tau_i)}-1\right)+\frac{N}{i\omega_r2(2n+1)}\left(e^{-i(2n+1)\omega_r(\tau_f-\tau_i)}-1\right)$$

$$-\frac{N}{i\omega_r2(2n-1)}\left(e^{i(2n-1)\omega_r(\tau_f-\tau_i)}-1\right)]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{e^{i\omega_r\tau_i}}{\omega_r(\tau_f-\tau_i)}\left[-\left(e^{-i\omega_r(\tau_f-\tau_i)}-1\right)+\frac{1}{2(2n+1)}\left(e^{-i(2n+1)\omega_r(\tau_f-\tau_i)}-1\right)\right.$$

$$\left.-\frac{1}{2(2n-1)}\left(e^{i(2n-1)\omega_r(\tau_f-\tau_i)}-1\right)\right]$$

$\tau_{c1} = \frac{4\pi}{n\omega_r}$. When $\tau \in \left[0,\frac{1}{8}\tau_{c1}\right]$, $\tau_f = \frac{1}{8}\tau_{c1}, \tau_i = 0, \omega_r(\tau_f-\tau_i) = \frac{1}{8}\times\frac{4\pi}{n} = \frac{\pi}{2n}$,

$$\overline{\widetilde{H}_{c_1}^{\mathrm{D}}}(\mu=-2, m=1)$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{2n}{\pi}[\left(e^{-i\frac{\pi}{2n}}-1\right)+\frac{1}{(4n+2)}\left(e^{-i(2n+1)\frac{\pi}{2n}}-1\right)$$

$$-\frac{1}{(4n-2)}\left(e^{i(2n-1)\frac{\pi}{2n}}-1\right)]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{2n}{\pi}\left[-\left(e^{-i\frac{\pi}{2n}}-1\right)-\frac{1}{(4n+2)}\left(e^{-i\frac{\pi}{2n}}+1\right)+\frac{1}{(4n-2)}\left(e^{-i\frac{\pi}{2n}}+1\right)\right]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{2n}{\pi}\left[-\left(e^{-i\frac{\pi}{2n}}-1\right)+\frac{1}{(4n^2-1)}\left(e^{-i\frac{\pi}{2n}}+1\right)\right]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{2n}{\pi}\left[2-\frac{4n^2}{(4n^2-1)}\left(e^{-i\frac{\pi}{2n}}+1\right)\right]$$

$$\overline{\widetilde{H}_{c\_1}^{\mathrm{D}}}(\mu=-2, m=1) = \frac{3n}{2\pi i}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\left[2-\frac{4n^2}{(4n^2-1)}\left(e^{-i\frac{\pi}{2n}}+1\right)\right] \qquad (6.9)$$

In $\tau \in \left[\frac{1}{8}\tau_{c1},\frac{5}{8}\tau_{c1}\right]$, $\tau_f = \frac{5}{8}\tau_{c1} = \frac{5}{8}\times\frac{4\pi}{n\omega_r} = \frac{5\pi}{2n\omega_r}, \tau_i = \frac{1}{8}\tau_{c1} = \frac{\pi}{2n\omega_r}, \tau_f-\tau_i = \frac{2\pi}{n\omega_r}$, we had:

$$\overline{\widetilde{H}^{\mathrm{D}}_{c\_4}}(\mu=-2,m=1)=\frac{n\omega_r e^{-i\frac{\pi}{2n}}}{2\pi}\int_0^{\frac{2\pi}{n\omega_r}}\sqrt{6}T^{\mathrm{D}}_{2,-2}\sqrt{\frac{3}{8}}\frac{[1-\cos 2(-\frac{\pi}{2}+n\omega_r t)]}{2}\omega^{\mathrm{D}}_{21}\exp[-i\omega_r t]$$

$$=\omega^{\mathrm{D}}_{21}\sqrt{6}T^{\mathrm{D}}_{2,-2}\frac{1}{4}\sqrt{\frac{3}{2}\frac{n\omega_r e^{-i\frac{\pi}{2n}}}{2\pi}}\int_0^{\frac{2\pi}{n\omega_r}}[1+\cos(2n\omega_r t)]]\exp[-i\omega_r t]$$

$$=\omega^{\mathrm{D}}_{21}T^{\mathrm{D}}_{2,-2}\frac{\sqrt{6}}{4}\sqrt{\frac{3}{2}\frac{n\omega_r e^{-i\frac{\pi}{2n}}}{2\pi}}\int_0^{\frac{2\pi}{n\omega_r}}[1+\frac{1}{2}(e^{-i2n\omega_r t}+e^{i2n\omega_r t})]\exp[-i\omega_r t]$$

$$=\omega^{\mathrm{D}}_{21}T^{\mathrm{D}}_{2,-2}\frac{\sqrt{6}}{4}\sqrt{\frac{3}{2}\frac{n\omega_r e^{-i\frac{\pi}{2n}}}{2\pi}}\int_0^{\frac{2\pi}{n\omega_r}}[e^{-i\omega_r t}+\frac{1}{2}(e^{-i(2n+1)\omega_r t}+e^{i(2n-1)\omega_r t})]$$

$$=\omega^{\mathrm{D}}_{21}T^{\mathrm{D}}_{2,-2}\frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}\frac{ne^{-i\frac{\pi}{2n}}}{2\pi}}$$

$$\Big[-(e^{-i\frac{2\pi}{n}}-1\Big)-\frac{1}{2(2n+1)}(e^{-i(2n+1)\frac{2\pi}{n}}-1)+\frac{1}{2(2n-1)}(e^{i(2n-1)\frac{2\pi}{n}}-1)]$$

$$=\omega^{\mathrm{D}}_{21}T^{\mathrm{D}}_{2,-2}\frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}\frac{ne^{-i\frac{\pi}{2n}}}{2\pi}}\Big[-(e^{-i\frac{2\pi}{n}}-1\Big)-\frac{1}{2(2n+1)}(e^{-i\frac{2\pi}{n}}-1)+\frac{1}{2(2n-1)}(e^{-i\frac{2\pi}{n}}-1)]$$

$$=\omega^{\mathrm{D}}_{21}T^{\mathrm{D}}_{2,-2}\frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}\frac{ne^{-i\frac{\pi}{2n}}}{2\pi}}\left(e^{-i\frac{2\pi}{n}}-1\right)[-1-\frac{1}{2(2n+1)}+\frac{1}{2(2n-1)}]$$

$$\overline{\widetilde{H}^{\mathrm{D}}_{c\_4}}(\mu=-2,m=1)=\omega^{\mathrm{D}}_{21}T^{\mathrm{D}}_{2,-2}\frac{3e^{-i\frac{\pi}{2n}}}{8\pi i}\left(\frac{2n-4n^3}{4n^2-1}\right)\left(e^{-i\frac{2\pi}{n}}-1\right) \tag{6.10}$$

In $\tau\in\left[\frac{5}{8}\tau_{c1},\tau_{c1}\right]$, $\tau_i=\frac{5}{8}\tau_{c1}=\frac{5}{8}\times\frac{4\pi}{n\omega_r}=\frac{5\pi}{2n\omega_r}, \tau_f=\tau_{c1}=\frac{4\pi}{n\omega_r}, \tau_f-\tau_i=\frac{3\pi}{2n\omega_r}$, we had the general form as:

$$=\frac{2n\omega_r\exp\left(-i\frac{5m\pi}{2n}\right)}{3\pi}\int_0^{\frac{3\pi}{2n\omega_r}}\sqrt{6}\sum_{\mu=-2}^{2}T^{\mathrm{D}}_{2\mu}\,d^2_{\mu0}[\frac{3\pi}{2}-n\omega_r t]\sum_{\substack{m=-2\\ m\neq0}}^{2}\omega^{\mathrm{D}}_{2m}\exp[-im\omega_r t]$$

So:

$$\overline{\widetilde{H}^{\mathrm{D}}_{c_3}}(\mu=-2,m=1)$$

$$= \frac{2n\omega_r e^{-i\frac{5\pi}{2n}}}{3\pi} \int_0^{\frac{3\pi}{2n\omega_r}} \sqrt{6} T^{\mathrm{D}}_{2,-2} \sqrt{\frac{3}{8}} \frac{[1 - \cos 2(\frac{3\pi}{2} - n\omega_r t)]}{2} \omega^{\mathrm{D}}_{21} \exp[-i\omega_r t]$$

$$= \omega^{\mathrm{D}}_{21} T^{\mathrm{D}}_{2,-2} \frac{\sqrt{6}}{2} \sqrt{\frac{3}{2}} \frac{n\omega_r e^{-i\frac{5\pi}{2n}}}{3\pi} \int_0^{\frac{3\pi}{2n\omega_r}} [1 + \cos(2n\omega_r t)]] \exp[-i\omega_r t]$$

$$= \omega^{\mathrm{D}}_{21} T^{\mathrm{D}}_{2,-2} \frac{\sqrt{6}}{2} \sqrt{\frac{3}{2}} \frac{n\omega_r e^{-i\frac{5\pi}{2n}}}{3\pi} \int_0^{\frac{3\pi}{2n\omega_r}} [e^{-i\omega_r t} + \frac{1}{2}(e^{-i(2n+1)\omega_r t} + e^{i(2n-1)\omega_r t})]$$

$$= \omega^{\mathrm{D}}_{21} T^{\mathrm{D}}_{2,-2} \frac{\sqrt{6}}{2} \sqrt{\frac{3}{2}} \frac{n e^{-i\frac{5\pi}{2n}}}{3\pi i} \left[-(e^{-i\frac{3\pi}{2n}} - 1\right) + \frac{1}{2(2n+1)}\left(e^{-i\frac{3\pi}{2n}} + 1\right) - \frac{1}{2(2n-1)}(e^{-i\frac{3\pi}{2n}} + 1)]$$

$$\overline{\widetilde{H}^{\mathrm{D}}_{c\_3}}(\mu = -2, m = 1) = \omega^{\mathrm{D}}_{21} T^{\mathrm{D}}_{2,-2} \frac{e^{-i\frac{5\pi}{2n}}}{2\pi i} [2n - \frac{4n^3}{(4n^2-1)}\left(e^{-i\frac{3\pi}{2n}} + 1\right)] \tag{6.11}$$

Together, combined, we have:

$$\overline{\widetilde{H}^{\mathrm{D}}_{c}}(\mu = -2, m = 1) = \frac{3n}{2\pi i} T^{\mathrm{D}}_{2,-2} \omega^{\mathrm{D}}_{21} \left[2 - \frac{4n^2}{(4n^2-1)}\left(e^{-i\frac{\pi}{2n}} + 1\right)\right]$$

$$+ \omega^{\mathrm{D}}_{21} T^{\mathrm{D}}_{2,-2} \frac{3e^{-i\frac{\pi}{2n}}}{8\pi i}\left(\frac{2n - 4n^3}{4n^2-1}\right)\left(e^{-i\frac{2\pi}{n}} - 1\right) + \omega^{\mathrm{D}}_{21} T^{\mathrm{D}}_{2,-2} \frac{e^{-i\frac{5\pi}{2n}}}{2\pi i} [2n - \frac{4n^3}{(4n^2-1)}\left(e^{-i\frac{3\pi}{2n}} + 1\right)]$$

$$\overline{\widetilde{H}^{\mathrm{D}}_{c}}(\mu = -2, m = 1) \tag{6.11}$$

$$= \frac{1}{\pi i} T^{\mathrm{D}}_{2,-2} \omega^{\mathrm{D}}_{21} [3n - \frac{6n^3}{(4n^2-1)}\left(e^{-i\frac{\pi}{2n}} + 1\right) + \frac{3e^{-i\frac{\pi}{2n}}}{8}\left(\frac{2n - 4n^3}{4n^2-1}\right)\left(e^{-i\frac{2\pi}{n}} - 1\right)$$

$$+ e^{-i\frac{5\pi}{2n}}[n - \frac{2n^3}{(4n^2-1)}\left(e^{-i\frac{3\pi}{2n}} + 1\right)]$$

Together we have to combine the three parts, and the final total $\overline{\widetilde{H}^{\mathrm{D}}_{SPCn}}(\mu = -2, m = 1) = 2\overline{\widetilde{H}^{\mathrm{D}}_{c}}(\mu = -2, m = 1)$ since we have the supercycle back to back. You will have the same kind of result for $\overline{\widetilde{H}^{\mathrm{D}}_{c}}(\mu = 2, m = -1)$ term for the recoupled dipolar interaction.

Recall $T^{2}_{\pm 2} = I^{\pm}S^{\pm}$. The scaling factor is the part excluding $T^{\mathrm{D}}_{2,\pm 2}$, which is quite complicated. You can use what we derived as a general formula, and plug in corresponding n value to get the scaling factor for postC7(n=7) and SPC5(n=5).

However, this result doesn't match with the result given in M. Hhwy et al. J. Chem. Phys. 108, 2686 (1998):

$$\kappa = \frac{3n^3 i[1 - \exp\left(i\frac{4\pi}{n}\right)]}{8\sqrt{2}\pi(4n^2 - 1)} \tag{6.12}$$

How could this be?

Let’s do the integration as on complete non-divided part for a C block, assuming the irradiation is on continuously without switching direction into sub-blocks:

$$\overline{H_{c1}^{\mathrm{D}}} = \sqrt{6}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{1}{\tau_f}\int_0^{\tau_f}\sqrt{\frac{3}{8}}\sin^2\beta(\tau)\ e^{-i\omega_r\tau}\,d\tau \tag{6.13}$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{1}{\omega_r\tau_f}$$

$$\left[-\left(e^{-i\omega_r\tau_f} - 1\right) + \frac{1}{2(2n+1)}\left(e^{-i(2n+1)\omega_r\tau_f} - 1\right) - \frac{1}{2(2n-1)}\left(e^{i(2n-1)\omega_r\tau_f} - 1\right)\right]$$

Here $\omega_r\tau_f = \omega_r\tau_{c1} = \frac{4\pi}{n}$

$$\frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{n}{4\pi}\left[-\left(e^{-i\frac{4\pi}{n}} - 1\right) + \frac{1}{2(2n+1)}\left(e^{-i\frac{4\pi}{n}} - 1\right) - \frac{1}{2(2n-1)}\left(e^{-i\frac{4\pi}{n}} - 1\right)\right]$$

$$= T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{\sqrt{6}}{16i}\sqrt{\frac{3}{2}}\frac{n}{\pi}\left\{\left(e^{-i\frac{4\pi}{n}} - 1\right)\left[-1 + \frac{1}{2(2n+1)} - \frac{1}{2(2n-1)}\right]\right\}$$

$$= T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{\sqrt{6}}{16i}\sqrt{\frac{3}{2}}\frac{n}{\pi}\left[\left(e^{-i\frac{4\pi}{n}} - 1\right)\frac{-8n^2 + 2 + 2n - 1 - 2n - 1}{2(4n^2 - 1)}\right]$$

$$= T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{\sqrt{6}}{16i}\sqrt{\frac{3}{2}}\frac{n}{\pi}\left[\left(e^{-i\frac{4\pi}{n}} - 1\right)\frac{-8n^2}{2(4n^2 - 1)}\right]$$

$$= T_{2,-2}^{\mathrm{D}}\omega_{21}^{\mathrm{D}}\frac{3i}{2\pi}\left[\left(e^{-i\frac{4\pi}{n}} - 1\right)\frac{n^3}{2(4n^2 - 1)}\right]$$

Where the scaling factor

$$\kappa = \frac{3i}{2\pi}\left[\left(e^{-i\frac{4\pi}{n}} - 1\right)\frac{n^3}{(4n^2 - 1)}\right]\omega_{21}^{\mathrm{D}}$$

$$= \frac{3i}{2\pi}\left[\left(e^{-i\frac{4\pi}{n}} - 1\right)\frac{n^3}{(4n^2 - 1)}\right] \times \left[-\frac{\boldsymbol{b_{IS}}}{\mathbf{2\sqrt{2}}}\mathbf{\sin 2}\boldsymbol{\beta}\ \boldsymbol{exp}(\boldsymbol{i\gamma})\right]$$

$$\kappa = \frac{3i}{4\sqrt{2}\pi}\left[\left(1-e^{-i\frac{4\pi}{n}}\right)\frac{n^3}{(4n^2-1)}\right]\boldsymbol{\sin 2\beta\, exp(i\gamma) b_{IS}} \tag{6.14}$$

It seems the given formula in the literature is not correct.

Homework: could you derive the average Hamiltonian of the original C7 (Chemical. Physics Letters 242, 304-309 (1995))?

You can show C7 selects $T^{\mathrm{D}}_{2,2}\omega^{\mathrm{D}}_{2-1}$ and $T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}$. The evolution of RF pulses of individual C block in C7 has two parts, instead of three:

In $\tau \in \left[0,\frac{1}{2}\tau_{c1}\right]$, $\tau_i = 0, \tau_f = \frac{1}{2}\tau_{c1} = \frac{2\pi}{7\omega_r}, \tau_f - \tau_i = \frac{2\pi}{7\omega_r}, \omega_{rf} = 7\omega_r$, $U = e^{-i\omega_{rf}\tau I_y} = e^{-i7\omega_r\tau I_y} = R(0,7\omega_r\tau,0)$, so

$$\overline{\widetilde{H}^{\mathrm{D}}_{c\_1}} = \frac{1}{\tau_f-\tau_i}\int_0^{\tau_f-\tau_i} R^{-1}(0,7\omega_r\tau,0)\sqrt{6}T^{\mathrm{D}}_{\lambda 0}\, R(0,7\omega_r\tau,0)\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r\tau)$$

$$= \frac{1}{\tau_f-\tau_i}\int_0^{\tau_f-\tau_i}\sqrt{6}\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}(-7\omega_r\tau)\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r\tau)$$

$$= \frac{1}{\tau_f-\tau_i}\int_0^{\tau_f-\tau_i}\sqrt{6}\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}(-7\omega_r\tau)\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r\tau)$$

We can plug in our integration formula derived for the first section of SPCn:

$$\overline{\widetilde{H}^{\mathrm{D}}_{c_1}} = \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\frac{1}{\omega_r(\tau_f-\tau_i)}[-\left(e^{-i\omega_r(\tau_f-\tau_i)}-1\right)+\frac{1}{2(2n+1)}\left(e^{-i(2n+1)\omega_r(\tau_f-\tau_i)}-1\right)$$

$$-\frac{1}{2(2n-1)}\left(e^{i(2n-1)\omega_r(\tau_f-\tau_i)}-1\right)]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\frac{7}{2\pi}$$

$$\left[-\left(e^{-i\frac{2\pi}{7}}-1\right)+\frac{1}{2(14+1)}\left(e^{-i(15)\frac{2\pi}{7}}-1\right)-\frac{1}{2(14-1)}\left(e^{i(13)\frac{2\pi}{7}}-1\right)\right]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\frac{7}{2\pi}\left[\left(e^{-i\frac{2\pi}{7}}-1\right)(-1+\frac{1}{2(14+1)}-\frac{1}{2(14-1)})\right]$$

$$= \frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\frac{7}{2\pi}\times\frac{-196}{195}\left[\left(e^{-i\frac{2\pi}{7}}-1\right)\right]$$

$$= \frac{1029}{390\pi i}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\left(1-e^{-i\frac{2\pi}{7}}\right)$$

In $\tau \in \left[\frac{1}{2}\tau_{c1},\tau_{c1}\right]$, $\tau_i = \frac{1}{2}\tau_{c1} = \frac{2\pi}{7\omega_r}, \tau_f = \tau_{c1} = \frac{4\pi}{7\omega_r}, \tau_f - \tau_i = \frac{2\pi}{7\omega_r}, \omega_{rf} = 7\omega_r$, $U = e^{-i2\pi I_y}e^{-i\omega_{rf}\tau I_y} = e^{-i(-7\omega_r\tau)I_y} = R(0,-7\omega_r\tau,0)$, so

$$\overline{\widetilde{H}^{\mathrm{D}}_{c\_2}} = \frac{1}{\tau_f-\tau_i}\int_{\tau_i}^{\tau_f} R^{-1}(0,-7\omega_r\tau,0)\sqrt{6}T^{\mathrm{D}}_{\lambda 0}\, R(0,-7\omega_r\tau,0)\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r\tau)$$

$$= \frac{e^{-im\omega_r\tau_i}}{\tau_f-\tau_i}\int_0^{\tau_f-\tau_i}\sqrt{6}\sum_{\mu=-2}^{2}T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}(7\omega_r\tau)\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r\tau)$$

$$= e^{-im\omega_r\tau_i}\overline{\widetilde{H}^{\mathrm{D}}_{c\_1}} = \frac{1029e^{-i\frac{2\pi}{7}}}{390\pi i}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\left[\left(1-e^{-i\frac{2\pi}{7}}\right)\right]$$

$$\overline{\widetilde{H}^{\mathrm{D}}_{c}} = \overline{\widetilde{H}^{\mathrm{D}}_{c\_1}} + \overline{\widetilde{H}^{\mathrm{D}}_{c\_2}} = \frac{1029}{390\pi i}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\left(1-e^{-i\frac{2\pi}{7}}\right)\left(1+e^{-i\frac{2\pi}{7}}\right) = \frac{1029}{390\pi i}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}(1-e^{-i\frac{4\pi}{7}})$$

$$= -\frac{1029}{390\pi i}T^{\mathrm{D}}_{2,-2}\omega^{\mathrm{D}}_{2,1}\left(1-e^{-i\frac{4\pi}{7}}\right)\times\frac{b_{IS}}{2\sqrt{2}}\sin 2\beta\, exp(i\gamma)$$

$$= -\frac{1029\sqrt{2}i}{1560\pi}\left(1-e^{-i\frac{4\pi}{7}}\right)b_{IS}\sin 2\beta\, exp(i\gamma)T^{\mathrm{D}}_{2,2}$$

$$\overline{\widetilde{H}^{\mathrm{D}}_{c}} = -\frac{343\sqrt{2}i}{520\pi}e^{-i\frac{2\pi}{7}}\left(e^{i\frac{2\pi}{7}}-e^{-i\frac{2\pi}{7}}\right)b_{IS}\sin 2\beta\, exp(i\gamma)T^{\mathrm{D}}_{2,-2} \tag{6.15}$$

Let's continue our discussion on SPC5. Now we know the form of recoupled homonuclear dipolar interaction. A critical question is, if the sequence kills isotropic and anisotropic chemical shift? You can apply the same analysis to both. They follow essentially the same derivation as our derivation above for SPC5, with different coefficients. You will find that although $T^{\mathrm{CS}}_{1,0}$ will be fully suppressed by the $2\pi-(-2\pi)$ or so called C^{44} block in C7, $T^{\mathrm{CS}}_{1,\pm 1}$ parts of both interactions still survive the single C block in C^{44}, and also in the later postC7 or SPC5 version C block of C^{143}.

I will not present the complete derivation here. You will find the average residual $T^{\mathrm{CS}}_{1,\pm 1}$ ratio between C^{44}: $C^{143} = (0.0708 + 0.390916i)$: $(0.07875 - 0.0734729i)$. Indeed, the C^{143} will work out better in terms of suppress both isotropic and anisotropic chemical shifts. But none is perfect. I will leave this as homework. You can show that with correctly applied transformation to interaction frame, you don't need higher order terms or simulations as in the postC7 paper to show the superiority of C^{143} vs. C^{44}.

The next questions is, assume we can neglect the residual chemical shifts, how will the system evolve under this double quantum interaction in experiments?

In Fig. 6.1, we see before the application of SPC5, the system stores the magnetization at the z axis. Since now we have pure double quantum Hamiltonian under SPC5, chemical shift (isotropic and anisotropic) are both averaged to ~ zero by SPC5. We can write the total Hamiltonian of the system in a simple form as:

$$\overline{H_{ij}^D} = b_{IS}(\beta)\left(e^{-i\gamma}I_i^+I_j^+ + e^{i\gamma}I_i^-I_j^-\right) \tag{6.16}$$
$$= b_{IS}(\beta)\exp[-i\frac{\gamma}{2}\left(I_{zi}+I_{zj}\right)](I_i^+I_j^+ + I_i^-I_j^-)\exp[i\frac{\gamma}{2}\left(I_{zi}+I_{zj}\right)]$$

Here we use the relationship:

$$\exp(-i\phi I_z)\, I^{\pm} \exp(i\phi I_z) = \exp(\mp i\phi)I^{\pm} \tag{6.17}$$

The exponential angle is $\frac{\gamma}{2}$, since we have double quantum operator, and each contributes $\frac{\gamma}{2}$. This transformation is critical, as it removes the heterogeneous phase factor in $\overline{H_{ij}^D}$ which will allow us to convert the Hamiltonian into fictitious spin space.

Recall now fictitious two spin operator sets, since we are dealing with two coupled spins:

$$I_2^x = \frac{1}{2}(I^+S^+ + I^-S^-); I_2^y = \frac{1}{2i}(I^+S^+ - I^-S^-); I_2^z = \frac{1}{2}(I_z + S_z)$$
$$I_0^z = \frac{1}{2}(I_z - S_z)$$

As we know, double quantum and zero quantum spins form their individual irreducible space, and commute with each other. So we can ignore the effect of SPC5 on I_0^z, as it will have no effect. Let's focus on I_2^z.

Rigorously, we can apply a transformation to the interaction frame of reference of the zero quantum Hamiltonian by $\widetilde{H_{ij}^D} = \exp(i\Delta I_0^z t)H_{ij}^D\exp(-i\Delta I_0^z t)$, where $\Delta = \omega_I^{iso} - \omega_S^{iso}$. However, as zero quantum commutes with double quantum operators, this transformation will leave H_{ij}^D unchanged:

$$\overline{H_{ij}^D} = b_{IS}(\beta)\exp\left(-i\frac{\gamma}{2}I_2^z\right)2I_2^x\exp\left(i\frac{\gamma}{2}I_2^z\right) \tag{6.18}$$
$$= 2b_{IS}(\beta)(I_2^x\cos\frac{\gamma}{2} + I_2^y\sin\frac{\gamma}{2})$$

To see how I_2^z evolves under SPC5 for an application time of t, we can evaluate I_2^z by density matrix:

$$I_2^z(t) = Tr\left\{I_2^z \exp\left(-iH_{ij}^D t\right) I_2^z \exp\left(iH_{ij}^D t\right) I_{zj}\right\} \tag{6.19}$$

Now recall the formula Eq. 5.2 we derived earlier:

$$\begin{aligned}\exp(-i\beta n \cdot J) &= \exp\left[-i\beta\left(I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta\right)\right]\\ &= \exp(i\varphi I_z)\,[\exp(-i\theta I_x)\exp(-i\beta I_z)\exp(i\theta I_x)]\exp(-i\varphi I_z)\end{aligned}$$

We can use this formula to rearrange out double quantum evolution, with $\varphi = \frac{\gamma}{2}$, and $\theta = \frac{\pi}{2}$:

$$\begin{aligned}\exp\left(-iH_{ij}^D t\right) &= \exp\left\{-i2b_{IS}(\beta)\left(I_2^x \cos\frac{\gamma}{2} + I_2^y \sin\frac{\gamma}{2}\right)t\right\} \\ &= \exp\left(i\frac{\gamma}{2}I_2^z\right)[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(-i2b_{IS}(\beta)tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)]\exp(-i\frac{\gamma}{2}I_2^z)\end{aligned} \tag{6.20}$$

$$\exp\left(iH_{ij}^D t\right) = \exp\left(i\frac{\gamma}{2}I_2^z\right)[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(i2b_{IS}(\beta)tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)]\exp(-i\frac{\gamma}{2}I_2^z)$$

To simplify the symbols, let's replace $2b_{IS}(\beta)t = \omega_D t$, and plug the evolution operator back into Eq. 6.19:

$$\begin{aligned}&I_2^z(t)\\ &= Tr\left\{\begin{matrix}I_2^z \exp\left(i\frac{\gamma}{2}I_2^z\right)\left[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(-i\omega_D tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)\right]\exp\left(-i\frac{\gamma}{2}I_2^z\right)I_2^z\exp\left(i\frac{\gamma}{2}I_2^z\right)\\ \left[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(i\omega_D tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)\right]\exp\left(-i\frac{\gamma}{2}I_2^z\right)\end{matrix}\right\}\\ &= Tr\left\{\begin{matrix}I_2^z \exp\left(i\frac{\gamma}{2}I_2^z\right)\left[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(-i\omega_D tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)\right]I_2^z\\ \left[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(i\omega_D tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)\right]\exp\left(-i\frac{\gamma}{2}I_2^z\right)\end{matrix}\right\}\end{aligned}$$

Now we can use our old tricks again: pick the exponential operator on the right and left closest to I_2^z, and they will give a simple single spin operator transformation according to Eq. 5.3. Pair by pair, we can work out the evolution:

$$\begin{aligned}&= Tr\left\{I_2^z \exp\left(i\frac{\gamma}{2}I_2^z\right)\left[\exp\left(-i\frac{\pi}{2}I_2^x\right)\exp(-i\omega_D tI_2^z)\right]I_2^y\left[\exp(i\omega_D tI_2^z)\exp\left(i\frac{\pi}{2}I_2^x\right)\right]\exp\left(-i\frac{\gamma}{2}I_2^z\right)\right\}\\ &= Tr\left\{I_2^z \exp\left(i\frac{\gamma}{2}I_2^z\right)\left[\exp\left(-i\frac{\pi}{2}I_2^x\right)\right]\left(I_2^y\cos\omega_D t - I_2^x\sin\omega_D t\right)\left[\exp\left(i\frac{\pi}{2}I_2^x\right)\right]\exp\left(-i\frac{\gamma}{2}I_2^z\right)\right\}\\ &= Tr\left\{I_2^z \exp\left(i\frac{\gamma}{2}I_2^z\right)\left(I_2^z\cos\omega_D t - I_2^x\sin\omega_D t\right)\exp\left(-i\frac{\gamma}{2}I_2^z\right)\right\}\\ &= Tr\left\{I_2^z[I_2^z\cos\omega_D t - \sin\omega_D t\left(I_2^x\cos\frac{\gamma}{2} + I_2^y\sin\frac{\gamma}{2}\right)]\right\}\end{aligned}$$

Hence the nonzero part of the trace will give us:

$$I_2^z(t) = \cos\omega_D t\, Tr\{(I_2^z)^2\} \tag{6.21}$$

Notice the evolution also generates a transverse component. If we evaluate $I_2^x(t)$ and $I_2^y(t)$, we will get:

$$I_2^x(t) = -\sin\omega_D t\cos\frac{\gamma}{2}Tr\{(I_2^x)^2\}, I_2^y(t) = -\sin\omega_D t\sin\frac{\gamma}{2}Tr\{(I_2^y)^2\} \tag{6.22}$$

You can plug in $(I_2^x)^2 = (I_2^y)^2 = (I_2^z)^2 = \frac{1}{3}1(1+1) = \frac{2}{3}$ to get the final numerical value. The spin quantum number of the fictitious spin 1 is 1.

The magnitude of the transverse component depends on the $\frac{\gamma}{2}$ angle (the angle that transform the molecule from its Principal Axis Frame to the rotor fixed frame), and oscillates with $-\sin\omega_D t$.

Therefore, the single quantum polarization before application of SPC5 will be converted to x, y, and z polarization of double quantum, with the magnitude of the double quantum polarization depends on:

$$\begin{gathered} I_2^z(t) = \frac{2}{3}\cos\omega_D t\,; \\ I_2^x(t) = -\frac{2}{3}\sin\omega_D t\cos\frac{\gamma}{2};\ I_2^y(t) = -\frac{2}{3}\sin\omega_D t\sin\frac{\gamma}{2}; \end{gathered} \tag{6.23}$$

At $t = 0$, we can see all the double quantum signal is along $I_2^z(t)$, and there is zero double quantum signal in the transverse plane. Gradually, the z polarization will be converted to the transverse double quantum polarization. At $t = \frac{\pi}{2\omega_D} = \frac{\pi}{4b_{IS}(\beta)}$, the transverse double quantum signal reaches maximum.

After SPC5 is turned off, the transverse double quantum coherence of two spins should evolve together at their Larmor frequency $\Sigma = \omega_i + \omega_j$, as only double quantum would survive from the second SPC5 to be converted back into observable single quantum(from the selection rule and you can also easily show that $I_{zi}(t)$ and $I_{zj}(t)$ under the effect of double quantum coupling won't give us any signal(Trace is zero), and that is why sequences like SPC5 are called double quantum FILTER).

Hence, in such a double quantum experiment, if you incorporate an indirect dimension after the first excitation SPC5, all sites will evolve at the addition of their chemical shifts and show up at the sum of their Larmor frequency in the recorded frequency spectrum.

At the same time, in the zero quantum space, $I_0^z(t) = I_0^z(0)$, since SPC5 will average out zero quantum terms, which means the zero quantum of the two nuclei would stay unchanged.

We can go back to evaluate the magnitude of $I_2^z(t)$ by combining the above two conditions:

$$\begin{gathered} I_2^z(t) = \frac{1}{2}\left[I_{zi}(t) + I_{zj}(t)\right] = \frac{1}{2}\cos[2b_{IS}(\beta)t]\left[I_{zi}(0) + I_{zj}(0)\right] \\ I_0^z(t) = \frac{1}{2}\left[I_{zi}(t) - I_{zj}(t)\right] = \frac{1}{2}\left[I_{zi}(0) - I_{zj}(0)\right] \end{gathered} \tag{6.24}$$

We can determine the polarization on each nucleus at any point of time:

$$I_{zi}(t) = \frac{[I_{zi}(0) + I_{zj}(0)]\cos[2b_{IS}(\beta)t] + [I_{zi}(0) - I_{zj}(0)]}{2} \tag{6.25}$$
$$= I_{zi}(0)\cos^2 b_{IS}(\beta)t - I_{zj}(0)\sin^2 b_{IS}(\beta)t$$

$$I_{zj}(t) = \frac{[I_{zi}(0) + I_{zj}(0)]\cos[2b_{IS}(\beta)t] - [I_{zi}(0) - I_{zj}(0)]}{2} \tag{6.26}$$
$$= I_{zj}(0)\cos^2 b_{IS}(\beta)t - I_{zi}(0)\sin^2 b_{IS}(\beta)t$$

We note that the oscillation of polarization between two nuclei only depends on the β angle of two nuclei, and has nothing to do with the γ angle of the two. Here recall β is the angle to rotate i and j spin from their principal axis frame to the rotor fixed frame. This is a γ encoded sequence, where the polarization transfer between any pair of nuclei has nothing to do with their γ. It has a stronger transfer efficiency than the pulse sequence depending on γ.

If initially j spin has zero polarization, all polarization is on i, then:

$$I_{zj}(t) = -I_{zi}(0)\sin^2 b_{IS}(\beta)t \tag{6.27}$$

Hence we see the sign of polarization is alternating between two directly double quantum coupled spins. This is opposite to the heteronuclear polarization transfer, Eq. 4.131 in Sect. 4.10 in Chapter 4. So the next spin bond to j but not with i will have the same sign with the polarization on nucleus i, and so on. This knowledge can be exploited in assignments.

As we commented in Chapter 4, section 4.11, we explained how to detect both x and y components indirectly in the double quantum (multiple quantum in general) space. To set up the indirect dimension of y component of double quantum, you just need to apply a $\frac{\pi}{4}$ phase shift to the excitation pulse sequence entirely.

To covert double quantum back to single quantum, we can use the same excitation sequence with an additional $\frac{\pi}{2}$ phase shift, which you can show that it will reverse the time evolution.

This will be all the knowledge, I believe, that you will need to code a pulse sequence in any spectrometer platform if you know the programming language.

6.2 Rotary resonance recoupling of homonuclear dipolar interaction

The decoupling of heteronuclear interactions gets complicated by the potential interference between rotations generated by RF irradiation and physical rotation by MAS. This was recognized by rotary resonance conditions at $\omega_{rf} = n\omega_r(Chem. Phys. Lett. 146, 71\ (1988))$, where n=1, 2, ... and ½. When n=1,2, we will have recoupling of heteronuclear through rotary resonance conditions. And when n=1/2, it is the HORROR sequence to recouple homonuclear dipolar interaction (JCP 101, 1805 (1994)).

All these rotary resonance conditions can be manifested by similar analysis as we did for our SPC5 sequence. Assume the RF irradiation is applied along the y axis (well, if it is applied to direction other than y, we can superimpose an additional phase shift to convert to y, so here make it y for simplicity). We can treat the interaction in general just like as a C block, assuming the irradiation is on continuously without switching direction. Recall the generic form of Hamiltonian under MAS:

$$H_{\Lambda} = \sum_{\mu=-\lambda}^{\lambda} T_{\lambda\mu}^{\Lambda}\, e^{-i\mu\alpha(\tau)} d_{\mu 0}^{\lambda}[-\beta(\tau)] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\, e^{-im\omega_r\tau}$$

If we have homonuclear dipolar interaction, under RF irradiation, it creates rotation on both spin operators in $T_{\lambda\mu}^{\Lambda}$, assume $\omega_{rf} = k\omega_r$, the rotation then should be $\beta(\tau) = k\omega_r\tau$. The average Hamiltonian over one rotor period is:

$$\overline{\widetilde{H}_{Homo}^{\mathrm{D}}} = \frac{1}{\tau_f}\int_0^{\tau_f} d\tau\sqrt{6} \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, e^{-i\mu\alpha(\tau)} d_{\mu 0}^{2}[-\beta(\tau)] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau} \tag{6.28}$$

$$= \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau (T_{2,-2}^{\mathrm{D}} + T_{2,2}^{\mathrm{D}}) \sqrt{\frac{3}{8}}\sin^2(-\beta) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

$$+ \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau (T_{2,-1}^{\mathrm{D}} - T_{2,1}^{\mathrm{D}}) \sqrt{\frac{3}{8}}\sin(-2\beta) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

$$+ \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau T_{2,0}^{\mathrm{D}} \frac{1}{2}(\cos^2(-\beta) - 1) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

Since the $T_{\lambda\mu}^{\Lambda}$, and $\omega_{2m}^{\mathrm{D}}$are just operators and parameters do not participate in the integration, the above equation can be rewritten as:

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\big(T_{2,-2}^{\mathrm{D}} + T_{2,2}^{\mathrm{D}}\big) \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \sqrt{\frac{3}{8}}\sin^2\beta\, e^{-im\omega_r\tau}$$

$$- \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\big(T_{2,-1}^{\mathrm{D}} - T_{2,1}^{\mathrm{D}}\big) \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \sqrt{\frac{3}{8}}\sin 2\beta\, e^{-im\omega_r\tau}$$

$$+\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}T_{2,0}^{\mathrm{D}}\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f}d\tau\frac{1}{2}(3\cos^2\beta-1)\,e^{-im\omega_r\tau}$$

$$=\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}(T_{2,-2}^{\mathrm{D}}+T_{2,2}^{\mathrm{D}})\,A-\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}(T_{2,-1}^{\mathrm{D}}-T_{2,1}^{\mathrm{D}})\,B+\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}T_{2,0}^{\mathrm{D}}\,C$$

We can then focus on the integral parts A, B and C one by one:

$$A=\frac{\sqrt{6}}{2}\sqrt{\frac{3}{2}}\frac{1}{\tau_f}\int_0^{\tau_f}\frac{1-\cos(2\beta)}{2}\;e^{-im\omega_r\tau}d\tau=\frac{1}{2}\sqrt{\frac{3}{2}}\frac{1}{\tau_f}\int_0^{\tau_f}\frac{1-\cos(2k\omega_r\tau)}{2}\;e^{-im\omega_r\tau}d\tau$$

$$=\frac{\sqrt{6}}{4}\sqrt{\frac{3}{2}}\frac{1}{\tau_f}\int_0^{\tau_f}\left[e^{-im\omega_r\tau}-\frac{1}{2}\left(e^{-i2k\omega_r\tau_f}+e^{i2k\omega_r\tau_f}\right)e^{-im\omega_r\tau}\right]d\tau$$

$$=\frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}\frac{1}{\omega_r\tau_f}\left[\begin{matrix}-\frac{1}{m}\left(e^{-i\omega_r\tau_f}-1\right)+\frac{1}{2(2k+m)}\left(e^{-i(2k+m)\omega_r\tau_f}-1\right)\\-\frac{1}{2(2k-m)}\left(e^{i(2k-m)\omega_r\tau_f}-1\right)\end{matrix}\right]$$

Here $\tau_f=\frac{2\pi}{\omega_r}$. $e^{-i\omega_r\tau_f}=e^{-i(2k+m)\omega_r\tau_f}=e^{i(2k-m)\omega_r\tau_f}=1$. So the integral would have been zero, unless $2k-m$ and $2k+m=0$. When $2k+m$ or $2k-m=0$, we can apply L'Hopital Rule in limit: $\lim\limits_{2k+m=0}\frac{1}{2(2k+m)}\left(e^{-i(2k+m)\omega_r\tau_f}-1\right)=\lim\limits_{x=0}\frac{1}{2x}\left(e^{-i\omega_r\tau_f x}-1\right)=-i\pi$. Or, $\lim\limits_{2k-m=0}\frac{1}{2(2k-m)}\left(e^{i(2k-m)\omega_r\tau_f}-1\right)=\lim\limits_{x=0}\frac{1}{2x}\left(e^{i\omega_r\tau_f x}-1\right)=i\pi$. Therefore, eitherway, the above equation will be:

$$A=\frac{\sqrt{6}}{4i}\sqrt{\frac{3}{2}}\frac{1}{\omega_r\tau_f}\times(-i\pi)=-\frac{\sqrt{6}}{4}\sqrt{\frac{3}{2}}\frac{1}{2}=-\frac{3}{8}\tag{6.29}$$

We see this will give us $k=1/2$, which is HORROR recoupling condition for the first term:

$$-\frac{3}{8}\left(T_{2,-2}^{\mathrm{D}}+T_{2,2}^{\mathrm{D}}\right)\left(\omega_{2,2k}^{\mathrm{D}}+\omega_{2,-2k}^{\mathrm{D}}\right),\tag{6.30}$$

$$with\;m=\pm 1\;for\;k=\frac{1}{2},and\;m=\pm 2\;for\;k=1$$

For the second term:

$$B=\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f}d\tau\sqrt{\frac{3}{8}}\sin 2\beta\,e^{-im\omega_r\tau}=\sqrt{\frac{3}{8}}\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f}d\tau\sin(2k\omega_r\tau)\,e^{-im\omega_r\tau}$$

$$= \frac{\sqrt{6}}{2i}\sqrt{\frac{3}{8}}\frac{1}{\tau_f}\int_0^{\tau_f} d\tau\left(e^{i2k\omega_r\tau} - e^{-i2k\omega_r\tau}\right) e^{-im\omega_r\tau}$$

$$= \frac{\sqrt{6}}{2i}\sqrt{\frac{3}{8}}\frac{1}{\tau_f}\int_0^{\tau_f} d\tau\left(e^{i(2k-m)\omega_r\tau} - e^{-i(2k+m)\omega_r\tau}\right)$$

$$= \frac{3}{4i}\frac{1}{\omega_r\tau_f}[\frac{1}{2k-m}\left(e^{i(2k-m)\omega_r\tau_f} - 1\right) + \frac{1}{2k+m}\left(e^{-i(2k+m)\omega_r\tau_f} - 1\right)]$$

Again, $e^{-i(2k+m)\omega_r\tau_f} = e^{i(2k-m)\omega_r\tau_f} = 1$, so the integral would have been zero, unless $2k - m$ and $2k + m = 0$. When $2k + m$ or $2k - m = 0$, we can apply L'Hopital Rule in limit: $\lim_{2k+m=0} \frac{1}{2(2k+m)}\left(e^{-i(2k+m)\omega_r\tau_f} - 1\right) = \lim_{x=0}\frac{1}{2x}\left(e^{-i\omega_r\tau_f x} - 1\right) = -\,i\pi$. Or, $\lim_{2k-m=0} \frac{1}{2(2k-m)}\left(e^{i(2k-m)\omega_r\tau_f} - 1\right) = \lim_{x=0}\frac{1}{2x}\left(e^{i\omega_r\tau_f x} - 1\right) = i\pi$. So eitherway, we have:

$$B = \frac{3}{8} \tag{6.31}$$

So the second term gives:

$$\frac{3}{8}\left(T^{\mathrm{D}}_{2,-1} - T^{\mathrm{D}}_{2,1}\right)(\omega^{\mathrm{D}}_{2,2k} + \omega^{\mathrm{D}}_{2,-2k}), \tag{6.32}$$

$$with\ m = \pm 1\ for\ k = \frac{1}{2}, and\ m = \pm 2\ for\ k = 1$$

The third term integral is:

$$C = \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau\frac{1}{2}(3\cos^2\beta - 1)e^{-im\omega_r\tau} = \frac{3}{2}\frac{1}{\tau_f}\int_0^{\tau_f} d\tau\cos^2(k\omega_r\tau)\, e^{-im\omega_r\tau}$$

$$= \frac{3}{2}\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau\frac{1 + \cos(2k\omega_r\tau)}{2} e^{-im\omega_r\tau}$$

$$= \frac{3}{4}\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau[e^{-im\omega_r\tau} + \frac{1}{2}\left(e^{-i2k\omega_r\tau_f} + e^{i2k\omega_r\tau_f}\right)e^{-im\omega_r\tau}]$$

$$= \frac{3}{4i}\frac{\sqrt{6}}{\omega_r\tau_f}[-\frac{1}{m}\left(e^{-i\omega_r\tau_f} - 1\right) - \frac{1}{2(2k+m)}\left(e^{-i(2k+m)\omega_r\tau_f} - 1\right)$$

$$+ \frac{1}{2(2k-m)}\left(e^{i(2k-m)\omega_r\tau_f} - 1\right)]$$

Again, $e^{-i(2k+m)\omega_r\tau_f} = e^{i(2k-m)\omega_r\tau_f} = 1$, so the integral would have been zero, unless $2k - m$ and $2k + m = 0$. When $2k + m$ or $2k - m = 0$, we can apply L'Hopital Rule in limit: $\lim_{2k+m=0} \frac{1}{2(2k+m)} \left(e^{-i(2k+m)\omega_r\tau_f} - 1\right) = \lim_{x=0} \frac{1}{2x} \left(e^{-i\omega_r\tau_f x} - 1\right) = -i\pi$. Or, $\lim_{2k-m=0} \frac{1}{2(2k-m)} \left(e^{i(2k-m)\omega_r\tau_f} - 1\right) = \lim_{x=0} \frac{1}{2x} \left(e^{i\omega_r\tau_f x} - 1\right) = i\pi$. So eitherway, we have:

$$C = \frac{3}{4i} \frac{\sqrt{6}}{\omega_r\tau_f} \times i\pi = \frac{3}{8}\sqrt{6} \tag{6.33}$$

So the third term gives us:

$$\frac{3}{8}\sqrt{6}T_{2,0}^{\mathrm{D}}\left(\omega_{2,2k}^{\mathrm{D}} + \omega_{2,-2k}^{\mathrm{D}}\right), \tag{6.34}$$

$$with\ m = \pm 1\ for\ k = \frac{1}{2}, and\ m = \pm 2\ for\ k = 1$$

Combined, the recoupled homonuclear dipolar interaction at rotary resonance condition when $\omega_{rf} = k\omega_r$, where $k = \frac{1}{2}, 1$:

$$\overline{H_{Homo}^{\mathrm{D}}} \tag{6.35}$$

$$= -\frac{3}{8}\left(T_{2,-2}^{\mathrm{D}} + T_{2,2}^{\mathrm{D}}\right)\left(\omega_{2,2k}^{\mathrm{D}} + \omega_{2,-2k}^{\mathrm{D}}\right) - \frac{3}{8}\left(T_{2,-1}^{\mathrm{D}} - T_{2,1}^{\mathrm{D}}\right)\left(\omega_{2,2k}^{\mathrm{D}} + \omega_{2,-2k}^{\mathrm{D}}\right)$$

$$+ \frac{3}{8}\sqrt{6}T_{2,0}^{\mathrm{D}}\left(\omega_{2,2k}^{\mathrm{D}} + \omega_{2,-2k}^{\mathrm{D}}\right)$$

At high field approximation, compared to $T_{2,0}^{\mathrm{D}}$, $T_{2,\pm1}^{\mathrm{D}}$ and $T_{2,\pm2}^{\mathrm{D}}$ involve spin operators I_x and I_y which are higher order terms(see Eq. 5.48 to 5.51), and you can prove that they are on the order of $\frac{1}{\omega_0}[\frac{3}{8}\left(\omega_{2,2k}^{\mathrm{D}} + \omega_{2,-2k}^{\mathrm{D}}\right)]^2$. The lowest order of surviving terms will be $\frac{3}{8}\sqrt{6}\left(\omega_{2,2k}^{\mathrm{D}} + \omega_{2,-2k}^{\mathrm{D}}\right)T_{2,0}^{\mathrm{D}}$. So we can say these rotary recoupling condition when RF irradiation at $\frac{1}{2}\omega_r$ or ω_r, we have recoupled homo nuclear dipolar interaction.

6.3 Rotary resonance recoupling of heteronuclear dipolar interaction

For heteronuclear dipolar Hamiltonian, when we apply RF irradiation along the y axis to only one of the nuclei, let's assume the RF irradiation is applied to I spin, among $T_{20}^{\mathrm{D}} = \frac{2}{\sqrt{6}} I_z S_z$, only the I_z is affected and endures spin rotation. The treatment of the averaged heteronuclear dipolar interaction is similar to Eq. 6.28 in:

$$\overline{H_{Heter}^{\mathrm{D}}} = \tag{6.36}$$

$$\frac{S_z}{\tau_f}\int_0^{\tau_f} d\tau\sqrt{6}\sum_{\mu=-1}^{1} T_{1\mu}^{\mathrm{D}}\, e^{-i\mu\alpha(\tau)} d_{\mu 0}^{1}[-\beta(\tau)] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

Since $d_{00}^{1}(\beta) = \cos\beta\,, d_{-10}^{1}(\beta) = -d_{10}^{1}(\beta) = \frac{1}{\sqrt{2}}\sin\beta$, we can separate these three terms and factor out those independent on time from the integral:

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} S_z\omega_{2m}^{\mathrm{D}}\left(T_{11}^{\mathrm{D}} - T_{1,-1}^{\mathrm{D}}\right)\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau\frac{1}{\sqrt{2}}\sin\beta\, e^{-im\omega_r\tau}$$

$$+ \sum_{\substack{m=-2\\ m\neq 0}}^{2} S_z\omega_{2m}^{\mathrm{D}} T_{10}^{\mathrm{D}}\frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau\cos\beta\, e^{-im\omega_r\tau}$$

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} S_z\omega_{2m}^{\mathrm{D}}(T_{11}^{\mathrm{D}} - T_{1,-1}^{\mathrm{D}})\, A + \sum_{\substack{m=-2\\ m\neq 0}}^{2} S_z\omega_{2m}^{\mathrm{D}} T_{10}^{\mathrm{D}}\, B$$

Recall $\beta = k\omega_r\tau$ Now things start to look similar to the homonuclear dipolar rotary recoupling:

$$A = \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau\frac{1}{\sqrt{2}}\sin\beta\, e^{-im\omega_r\tau} = \frac{\sqrt{6}}{\sqrt{2}\tau_f}\int_0^{\tau_f} d\tau\frac{1}{2i}\left(e^{ik\omega_r\tau} - e^{-ik\omega_r\tau}\right)e^{-im\omega_r\tau}$$

$$= \frac{\sqrt{6}}{\sqrt{2}\tau_f}\int_0^{\tau_f} d\tau\frac{1}{2i}\left(e^{i(k-m)\omega_r\tau} - e^{-i(k+m)\omega_r\tau}\right)$$

$$= \frac{\sqrt{6}}{i2\sqrt{2}\omega_r\tau_f}[\frac{1}{(k-m)}\left(e^{i(k-m)\omega_r\tau_f} - 1\right) + \frac{1}{(k+m)}\left(e^{-i(k+m)\omega_r\tau_f} - 1\right)]$$

Again, $e^{-i(k+m)\omega_r\tau_f} = e^{i(k-m)\omega_r\tau_f} = 1$, so the integral would have been zero, unless $k-m$ and $k+m=0$. When $k+m$ or $k-m=0$, we can apply L'Hopital Rule in limit: $\lim_{k+m=0}\frac{1}{(k+m)}\left(e^{-i(k+m)\omega_r\tau_f} - 1\right) = \lim_{x=0}\frac{1}{x}\left(e^{-i\omega_r\tau_f x} - 1\right) = -2\pi i$. Or, $\lim_{k-m=0}\frac{1}{(k-m)}\left(e^{i(k-m)\omega_r\tau_f} - 1\right) = \lim_{x=0}\frac{1}{x}\left(e^{i\omega_r\tau_f x} - 1\right) = 2\pi i$. Eitherway, we have:

$$A = \frac{\sqrt{6}}{i2\sqrt{2}\omega_r\tau_f} \times \pm 2\pi i = \begin{cases} -\frac{\sqrt{3}}{2}, m = -k \\ \frac{\sqrt{3}}{2}, m = k \end{cases} \tag{6.37}$$

This means the $T_{1\pm1}^{\mathrm{D}}$ part of the heteronuclear dipolar interaction will be recoupled if RF irradiation at ω_r or $2\omega_r$ with:

$$\frac{\sqrt{3}}{2}S_z\left(T_{11}^{\mathrm{D}} - T_{1,-1}^{\mathrm{D}}\right)[\omega_{2m}^{\mathrm{D}} - \omega_{2m}^{\mathrm{D}}] = \frac{\sqrt{3}}{2}\left(T_{21}^{\mathrm{D}} - T_{2,-1}^{\mathrm{D}}\right)[\omega_{2m}^{\mathrm{D}} - \omega_{2m}^{\mathrm{D}}], m = 1,2$$

Similarly, you can show:

$$B = \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \cos\beta\, e^{-im\omega_r\tau} = \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{2}\left(e^{ik\omega_r\tau} + e^{-ik\omega_r\tau}\right)e^{-im\omega_r\tau}$$

$$= \frac{\sqrt{6}}{i2\omega_r\tau_f}\left[\frac{1}{(k-m)}\left(e^{i(k-m)\omega_r\tau_f} - 1\right) - \frac{1}{(k+m)}\left(e^{-i(k+m)\omega_r\tau_f} - 1\right)\right]$$

Take the limit when When $k + m$ or $k - m = 0$:

$$B = \frac{\sqrt{6}}{i2\omega_r\tau_f} \times i2\pi = \frac{\sqrt{6}}{2}, m = \pm k \tag{6.38}$$

This means the second term will be:

$$\frac{\sqrt{6}}{2}S_z(\omega_{2k}^{\mathrm{D}} + \omega_{2,-k}^{\mathrm{D}})T_{10}^{\mathrm{D}} = \frac{\sqrt{6}}{2}(\omega_{2k}^{\mathrm{D}} + \omega_{2,-k}^{\mathrm{D}})T_{20}^{\mathrm{D}}$$

Combined, we have recoupled heteronuclear dipolar interaction at rotary resonance condition when $\omega_{rf} = k\omega_r$, where $k = 1, 2$:

$$\overline{H_{Heter}^{\mathrm{D}}} = \frac{\sqrt{3}}{2}\left(T_{21}^{\mathrm{D}} - T_{2,-1}^{\mathrm{D}}\right)\left[\omega_{2k}^{\mathrm{D}} - \omega_{2k}^{\mathrm{D}}\right] + \frac{\sqrt{6}}{2}(\omega_{2k}^{\mathrm{D}} + \omega_{2,-k}^{\mathrm{D}})T_{20}^{\mathrm{D}} \tag{6.39}$$

Again, $T_{2,\pm 1}^{\mathrm{D}}$ spin operators I_x and I_y which are higher order terms(see Eq. 5.48 to 5.51), so the lowest order surviving term will be T_{20}^{D}.

The implication of rotary resonance recoupling of heteronuclear dipolar interaction is, for decoupling sequence of ^{1}H-^{13}C heteronuclear dipolar interaction to achieve best performance, we need to avoid such rotary resonances. Hence, we require high power ^{1}H-^{13}C decoupling field to be at least more than $\omega_{rf} = 2\omega_r$. Recall the C-symmetry sequences we introduced earlier, the recoupling of double quantum by the sequence requires carbon channel field to be at least $\omega_{rf}(^{13}C) = \frac{2n}{N}\omega_r$, which means for we need $\omega_{rf}(^{13}C)$ to be at 7 fold and 5 fold MAS speed for postC7 and SPC5 respectively. On top of this, they also need thorough ^{1}H-^{13}C heteronuclear dipolar decoupling. Therefore, SPC5 will have less trouble to satisfy this with a reasonable MAS speed if we spin at MAS less than 12 kHz, as normally we don't push ^{1}H-^{13}C heteronuclear dipolar decoupling to be more than 120 kHz.

6.4 Rotary resonance recoupling of homonuclear dipolar interaction due to isotropic chemical shift difference

With the analysis of heteronuclear dipolar interaction recoupling, you can easily see if we have chemical shift differences between two nuclei that matches multiples of rotation frequencies, it will also recouple the dipolar interactions between these two spins at the rotary resonance condition. To see how this works, we will inspect the interference effect between different terms of the system Hamiltonian.

Let's assume we only have chemical shifts and dipolar interactions present in the system of two spins. Recall that the tensor representation of the chemical shift anisotropy of one nucleus is represented by:

$$H^{cs} = \omega_0 \delta_{\mathrm{iso}} I_z + I_z \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa}} \exp(im\omega_r t) = \omega_0^{iso} I_z + I_z \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa}} \exp(im\omega_r t)$$

Now if we have two nuclei, I_{zi} and I_{zj}:

$$H_i^{cs} = \omega_i^{iso} I_{zi} + I_{zi} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa\_i}} \exp(im\omega_r t) \tag{6.40}$$

$$H_j^{cs} = \omega_j^{iso} I_{zj} + I_{zj} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa\_j}} \exp(im\omega_r t) \tag{6.41}$$

$$H^{D} = \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r \tau} \tag{6.42}$$

In the following analysis, we will show that the interference effect between the difference of isotropic chemical shifts and MAS is manifested in a similar fashion as the intentional recoupling caused by RF irradiation. You will see that, if the difference of the chemical shifts of two sites also matches with the above rotary resonance condition, the evolution of chemical shifts produces the phase shift in the spin space with a frequency synchronized with the physical rotation frequency, and leads to similar rotary resonance conditions. To get better insights how the system behaves, we need to switch to the fictitious coupled spin 2 and spin 0 space:

$I_2^x = \frac{1}{2}(I^+S^+ + I^-S^-) = I_x S_x - I_y S_y$; $\quad I_0^x = \frac{1}{2}(I^+S^- + I^-S^+) = I_x S_x + I_y S_y$

$I_2^y = \frac{1}{2i}(I^+S^+ - I^-S^-) = I_x S_y + I_y S_x$; $\quad I_0^y = \frac{1}{2i}(I^+S^- - I^-S^+) = I_y S_x - I_x S_y$

$I_2^z = \frac{1}{2}(I_z + S_z)$; $\quad I_0^z = \frac{1}{2}(I_z - S_z)$

Then we can use the formula Eq. 4.158:

$$AI_z + BS_z = (A+B)I_2^z + (A-B)I_0^z$$

We can convert the system Hamiltonian into:

$$H^{cs} = \Sigma_{iso} I_2^z + \Delta_{iso} I_0^z \tag{6.43}$$
$$+I_2^z \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa\_}\Sigma} \exp(im\omega_r t) + I_0^z \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa\_}\Delta} \exp(im\omega_r t)$$

Where $\Sigma_{iso} = \omega_i^{iso} + \omega_j^{iso}, \Delta_{iso} = \omega_i^{iso} - \omega_j^{iso}$, $\omega_{2m}^{\mathrm{csa\_}\Sigma} = \omega_{2m}^{\mathrm{csa\_i}} + \omega_{2m}^{\mathrm{csa\_j}}$, $\omega_{2m}^{\mathrm{csa\_}\Delta} = \omega_{2m}^{\mathrm{csa\_i}} - \omega_{2m}^{\mathrm{csa\_j}}$.

After this conversion, we have the system in the double and zero quantum coupled spin spaces. The spin operators of each fictitious spin live in their own separated spin spaces, just like spins of two different gyromagnetic ratios. They won't interact with each other.

Therefore, we can apply transformation to their own rotating frame at their respective Larmor frequencies Σ_{iso} and Δ_{iso}. Equivalently, you can say we perform a transformation to the interaction frame of double and zero quantum by multiple each term A (other than the isotropic chemical shift terms) with:

$$\tilde{A} = exp^{i\Delta_{iso}I_0^z t} exp^{i\Sigma_{iso}I_2^z t} A exp^{-i\Sigma_{iso}I_2^z t} exp^{-i\Delta_{iso}I_0^z t} \tag{6.44}$$

This transformation allows us to remove the isotropic chemical shifts present in the system Hamiltonian and focus on the remaining terms, while retaining the potential interference effect from removed terms.

When we apply such transformation, the exponent of respective double and zero quantum operators will only affect terms containing operators of their corresponding species, just as if they are two different nuclei. Hence:

$$\widetilde{H}^{cs} = exp^{i\Delta_{iso}I_0^z t} exp^{i\Sigma_{iso}I_2^z t} H^{cs} exp^{-i\Sigma_{iso}I_2^z t} exp^{-i\Delta_{iso}I_0^z t} \tag{6.45}$$
$$= exp^{i\Delta_{iso}I_0^z t} exp^{i\Sigma_{iso}I_2^z t} \left[I_2^z \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa}_\Sigma} \exp(im\omega_r t) \right] exp^{-i\Sigma_{iso}I_2^z t} exp^{-i\Delta_{iso}I_0^z t}$$
$$+exp^{i\Delta_{iso}I_0^z t} exp^{i\Sigma_{iso}I_2^z t} [I_0^z \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa}_\Delta} \exp(im\omega_r t)] exp^{-i\Sigma_{iso}I_2^z t} exp^{-i\Delta_{iso}I_0^z t}$$
$$\widetilde{H}^{cs} = exp^{i\Sigma_{iso}I_2^z t} \left[I_2^z \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa}_\Sigma} \exp(im\omega_r t) \right] exp^{-i\Sigma_{iso}I_2^z t}$$
$$+exp^{i\Delta_{iso}I_0^z t} \left[I_0^z \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{csa}_\Delta} \exp(im\omega_r t) \right] exp^{-i\Delta_{iso}I_0^z t}$$

$$= exp^{i\Sigma_{iso}I_2^z t}[I_2^z]exp^{-i\Sigma_{iso}I_2^z t}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{csa}_{\Sigma}}\exp(im\omega_r t)$$

$$+exp^{i\Delta_{iso}I_0^z t}[I_0^z]exp^{-i\Delta_{iso}I_0^z t}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{csa}_{\Delta}}\exp(im\omega_r t)$$

$$\widetilde{H}^{cs} = I_2^z\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{csa\_\Sigma}}\exp(im\omega_r t) + I_0^z\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{csa\_\Delta}}\exp(im\omega_r t)$$

These terms don't change much, except the anisotropic parameters now change to the coupled double and zero quantum pieces. They will only change the energy levels from individual spins to corresponding values in double and zero quantum space, and produce their associated side bands, if you follow the same derivation presented in section 5.5. Nonetheless, their averages over a complete rotor period will still be zero, and don't contribute to line broadening (well, this won't be long, as we will show later when we add Homonucler dipolar interaction in).

However, when we apply this to the dipolar interaction, things become very different:

$$\widetilde{H}^{D} \tag{6.46}$$

$$= exp^{i\Delta_{iso}I_0^z t}exp^{i\Sigma_{iso}I_2^z t}\left[\sqrt{6}T_{20}^{\mathrm{D}}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}\right]exp^{-i\Sigma_{iso}I_2^z t}exp^{-i\Delta_{iso}I_0^z t}$$

$$= \sqrt{6}(exp^{i\Delta_{iso}I_0^z t}exp^{i\Sigma_{iso}I_2^z t}T_{20}^{\mathrm{D}}exp^{-i\Sigma_{iso}I_2^z t}exp^{-i\Delta_{iso}I_0^z t})\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

Where we recall:

$$T_{20}^{\mathrm{D}} = \frac{1}{\sqrt{6}}(3\mathrm{I}_{z1}\mathrm{I}_{z2} - \mathrm{I}_1\cdot\mathrm{I}_2) = \frac{1}{\sqrt{6}}\left[\frac{1}{2}(I^+S^- + I^-S^+) + 2I_zS_z\right] = \frac{1}{\sqrt{6}}(I_0^x + 2I_zS_z)$$

$$T_{20}^{\mathrm{D}} = (\frac{1}{\sqrt{6}}I_0^x + \sqrt{\frac{2}{3}}I_zS_z) \tag{6.47}$$

The I_zS_z part won't interact with the transformation of interaction (Why? I will leave it to you to show this). We can drop it from our derivation for now. However, I_0^x will be affected, in a manner reminiscent of our analysis of polarization evolution during SPC5 in Sect 6.1:

$$exp^{i\Delta_{iso}I_0^z t}exp^{i\Sigma_{iso}I_2^z t}T_{20}^{\mathrm{D}}exp^{-i\Sigma_{iso}I_2^z t}exp^{-i\Delta_{iso}I_0^z t}$$

$$= \frac{1}{\sqrt{6}}\left(exp^{i\Delta_{iso}I_0^z t} I_0^x exp^{-i\Delta_{iso}I_0^z t}\right) = \frac{1}{\sqrt{6}}[I_0^x \cos(\Delta_{iso}t) - I_0^y \sin(\Delta_{iso}t)]$$

Obviously, this cosine and sine part can interfere with $e^{-im\omega_r\tau}$ if $\Delta_{iso} = k\omega_r$ and lead to nonzero average over MAS rotation period:

$$\widetilde{H}^D = \sqrt{6}\frac{1}{\sqrt{6}}[I_0^x \cos(\Delta_{iso}t) - I_0^y \sin(\Delta_{iso}t)] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

$$\overline{\widetilde{H}^D} = \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{\sqrt{6}}\left[I_0^x \cos(\Delta_{iso}t) - I_0^y \sin(\Delta_{iso}t)\right] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r\tau}$$

$$= \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{\sqrt{6}}\left[I_0^x \cos(\Delta_{iso}t) - I_0^y \sin(\Delta_{iso}t)\right] e^{-im\omega_r\tau}$$

$$\overline{\widetilde{H}^D} = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \left[I_0^x \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{\sqrt{6}} \cos(\Delta_{iso}t)\, e^{-im\omega_r\tau} - I_0^y \frac{\sqrt{6}}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{\sqrt{6}} \sin(\Delta_{iso}t)\, e^{-im\omega_r\tau}\right] \tag{6.48}$$

$$\overline{\widetilde{H}^D} = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, [I_0^x A - I_0^y B]$$

Let’s evaluate the time-dependent terms A and B separately:

$$A = \frac{1}{\tau_f}\int_0^{\tau_f} d\tau \cos(\Delta_{iso}t)\, e^{-im\omega_r\tau} = \frac{1}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{2}(e^{i\Delta_{iso}t} + e^{-i\Delta_{iso}t})e^{-im\omega_r\tau}$$

Now let’s assume:

$$\Delta_{iso} = k\omega_r, k = 1,2$$

At once, you can see the integral part becomes the same with what we derived for recoupling of heteronuclear dipolar interaction at rotary resonance condition, except the factor of $\sqrt{\frac{2}{3}}$:

$$\frac{1}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{2}\left(e^{ik\omega_r\tau} + e^{-ik\omega_r\tau}\right)e^{-im\omega_r\tau}$$

$$= \frac{1}{i2\omega_r\tau_f}\left[\frac{1}{(k-m)}\left(e^{i(k-m)\omega_r\tau_f} - 1\right) - \frac{1}{(k+m)}\left(e^{-i(k+m)\omega_r\tau_f} - 1\right)\right]$$

You can repeat the derivation steps over, but let's just plug in the result: When $k+m$ or $k-m=0$:

$$A = \frac{1}{i2\omega_r \tau_f} \times 2\pi i = \frac{1}{2}, m = \pm k$$

This means the first term will be:

$$\frac{1}{2} I_0^x \sum_{\substack{k=-2 \\ k\neq 0}}^{2} \omega_{2k}^{\mathrm{D}} = \frac{1}{4}(I^+S^- + I^-S^+) \sum_{\substack{k=-2 \\ k\neq 0}}^{2} \omega_{2k}^{\mathrm{D}}$$

Now let's evaluate B:

$$B = \frac{1}{\tau_f}\int_0^{\tau_f} d\tau \sin(\Delta_{iso} t)\, e^{-im\omega_r \tau} = \frac{1}{\tau_f}\int_0^{\tau_f} d\tau \frac{1}{2i}(e^{i\Delta_{iso}t} - e^{-i\Delta_{iso}t})e^{-im\omega_r \tau}$$

You can complete the integral and show that:

$$B = \frac{1}{i2\omega_r \tau_f} \times \pm 2\pi i = \frac{(-1)^m}{2}, m = \pm k$$

So the second term becomes:

$$\frac{1}{2} I_0^y \sum_{\substack{m=-2 \\ m\neq 0}}^{2} (-1)^m \omega_{2m}^{\mathrm{D}} = \frac{1}{4i}(I^+S^- - I^-S^+) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} (-1)^m \omega_{2m}^{\mathrm{D}}$$

Combined, we see when the difference of isotropic chemical shifts of two homonuclear sites matches the multiples of rotation frequency, or so called rotary resonance condition: $\Delta_{iso} = k\omega_r, k = 1,2$

We have the homonuclear dipolar interaction recoupled:

$$\overline{\widetilde{H}^D} = \frac{1}{4} \sum_{\substack{k=-2 \\ k\neq 0}}^{2} \omega_{2k}^{\mathrm{D}} \left[(I^+S^- + I^-S^+) - i(-1)^k (I^+S^- - I^-S^+)\right] \tag{6.49}$$

$$= \frac{1}{2} \sum_{\substack{k=-2 \\ k\neq 0}}^{2} \omega_{2k}^{\mathrm{D}} (I_0^x + (-1)^k I_0^y]$$

What does this mean, then?

This interference effect does not need active application of RF pulses, as long as the difference of chemical shifts of two sites matches the recoupling condition similar to the rotary resonance. So in experiment setup, we have to watch out such recoupling, as this recoupling will lead to broadening of spectral linewidth. To do so, we need to make sure the first and second spinning sidebands from any part of the spectral do not fall onto any other part of the spectrum.

Reversely, we can actively engage this effect to our advantage. This is used in so called Dipolar Assisted Rotational Resonance sequence, or DARR. We will review briefly below.

6.5 Dipolar Assisted Rotary Resonance recoupling of homonuclear dipolar interaction

DARR is probably one of the most user friendly homonuclear recoupling sequence, and is used frequently at low MAS speeds. It was show by K. Takegoshi et al. in "^{13}C-^{1}H dipolar-assisted rotational resonance in magic-angle spinning NMR", Chem. Phys. Lett. 344 631-637 (2001). All we need to do is to apply RF irradiation matching ω_r on ^{1}H channel, and we get ^{13}C-^{13}C dipolar interaction recoupled to allow efficient propagation of polarization between ^{13}C sites. Then ^{13}C-^{13}C crosspeaks will be generated to resolve spatial correlation between ^{13}C sites.

The principal of this sequence is in fact an actively controlled recoupling of homonuclear dipolar interaction by chemical shift difference. Well, you may say: hold on, hold on! How is that possible? I know now with the naturally coincident isotropic chemical shift difference, ^{13}C pairs would have been recoupled. But in normal experiment setup, we have avoided such coincidents by carefully position the carrier frequency to displace the rotational resonance at ω_r. You just showed me homonuclear dipolar interaction can be recoupled, but you need to apply RF irradiation on corresponding nuclear involved in the interaction, How could you do something to ^{1}H channel to resurrect ^{13}C homonuclear interaction? This must be black magic!

Well, if you watched some Chinese martial arts movie, you might have heard of a technique called "隔山打牛"。It is hard to translate this to English directly, but actually DARR is the perfect correspondence of 隔山打牛 in ssNMR.

This is easier to explain now after we just went through all the rotary resonance effect above. Basically it recouples ^{1}H-^{13}C heteronuclear interaction by irradiating on ^{1}H channel at ω_r, and then combines the isotropic chemical shift difference driven recoupling between different ^{13}C nuclei, the ^{13}C-^{13}C homonuclear interaction is resurrected. Let's see in detail now.

First, we can directly quote from our previous derivation the effect of irradiating on ^{1}H channel at ω_r will give us the first order recoupled ^{1}H-^{13}C heteronuclear interaction:

$$\bar{H}^{\mathrm{D}}_{Heter} = \frac{\sqrt{6}}{2}(\omega^{\mathrm{D}}_{2k} + \omega^{\mathrm{D}}_{2,-k})T^{\mathrm{D}}_{20} = \frac{1}{2}(\omega^{\mathrm{D}}_{2k} + \omega^{\mathrm{D}}_{2,-k})2I_zS_z \tag{6.50}$$

Here $k = 1$ as we pick $\omega_{rf} = \omega_r$

Let's use I to represent the proton spin, and S to represent the carbon spin.

Now without this term, the isotropic chemical shift difference between ^{13}C pairs would already exist

$$H_{cs} = \omega_i^{iso} S_{zi} + \omega_j^{iso} S_{zj}$$

Again, let's convert to fictitious double and zero quantum spins:

$$H_{cs} = \Sigma_{iso} S_2^z + \Delta_{iso} S_0^z \tag{6.51}$$

But at this point by $\Delta_{iso} S_0^z$ alone will only produce recoupling of dipolar interaction between ^{13}C pairs, if the chemical shift difference between the pair matches the rotary resonance condition. However, such rotary resonance conditions are intentionally avoided in experimental setup for spectral resolution as we commented in previous section.

This can be achieved trivially, normally the actual chemical shift difference between carbon sites are either too small in the range $[0, 60]\ ppm$ (for aliphatic site pairs or pairs of aromatic/C' sites, or too large in the range $(110, 170) ppm$, and we can easily set our MAS speed to avoid these conditions.

But let's take both isotropic chemical shift difference and $\bar{H}_{Heter}^{\mathrm{D}}$ together into account, since the spin part of $\bar{H}_{Heter}^{\mathrm{D}}$ also contains S_z and will affect $\bar{H}_{Homo}^{\mathrm{D}}$ between carbons the same way:

$$H_{DARR} = \Delta_{iso} S_0^z + \frac{1}{2}(\omega_{21}^{\mathrm{D}} + \omega_{2,-1}^{\mathrm{D}}) 2 I_z S_{zi} \tag{6.52}$$

Things immediately become different. The size of the second term scales with normal dipolar interactions by a factor $(\omega_{21}^{\mathrm{D}} + \omega_{2,-1}^{\mathrm{D}}) I_z$, so it will be $\pm\frac{1}{2}$ (since I_z can be $\pm\frac{1}{2}$) of the static dipolar interaction strength, multiplied by $(\omega_{21}^{\mathrm{D}} + \omega_{2,-1}^{\mathrm{D}})$:

$$\frac{1}{2}(\omega_{21}^{\mathrm{D}} + \omega_{2,-1}^{\mathrm{D}}) 2 I_z S_{zi} \tag{6.53}$$

$$= \pm\frac{1}{2} \times \frac{b_{IS}}{2\sqrt{2}} \sin 2\beta \, [exp(i\gamma) + exp(-i\gamma)] = \pm\frac{1}{2\sqrt{2}} \sin 2\beta \cos\gamma \, b_{IS}$$

(in unit of rad/s).

As the powder angle β can vary between $[0, \pi]$, and γ can vary between $[0, 2\pi]$, the recoupled ^{1}H-^{13}C heteronuclear interaction will essentially provide a flexible offset in the range $[-\frac{1}{2}, \frac{1}{2}]\ \frac{b_{IS}}{\sqrt{2}}$ in rad/s. Recall directly bonded ^{1}H-^{13}C heteronuclear interaction is 21.5 kHz, it means the second term will provide ~ $[-7.6, 7.6]$ kHz flexible matching buffer. The actual value should be slightly larger than this, since we also have higher order term ^{1}H-^{13}C $\frac{\sqrt{3}}{2}(T_{2-1}^{\mathrm{D}} - T_{21}^{\mathrm{D}})[\omega_{2k}^{\mathrm{D}} - \omega_{2k}^{\mathrm{D}}]$ shown in Eq. 6.39.

Let's do a simple estimation to see how DARR helps ^{13}C-^{13}C nuclear pair recouple. Assume the experiment is performed at 600 MHz field. Then $\bar{H}_{Heter}^{\mathrm{D}}$ will provide additional $[-7.6, 7.6]$kHz ~ $[-50, 50]\ ppm$ matching buffer for rotary resonance condition. We will consider one-bond transfer only here, as multi-bond transfer can be achieved by relay of one-bond transfer. For typical Ca-C' one-bond, $\Delta_{iso}^{\mathrm{Ca-C'}} \sim [100{,}120]\ ppm$, for typical Ca-Cb one-bond,

$\Delta_{iso}^{\mathrm{Ca-Cb}} \sim [10, 30]\ ppm$. Therefore, combining the assisted ^{1}H-^{13}C dipolar interaction, the required rotary resonance condition is $\sim[50 - 150, 75 - 170]\ ppm$ for Ca-C' and $\sim[-40 - 60, -20 - 70]\ ppm$ for Ca-Cb transfer.

This indicates that DARR would enable stable recoupling at rotary resonance $\omega_{rf} = \omega_r$, which is 0-60*150 Hz=9 kHz for $\Delta_{iso}^{\mathrm{Ca-Cb}} = 10\ ppm$, and 0-70*150 Hz= 11.5 kHz for $\Delta_{iso}^{\mathrm{Ca-Cb}} = 35\ ppm$. And you can show the condition for Ca-C' using the parameters estimated above.

In reality, if the Ca-Cb or Ca-C' pairs don't exactly match the MAS for rotary resonance at MAS speed between, the Ca and farther side chain will have larger chemical shift differences, and potentially will satisfy the rotary resonance condition and produce strong coupling than direct Ca-Cb transfer under DARR. Then such non-directly bonded pairs of Carbon may very well give us more efficient recoupling and transfer of polarization than the directly bonded pairs in such MAS regions.

At higher MAS speed or high magnetic field conditions, the buffering effect from $\overline{H}_{Heter}^{\mathrm{D}}$ would gradually diminish, as the increasing separation of resonance condition will exceed the buffer effect from Eq. 6.53. The upper limit would probably be somewhere near the buffered upper range for Ca-C', which is ~ 170 ppm ~ $\omega_r = 25.5\ kHz$.

In practice, we will have polarization transfer between carbon sites even without DARR. This is because spin diffusion effect and coupling between ^{13}C-^{13}C nuclear pairs still exist without the rotary resonance matching, due to the inhomogeneous homonuclear dipolar interaction. As we demonstrated at the end of Sect. 5.5, these inhomogeneous interactions do not commute with itself or each other, nor with other interactions. They combined will lead to some intrinsic broadened linewidth under MAS. As we will show in Chapter 7, this interference is the dominant hurdle for heteronuclear decoupling.

In any case, if you followed through the above derivation, you probably can appreciate this imcommutable effect will also produce interference effect similar to the rotary resonance effect, and lead to broadening of the spectrum at this step.

In Chapter 7, we will show these rotary resonance conditions will naturally arise from the analyses of the Average Hamiltonian Theory, or the Floquet theory.

Recall SPC5 (C symmetry) sequence, the recoupling condition works best also at mid-low MAS speed. What alternatives do we have for ^{13}C-^{13}C homonuclear dipolar recoupling to establish the through-space correlation between sites, especially at high MAS, and less a problem at high field?

There are a range of pulse sequences we can employ for that purpose. One of the best detailed review of such sequences is Robert Tycko's "Homonuclear Dipolar Recoupling in Solid State NMR: Analysis with Average Hamiltonian Theory", available online at 2008 Winter School on Biomolecular ssNMR or Encyclopedia of Magnetic Resonance. His derivation utilizes the single spin operators, which probably requires higher awareness of what you do in terms of symmetry. We will just demonstrate the analysis of the finite pulse RFDR using irreducible tensor representation, which the symmetry will manifest itself as you go.

6.6 Finite pulse effect during the recoupling of dipolar interaction

RF driven recoupling (RFDR) sequence was discovered by A. E. Bennett et al (JCP, 96, 8624 (1992), JCP 108, 9463 (1998)). It employs the chemical shift differences to recouple dipolar interactions in a similar fashion to what we explained in Sect. 6.4. It is deployed by a strong π pulse in each rotation period. Therefore, only those sites with large chemical shift offsets would be strongly recoupled. You can read the analysis in either the original papers, or more detailed derivation in Tycko's lecture note cited above. In such analyses, the π pulse was approximated as δ pulse with infinite strength and zero duration.

Y. Ishii then showed that things are not exactly the same if we account for the actual pulse width instead of a δ pulse, with its finite strength and duration. When the duration of the pulse is accounted for, instead of a δ pulse, the homonuclear dipolar interaction is recoupled to be $3I_{z1}I_{z2} - I_1 \cdot I_2$, in the same format of that in the static sample. He named this finite pulse RFDR (fpRFDR) in short.

For this to work, the phase of π pulses in the sequence should be set to be XY-4 (x,y,x,y) XY-8(x,y,x,y; y,x,y,x) or XY-16(x,y,x,y; y,x,y,x; -x,-y,-x,-y; -y,-x,-y,-x) fashion. This phase cycling scheme was proposed by Terry Gullion to help suppress errors of rotation associated with pulse imperfection in J. Magn. Reson. 89, 479 (1990). In the fpRFDR, this cycling is the key to achieve the spin part of recoupled homonuclear dipolar interaction to be $3I_{z1}I_{z2} - I_1 \cdot I_2$.

Let's revisit this finite pulse effect. Assume each π pulse is in the middle of each rotor period, with length τ_p, so:

$$\pi = \omega_r \tau_p \tag{6.54}$$

Let's see how this can be interpreted by Tensor format derivation:

$$e^{i\hat{H}_1\tau} R(\omega_r\tau, 0,0) \left[T^{\Lambda}_{\lambda 0} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\Lambda}_{2m} \exp(im\omega_r t) \right] R^{-1}(\omega_r\tau, 0,0) e^{-i\hat{H}_1\tau}$$
$$= \sum_{\mu=-\lambda}^{\lambda} T^{\Lambda}_{\lambda\mu}\, e^{-i\mu\alpha(\tau)} d^{\lambda}_{\mu 0}[-\beta(\tau)] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\Lambda}_{2m}\, e^{-im\omega_r\tau}$$

You may feel a bit lost how can we apply the rotation of tensors to such a pulse sequence where pulses have alternating phases and are not continuous irradiation like the SPC5 sequence?

Well, we just have to follow the same principal by transforming the Hamiltonian of the interaction to the interaction frame of the RF pulse sequence:

$$\widetilde{H}^{\Lambda} = e^{i\widehat{H}_1\tau}[T_{\lambda 0}^{\Lambda} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda} \exp(im\omega_r t)]e^{-i\widehat{H}_1\tau}$$

The only caviar is now:

$$e^{i\widehat{H}_1\tau} = U^{-1}$$

$$U = \vec{T}\exp\{-i\int_0^t H_{RF}(t')dt'\}$$

Where U is the evolution operator, and $\vec{T}$ is the Dyson time-ordering operator.

To be more explicit, the $H_{RF}(t')$ is time-dependent. We can divide $H_{RF}(t')$ into N different segments, each with a constant RF pulse: H_{rf1} in interval τ_1 between $[0, t_1]$, H_{rf2} in interval τ_2 between $[t_1, t_2]$, … in interval τ_i between $[t_{i-1}, t_i]$, and H_{rfN} in interval τ_N between$[t_{N-1}, t_N]$. An interval with no RF pulse output can be treated as with 0 constant RF as well. Then we can naturally express explicitly:

$$U = e^{-iH_{rfN}\tau_N} \dots e^{-iH_{rfi}\tau_i} \dots e^{-iH_{rf2}\tau_2} e^{-iH_{rf1}\tau_1} \tag{6.55}$$
$$e^{i\widehat{H}_1\tau} = e^{iH_{rf1}\tau_1} e^{iH_{rf2}\tau_2} \dots e^{iH_{rfi}\tau_i} \dots e^{iH_{rfN}\tau_N}$$

Together, we have:

$$\widetilde{H}^{\Lambda} = e^{iH_{rf1}\tau_1} e^{iH_{rf2}\tau_2} \dots e^{iH_{rfi}\tau_i} \dots e^{iH_{rfN}\tau_N} \left[T_{\lambda 0}^{\Lambda} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda} \exp(im\omega_r t) \right] e^{-iH_{rfN}\tau_N} \dots e^{-iH_{rfi}\tau_i} \dots e^{-iH_{rf2}\tau_2} e^{-iH_{rf1}\tau_1} \tag{6.56}$$

Please pay very close attention to the order of the segmental Hamiltonian. The earlier applied pulse will be on the outside of the sandwiching exponential operators.

This mean at all time points in the pulse sequence, we need to compute both the spin and physical rotation by referring to time zero. If the pulse is on, please count its finite pulse effect by integration of both the spin rotation and physical rotation. They may interfere with each other.

Just like actions in real life, our current life is affected by our past history, when we consider the the system status in a specific time interval, not only do we have to use Eq. 5.65 to compute the effect of pulse and MAS rotation in current time interval, the effect of the spin and physical rotation occurred before current time interval have to be computed as well, as we will show in the derivation of the fpRFDR Hamiltonian.

Please remember, even if there is a period with no RF irradiation, we still need to account for the spin rotation of previous pulses in the evolution of Hamiltonian, and remember the physical rotation always referred to time zero, as MAS is on all the time. It is that simple. Just keep your eyes on the pulse sequence, and add appropriate spin rotation corresponding to the pulse, and keep the $e^{-im\omega_r\tau}$ running all the time.

For example, when we evaluate the finite pulse effect of ith pulse in $[t_{i-1}, t_i]$, we have to do time-dependent integration for this pulse. In addition, we need take into account the effect of all previously applied pulses. But the effects of these earlier pulses can be computed by definite rotation angles without integration, since their executions were already completed before current time interval, and so were the physical rotation angles.

It is fairly clearly we can keep exploiting the unified transformation pattern by Wigner-Eckart theorem. To address the alternating or varying phases, we need to convert all pulses to the z-y-z rotation format that is consistent with the convention for the Wigner-Eckart theorem. After all those demonstrations in chapter 5, I am sure you are well versed to complete such convertions.

Now let’s see how homonuclear dipolar interaction is affected by the fpRFDR pulse train.

In our previous analyses, the sequence either has an explicit periodic cycle (SPC5), or it extends indefinitely (rotary resonances). Our analyses naturally stops with the sequence, or assume it goes on for ever.

In general, the analysis of a pulse sequence needs to have a defined cycle. We need to select this cycle synchronizing with the period of the pulse, since the system is restored after a periodic spin and physical rotation, as if nothing happened. This is the principle for the so called Average Hamiltonian Theory. Some pulse sequences have time reversal symmetry, which can be exploited to further simplify the analysis. For example, the odd expansion terms in the Floquet theory are zero due to this principle in the analysis of the decoupling pulses with time reversal symmetry.

The shortest cycle period of the fpRFDR is XY-4 (x,y,x,y), so will be our derivation.

All we need to do is to transform the Hamiltonian of an interaction to be considered into the interaction frame of the RF pulse train:

$$e^{i\hat{H}_1\tau}[T_{\lambda 0}^{\Lambda}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega_{2m}^{\Lambda}\exp(-im\omega_r t)]e^{-i\hat{H}_1\tau}$$

As the first pulse is along the x axis, we need to convert to z-y-z convention, using Eq. 5.14:

$$R_{rf}(t) = \exp(-i\beta I_x) = \exp\left(i\frac{\pi}{2}I_z\right)\exp\left(-i\beta I_y\right)\exp\left(-i\frac{\pi}{2}I_z\right)$$
$$= \exp\left(i\frac{\pi}{2}I_z\right)\exp\left(-i\beta I_y\right)\exp\left(-i\frac{\pi}{2}I_z\right)$$

$$R_{rf}(t) = R\left(-\frac{\pi}{2},\beta,\frac{\pi}{2}\right) = R^{-1}\left(-\frac{\pi}{2},-\beta,\frac{\pi}{2}\right) \tag{6.57}$$

Also remember:

$$e^{i\hat{H}_1\tau} =$$

$$R_{rf}^{-1}(t) = \ (\exp\left(i\frac{\pi}{2}I_z\right)\exp(-i\beta I_y)\exp\left(-i\frac{\pi}{2}I_z\right))^{-1}$$

$$= (\exp\left(-i\frac{\pi}{2}I_z\right))^{-1}(\exp(-i\beta I_y))^{-1}(\exp\left(i\frac{\pi}{2}I_z\right))^{-1}$$

$$= \exp\left(i\frac{\pi}{2}I_z\right)\exp(i\beta I_y)\exp\left(-i\frac{\pi}{2}I_z\right) = R(-\frac{\pi}{2},-\beta,\frac{\pi}{2})$$

So together, the average homonuclear dipolar interaction in the interaction frame of the RF pulse along the x axis in the first rotor period is:

$$\overline{\tilde{H}_{homo}^{D}}([0,\tau_r]) \tag{6.58}$$

$$= \frac{1}{\tau_r}\int_0^{\tau_r} dt R^{-1}\left(-\frac{\pi}{2},\beta,\frac{\pi}{2}\right)\left[\sqrt{6}T_{20}^{\mathrm{D}}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\exp(-im\omega_r t)\right]R\left(-\frac{\pi}{2},\beta,\frac{\pi}{2}\right)$$

$$= \frac{2\sqrt{6}}{\tau_r-\tau_p}\int_0^{\frac{1}{2}(\tau_r-\tau_p)} dt\, T_{20}^{\mathrm{D}}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\exp(-im\omega_r t)$$

$$+\frac{\sqrt{6}}{\tau_p}\int_{\frac{1}{2}(\tau_r-\tau_p)}^{\frac{1}{2}(\tau_r+\tau_p)}\sum_{\mu=-2}^{2}T_{2\mu}^{\mathrm{D}}\, e^{i\mu\left(\frac{\pi}{2}\right)}d_{\mu 0}^{2}\left\{-\omega_{rf}\left[t-\frac{1}{2}(\tau_r-\tau_p)\right]\right\}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}$$

$$+\frac{2\sqrt{6}}{\tau_r-\tau_p}\int_{\frac{1}{2}(\tau_r+\tau_p)}^{\tau_r} dt\sum_{\mu=-2}^{2}T_{2\mu}^{\mathrm{D}}\, e^{i\mu\frac{\pi}{2}}d_{\mu 0}^{2}(-\pi)\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2m}^{\mathrm{D}}\exp(-im\omega_r t)$$

Here we applied the time-dependent condition of β, it is zero in $[0,\frac{1}{2}(\tau_r-\tau_p)]$, and $\beta = \omega_{rf}\left[t-\frac{1}{2}(\tau_r-\tau_p)\right]$ between $[\frac{1}{2}(\tau_r-\tau_p),\frac{1}{2}(\tau_r+\tau_p)]$, and $\beta=\pi$ in $[\frac{1}{2}(\tau_r+\tau_p),\tau_r]$.

So when $\beta = \omega_{rf}\left[t-\frac{1}{2}(\tau_r-\tau_p)\right]$, we can apply the Wigner rotation matrix:

$$T'_{km} = R(\alpha\beta\gamma)T_{km}R^{-1}(\alpha\beta\gamma) = \sum_{p=-k}^{k}T_{kp}\,D_{pm}^{k}(\alpha\beta\gamma) = \sum_{p=-k}^{k}T_{kp}\,d_{pm}^{k}(\alpha\beta\gamma)e^{-ip\alpha}e^{-ik\gamma}$$

We can do a change of the integral argument for the second and third segment. In the second integral, we can replace $t = t' + \frac{1}{2}(\tau_r-\tau_p)$, so the limit of integral is changed from

$[\frac{1}{2}(\tau_r-\tau_p),\frac{1}{2}(\tau_r+\tau_p)]$ to $[0,\tau_p]$. In the third integral, we can replace $t=t'+\frac{1}{2}(\tau_r+\tau_p)$, so the limit of integral is changed from $[\frac{1}{2}(\tau_r+\tau_p),\tau_r]$ to $[0,\frac{1}{2}(\tau_r-\tau_p)]$. Eq. 6.58 becomes:

$$\begin{aligned}
\overline{\widetilde{H}^{D}_{homo}}([0,\tau_r]) ={}& \frac{2\sqrt{6}}{\tau_r-\tau_p}\int_{0}^{\frac{1}{2}(\tau_r-\tau_p)} dt\, T^{\mathrm{D}}_{20}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t) \\
&+\frac{\sqrt{6}}{\tau_p}\int_{\frac{1}{2}(\tau_r-\tau_p)}^{\frac{1}{2}(\tau_r+\tau_p)} dt\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, e^{i\mu\frac{\pi}{2}} d^{2}_{\mu 0}\left\{-\omega_{rf}\left[t-\frac{1}{2}(\tau_r-\tau_p)\right]\right\}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\, e^{-im\omega_r t} \\
&+\frac{2\sqrt{6}e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)}}{\tau_r-\tau_p}\int_{0}^{\frac{1}{2}(\tau_r-\tau_p)} dt\, \boldsymbol{T^{\mathrm{D}}_{20}}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t) \\
={}& \frac{e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sqrt{6}}{\tau_p}\int_{0}^{\tau_p} dt'\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, e^{i\mu\frac{\pi}{2}} d^{2}_{\mu 0}(-\omega_{rf}t')\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\, e^{-im\omega_r t'} \\
&+\frac{2(1+e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)})\sqrt{6}}{\tau_r-\tau_p}\int_{0}^{\frac{1}{2}(\tau_r-\tau_p)} dt\, \boldsymbol{T^{\mathrm{D}}_{20}}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t)
\end{aligned} \tag{6.59}$$

$$\overline{\widetilde{H}^{D}_{homo}}([0,\tau_r]) = e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sum_{\mu=-2}^{2} e^{i\mu\frac{\pi}{2}}B + A[1+e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)}] \tag{6.60}$$

Here:

$$A=\frac{2\sqrt{6}}{\tau_r-\tau_p}\int_{0}^{\frac{1}{2}(\tau_r-\tau_p)} dt\ T^{\mathrm{D}}_{20}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t)$$

$$B=\frac{\sqrt{6}}{\tau_p}\int_{0}^{\tau_p} dt'\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^{2}_{\mu 0}(-\omega_{rf}t')\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\, e^{-im\omega_r t'}$$

We bolded the last $\boldsymbol{T^{\mathrm{D}}_{20}}$**,** because it is in fact:

$$\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, e^{i\mu\frac{\pi}{2}} d^{2}_{\mu 0}(-\pi) = \boldsymbol{T^{\mathrm{D}}_{20}}$$

Please prove it yourself.

Now for the second rotor period, we have a π pulse along y axis, $e^{i\hat{H}_1\tau}=R^{-1}_{rf}(t)=(R(0,\beta,0)R(-\frac{\pi}{2},\pi,\frac{\pi}{2}))^{-1}=R^{-1}\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right)R^{-1}(0,\beta,0)=$ $R(-\frac{\pi}{2},-\pi,\frac{\pi}{2})R(0,-\beta,0)$. Note the previous x pulse is accounted as well.

$$\overline{\widetilde{H}^{D}_{homo}}([\tau_r, 2\tau_r]) = \frac{e^{-im\omega_r\tau_r}}{\tau_r}\int_{\tau_r}^{2\tau_r} R^{-1}\left(-\frac{\pi}{2},-\pi,\frac{\pi}{2}\right) R^{-1}(0,\beta,0)\left[\sqrt{6}\,T^{\mathrm{D}}_{20}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t)\right] R(0,\beta,0)R((-\frac{\pi}{2},-\pi,\frac{\pi}{2})$$

We note that $e^{-im\omega_r\tau_r} = 1$, so:

$$\overline{\widetilde{H}^{D}_{homo}}([\tau_r, 2\tau_r]) = \frac{1}{\tau_r}\int_{\tau_r}^{2\tau_r} R^{-1}(-\frac{\pi}{2},-\pi,\frac{\pi}{2}) R^{-1}(0,\beta,0)\left[\sqrt{6}\,T^{\mathrm{D}}_{20}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t)\right] R(0,\beta,0)R(-\frac{\pi}{2},-\pi,\frac{\pi}{2}) \tag{6.61}$$

We will omit this phase factor due to MAS in our analysis of subsequent rotor periods, as they are unity. But you should always be aware that they do exist.

Here again we have the time-dependent condition of β: it is zero in $[\tau_r, \tau_r + \frac{1}{2}(\tau_r - \tau_p)]$, and $\beta = \omega_{rf}\left[t - \frac{1}{2}(\tau_r - \tau_p) - \tau_r\right]$ between $[\,\tau_r + \frac{1}{2}(\tau_r - \tau_p), \tau_r + \frac{1}{2}(\tau_r + \tau_p)]$, and $\beta = \pi$ in $[\tau_r + \frac{1}{2}(\tau_r + \tau_p), 2\tau_r]$.

We can first compute the time-dependent spin rotation:

$$\overline{\widetilde{H}_D}([\tau_r, 2\tau_r]) = R^{-1}(0,\beta,0)\, T^{\mathrm{D}}_{20}\, R(0,\beta,0)$$

After change the argument from $t = t' - \tau_r$ for the first interval, and $t = t' - \tau_r - \frac{1}{2}(\tau_r - \tau_p)$ for the second interval, and $t = t' - \tau_r - \frac{1}{2}(\tau_r + \tau_p)$ for the third interval, we have:

$$\begin{aligned}\overline{\widetilde{H}_D}([\tau_r, 2\tau_r]) &= \frac{2\sqrt{6}}{\tau_r - \tau_p}\int_0^{\frac{1}{2}(\tau_r-\tau_p)} dt\;\; T^{\mathrm{D}}_{20}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t)\\ &+\frac{e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sqrt{6}}{\tau_p}\int_0^{\tau_p} dt\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}[-\omega_{rf}t]\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\, e^{-im\omega_r t}\\ &+\frac{2e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)}\sqrt{6}}{\tau_r - \tau_p}\int_0^{\frac{1}{2}(\tau_r-\tau_p)} dt\sum_{\mu=-2}^{2} T^{\mathrm{D}}_{2\mu}\, d^2_{\mu 0}[-\pi]\sum_{\substack{m=-2\\ m\neq 0}}^{2}\omega^{\mathrm{D}}_{2m}\exp(-im\omega_r t)\end{aligned}$$

$$\overline{\widetilde{H}_D}([\tau_r, 2\tau_r]) = e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)} \sum_{\mu=-2}^{2} B + A[e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)} + 1] \tag{6.62}$$

For the rotation applied to A:

$$R^{-1}(-\frac{\pi}{2}, -\pi, \frac{\pi}{2})[\, T_{20}^{\mathrm{D}}]R(-\frac{\pi}{2}, -\pi, \frac{\pi}{2}) = \sum_{\mu=-2}^{2} T_{2\mu}^{\mathrm{D}}\, e^{-i\mu\frac{\pi}{2}} d_{\mu 0}^{2}(-\pi) = \boldsymbol{T_{20}^{\mathrm{D}}}$$

For the rotation applied to second term containing B:

$$\frac{\sqrt{6}}{\tau_p} \int_0^{\tau_p} \sum_{\mu,\nu=-2}^{2} T_{2\nu}^{\mathrm{D}}\, e^{-i(\mu-\nu)\frac{\pi}{2}} d_{\nu\mu}^{2}[-\pi] d_{\mu 0}^{2}[-\omega_{rf} t] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}$$

So for the second rotor period:

$$\overline{\widetilde{H}_{homo}^{D}}([\tau_r, 2\tau_r]) \tag{6.63}$$
$$= \left[e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)} + 1 \right] A$$
$$+ \frac{e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sqrt{6}}{\tau_p} \int_0^{\tau_p} \sum_{\mu,\nu=-2}^{2} T_{2\nu}^{\mathrm{D}}\, e^{-i(\mu-\nu)\frac{\pi}{2}} d_{\nu\mu}^{2}[-\pi] d_{\mu 0}^{2}[-\omega_r \tau_p] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}$$

Let’s leave the integral at this step, and proceed to see the remaining two rotor periods.

For the third rotor period,

$$e^{i\widehat{H}_1\tau} = R_{rf}^{-1}(t) = (R(\frac{\pi}{2}, \beta, -\frac{\pi}{2})R(0, \pi, 0)R(-\frac{\pi}{2}, \pi, \frac{\pi}{2}))^{-1} =$$
$$R^{-1}(-\frac{\pi}{2}, \pi, \frac{\pi}{2})R^{-1}(0, \pi, 0)R^{-1}(-\frac{\pi}{2}, \beta, \frac{\pi}{2})$$

Note the time-dependent condition of β, it is zero in $[\, 2\tau_r, 2\tau_r + \frac{1}{2}(\tau_r - \tau_p)]$, and $\beta = \omega_{rf}\left[t - \frac{1}{2}(\tau_r - \tau_p) - 2\tau_r\right]$ between $[\, 2\tau_r + \frac{1}{2}(\tau_r - \tau_p), 2\tau_r + \frac{1}{2}(\tau_r + \tau_p)]$, and $\beta = \pi$ in $[2\tau_r + \frac{1}{2}(\tau_r + \tau_p), 3\tau_r]$.

Therefore, we have

$$\overline{\widetilde{H}_{homo}^{D}}([2\tau_r, 3\tau_r])$$
$$= \frac{1}{\tau_r} \int_{2\tau_r}^{3\tau_r} R\left(-\frac{\pi}{2}, -\pi, \frac{\pi}{2}\right) R(0, -\pi, 0) R\left(-\frac{\pi}{2}, -\beta, \frac{\pi}{2}\right) \left[\sqrt{6}\, T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp(-im\omega_r t) \right]$$
$$R^{-1}(-\frac{\pi}{2}, \beta, \frac{\pi}{2}) R^{-1}(0, -\pi, 0) R^{-1}(-\frac{\pi}{2}, \pi, \frac{\pi}{2})$$

Again, we can separate the spin part rotation to evaluate by itself, and compute the time-independent spin rotation after the integration. The time-dependent integration part is exactly same as the first rotor period $\overline{\widetilde{H}^{D}_{homo}}([0,\tau_r])$

$$\overline{\widetilde{H}^{D}_{homo}}([2\tau_r,3\tau_r])$$

$$= R\left(-\frac{\pi}{2},-\pi,\frac{\pi}{2}\right)R(0,-\pi,0)\{e^{im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sum_{\mu=-2}^{2}e^{i\mu\frac{\pi}{2}}B + A[e^{im\omega_r\frac{1}{2}(\tau_r+\tau_p)}$$

$$+1]\}R^{-1}(0,-\pi,0)R^{-1}(-\frac{\pi}{2},\pi,\frac{\pi}{2})$$

Again, the A is not affected by the rotation, as A is just T^{D}_{20}.

Before we compute the rotation on B, note that we have two rotations each with a nonzero rotation around the y axis. Let's simplify it first into a single round of rotation in the standard z-y-z format, so we don't have to apply the Wigner-Eckart theorem twice:

$$R(0,\pi,0)R\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right) = e^{i\pi I_y}\exp\left(i\frac{\pi}{2}I_z\right)\exp\left(-i\pi I_y\right)\exp\left(-i\frac{\pi}{2}I_z\right)$$

$$= [e^{i\pi I_y}\exp\left(i\frac{\pi}{2}I_z\right)\exp\left(-i\pi I_y\right)]\exp\left(-i\frac{\pi}{2}I_z\right) = \exp\left(-i\frac{\pi}{2}I_z\right)\exp\left(-i\frac{\pi}{2}I_z\right) = \exp(-i\pi I_z)$$

This combination of rotation trick was also used in Tycko's derivation of the fpRFDR. However, there the recognition of the combination of two into a single π phase shift demands more conscious awareness due to strong expertise. Here, it comes naturally as long as you follow the Wigner-Eckart theory. After this simplication, we have:

$$R\left(-\frac{\pi}{2},-\pi,\frac{\pi}{2}\right)R(0,-\pi,0)\left[\sum_{\mu=-2}^{2}e^{i\mu\frac{\pi}{2}}B\right]R^{-1}(0,-\pi,0)R^{-1}\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right)$$

$$= R^{-1}(\pi,0,0)\left[\sum_{\mu=-2}^{2}e^{i\mu\frac{\pi}{2}}B\right]R(\pi,0,0) = \sum_{\mu=-2}^{2}e^{-i\mu\frac{\pi}{2}}B$$

Hence we have:

$$\overline{\widetilde{H}^{D}_{homo}}([2\tau_r,3\tau_r]) \tag{6.64}$$

$$= [e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)}+1]A + e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sum_{\mu=-2}^{2}e^{-i\mu\frac{\pi}{2}}B$$

Now let's see what is the fourth integral:

$$e^{i\hat{H}_1\tau} = R_{rf}^{-1}(t) = (R(0,\beta,0)R\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right)R(0,\pi,0)R\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right))^{-1}$$

$$= R^{-1}\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right)R^{-1}(0,\pi,0)R^{-1}\left(-\frac{\pi}{2},\pi,\frac{\pi}{2}\right)R^{-1}(0,\beta,0)$$

$$= R\left(-\frac{\pi}{2},-\pi,\frac{\pi}{2}\right)R(0,-\pi,0)R\left(-\frac{\pi}{2},-\pi,\frac{\pi}{2}\right)R(0,-\beta,0)$$

So

$$\overline{\widetilde{H}^{D}_{homo}}([3\tau_r, 4\tau_r])$$

$$= \frac{1}{\tau_r}\int_{3\tau_r}^{4\tau_r} R^{-1}(-\frac{\pi}{2}, \pi, \frac{\pi}{2}) R^{-1}(0, \pi, 0) R^{-1}(-\frac{\pi}{2}, \pi, \frac{\pi}{2}) R^{-1}(0, \beta, 0)\left[T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \exp(-im\omega_r t)\right]$$
$$R(0, \beta, 0) R\left(-\frac{\pi}{2}, \pi, \frac{\pi}{2}\right) R(0, \pi, 0) R\left(-\frac{\pi}{2}, \pi, \frac{\pi}{2}\right)$$

The time-dependent part of rotation can be computed together with the integral, and it will be the same as the time-dependent integration in the second rotor period:

$$e^{-im\omega_r \frac{1}{2}(\tau_r - \tau_p)} \sum_{\mu=-2}^{2} B + A[e^{-im\omega_r \frac{1}{2}(\tau_r + \tau_p)} + 1]$$

Then the outside time-independent rotation can be applied to these two terms after integration. Again, A term will not be affected, as A is just T_{20}^{D}. Before we evaluate the linear combination of second rank tensors $\sum_{\mu=-2}^{2} B$, let's simplify:

$$R\left(-\frac{\pi}{2}, -\pi, \frac{\pi}{2}\right) R(0, -\pi, 0) R\left(-\frac{\pi}{2}, -\pi, \frac{\pi}{2}\right) = R\left(-\frac{\pi}{2}, -\pi, \frac{\pi}{2}\right) \exp(-i\pi I_z) = R\left(-\frac{\pi}{2}, -\pi, -\frac{\pi}{2}\right)$$

Hence we have:

$$\overline{\widetilde{H}^{D}_{homo}}([3\tau_r, 4\tau_r]) = \left[e^{-im\omega_r \frac{1}{2}(\tau_r + \tau_p)} + 1\right] A \tag{6.65}$$
$$+ \frac{e^{-im\omega_r \frac{1}{2}(\tau_r - \tau_p)}\sqrt{6}}{\tau_p} \int_0^{\tau_p} dt \sum_{\mu,\nu=-2}^{2} T_{2\nu}^{\mathrm{D}}\, e^{i(\nu+\mu)\frac{\pi}{2}} d_{\nu\mu}^{2}[-\pi] d_{\mu 0}^{2}[-\omega_r \tau_p] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}$$

Combining four rotor periods Eq. 6.60, 6.63 to 6.65, we have:

$$\overline{\widetilde{H}^{D}_{homo}}([0, 4\tau_r]) = \frac{1}{4}\{\left[e^{-im\omega_r \frac{1}{2}(\tau_r + \tau_p)} + 1\right] A \times 4 \tag{6.66}$$
$$+ \frac{e^{-im\omega_r \frac{1}{2}(\tau_r - \tau_p)}\sqrt{6}}{\tau_p} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t} \int_0^{\tau_p} dt \sum_{\mu=-2}^{2} \left[\sum_{\nu=-2}^{2} T_{2\nu}^{\mathrm{D}} \left(e^{-i(\mu-\nu)\frac{\pi}{2}} + e^{i(\mu+\nu)\frac{\pi}{2}}\right) d_{\nu\mu}^{2}(-\pi)\right.$$
$$\left. + T_{2\mu}^{D} \left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right)\right] d_{\mu 0}^{2}(-\omega_r \tau_p)\} = \frac{1}{4}\{\left[e^{-im\omega_r \frac{1}{2}(\tau_r + \tau_p)} + 1\right] A \times 4 +$$
$$\frac{e^{-im\omega_r \frac{1}{2}(\tau_r - \tau_p)}\sqrt{6}}{\tau_p} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t} \int_0^{\tau_p} dt \sum_{\mu=-2}^{2} \left[\sum_{\nu=-2}^{2} T_{2\nu}^{\mathrm{D}}\, e^{i\nu\frac{\pi}{2}} \left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) d_{\nu\mu}^{2}(-\pi)\right.$$
$$\left. + T_{2\mu}^{D} \left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right)\right] d_{\mu 0}^{2}(-\omega_r \tau_p)\}$$

Let's look at the second integral:

When $\mu = \pm 1, e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}} = 0$. So the second term is always zero.

When $\mu = \pm 2$,$T^{D}_{2\mu}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) = -2T^{D}_{22}$,

$$\sum_{\nu=-2}^{2} T^{D}_{2\nu} e^{i\nu\frac{\pi}{2}}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) d^{2}_{\nu 2}(-\pi) = -2\sum_{\nu=-2}^{2} T^{D}_{2\nu} e^{i\nu\frac{\pi}{2}} d^{2}_{\nu,2}(-\pi)$$

When $\nu = 0, \pm 1,\ d^{2}_{\nu\pm 2}(-\pi) = 0$.

When $\nu = \pm 2, -\sum_{\nu=-2}^{2} T^{D}_{2\nu} e^{i\nu\frac{\pi}{2}} d^{2}_{\nu,2}(-\pi) = 2\left[T^{D}_{22} d^{2}_{2,2}(-\pi) + T^{D}_{2,-2} d^{2}_{-2,2}(-\pi)\right] = 2T^{D}_{2,-2}$

Here $d^{2}_{2,2}(-\pi)$=$d^{2}_{-2,2}(-\pi)$=1. This will just cancel with the other term $T^{D}_{2\mu}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right)$

When $\mu = 0, \nu = 0$, $d^{2}_{0,0}(\pi) = 1$. $\sum_{\nu=-2}^{2} T^{\mathrm{D}}_{2\nu}\, e^{i\nu\frac{\pi}{2}}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) d^{2}_{\nu\mu}(-\pi) + T^{D}_{2\mu}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) = 4T^{\mathrm{D}}_{20}$. Hence, combined, we have:

$$\begin{aligned} &\overline{H^{D}_{homo}}([0, 4\tau_r]) \\ &= [e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)} + 1]A + \frac{e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sqrt{6}}{\tau_p}\int_0^{\tau_p} dt T^{\mathrm{D}}_{20} d^{2}_{00}(-\omega_{rf}t) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\mathrm{D}}_{2m}\, e^{-im\omega_r t}] \\ &= [e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)} + 1]A + e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}B] \end{aligned}$$

Both the spin part of A and B are T^{D}_{20}. Therefore, even without further computation of the integral, we can appreciate the final form of the spin part of the Hamiltonian is T^{D}_{20}, so we proved that the recoupled interaction shares the same format as the static homonuclear dipolar interaction.

$$\begin{aligned} A &= \frac{2\sqrt{6}}{\tau_r - \tau_p}\int_0^{\frac{1}{2}(\tau_r-\tau_p)} dt\ \ T^{\mathrm{D}}_{20} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\mathrm{D}}_{2m} \exp(-im\omega_r t) \\ &= T^{\mathrm{D}}_{20} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\mathrm{D}}_{2m} \frac{2\sqrt{6}}{m\omega_r(\tau_r-\tau_p)i}\{1 - \exp[-im\omega_r \frac{1}{2}(\tau_r-\tau_p)]\} \end{aligned}$$

Now assume $\tau_r - \tau_p = \frac{n}{N}\tau_r, m\omega_r(\tau_r - \tau_p) = \frac{2mn\pi}{N}$. In addition, $\omega_{rf}\tau_p = \omega_{rf}\left(\frac{N-n}{N}\right)\tau_r = \pi = \frac{1}{2}\omega_r\tau_r$, so $\omega_{rf} = \frac{N}{2(N-n)}\omega_r$. So we have:

$$A = \sqrt{6}\, T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\left[1 - \mathrm{e}^{-i\frac{mn\pi}{N}}\right] \tag{6.67}$$

So the first term is:

$$\begin{aligned} &\left[e^{-im\omega_r\frac{1}{2}(\tau_r+\tau_p)} + 1\right] A \\ = &\ (1 + \mathrm{e}^{i\frac{mn\pi}{N}}) T_{20}^{\mathrm{D}} \sqrt{6} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\left[1 - \mathrm{e}^{-i\frac{mn\pi}{N}}\right] \\ &= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\left[1 - \mathrm{e}^{-i\frac{2\pi mn}{N}}\right] \end{aligned} \tag{6.68}$$

For the second term, we have:

$$B = \frac{\sqrt{6}}{\tau_p}\int_0^{\tau_p} dt\, T_{20}^{\mathrm{D}} d_{00}^{2}(-\omega_{rf}t) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}$$

$$= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{\tau_p}\int_0^{\tau_p} dt\, d_{00}^{2}(-\omega_{rf}t) e^{-im\omega_r t}$$

$$= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{\tau_p}\int_0^{\tau_p} dt\, \frac{1}{2}\left(3\cos^2\left(\omega_{rf}t\right) - 1\right) e^{-im\omega_r t}$$

$$= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{2\tau_p}\int_0^{\tau_p} dt\, \{3\frac{[1 + \cos 2\left(\omega_{rf}t\right)]}{2} - 1\} e^{-im\omega_r t}$$

$$= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{4\tau_p}\int_0^{\tau_p} dt\, [3\cos(\frac{N}{N-n}\omega_r t) - 1] e^{-im\omega_r t}$$

$$= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{4\tau_p}\int_0^{\tau_p} dt\, [\frac{3}{2} e^{i\frac{N}{(N-n)}\omega_r t} + \frac{3}{2} e^{-i\frac{N}{(N-n)}\omega_r t} - 1] e^{-im\omega_r t}$$

$$= \sqrt{6} T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{4\tau_p}\int_0^{\tau_p} dt\, [\frac{3}{2} e^{i[\frac{N-m(N-n)}{(N-n)}\omega_r t} + \frac{3}{2} e^{-i\frac{N+m(N-n)}{(N-n)}\omega_r t} - e^{-im\omega_r t}]$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{1}{4\omega_r\tau_p i}\left\{\frac{3(\mathrm{N-n})}{2[N-m(N-n)]}\left(e^{i\frac{[N-m(N-n)]\omega_r\tau_p}{(N-n)}}-1\right)\right.$$

$$\left.-\frac{3(\mathrm{N-n})}{2[N+m(N-n)]}\left(e^{-i\frac{[N+m(N-n)]\omega_r\tau_p}{(N-n)}}-1\right)+\frac{1}{m}(e^{-im\omega_r\tau_p}-1)\right\}$$

Since $\omega_r\tau_p = \omega_r\left(\frac{N-n}{N}\right)\tau_r = 2\pi\left(\frac{N-n}{N}\right)$, we have:

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{8\pi(N-n)i}\left\{\frac{3(\mathrm{N-n})}{2[N-m(N-n)]}\left(e^{i\frac{2\pi[N-m(N-n)]}{N}}-1\right)\right.$$

$$\left.-\frac{3(\mathrm{N-n})}{2[N+m(N-n)]}\left(e^{-i\frac{2\pi[N+m(N-n)]}{N}}-1\right)+\frac{1}{m}\left(e^{-i2\pi m\left(\frac{N-n}{N}\right)}-1\right)\right\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{8\pi(N-n)i}\left\{\frac{3(\mathrm{N-n})}{2[N-m(N-n)]}\left(e^{-i\frac{2\pi m(N-n)}{N}}-1\right)\right.$$

$$\left.-\frac{3(\mathrm{N-n})}{2[N+m(N-n)]}\left(e^{-i\frac{2\pi m(N-n)}{N}}-1\right)+\frac{1}{m}\left(e^{-i2\pi\left(\frac{N-n}{N}\right)}-1\right)\right\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{8\pi(N-n)i}\left\{\left[\frac{3(\mathrm{N-n})}{2[N-m(N-n)]}+\frac{3(\mathrm{N-n})}{2[N+m(N-n)]}\right]\left(e^{-i\frac{2\pi m(N-n)}{N}}-1\right)\right.$$

$$\left.+\frac{1}{m}\left(e^{-i2\pi m\left(\frac{N-n}{N}\right)}-1\right)\right\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{8\pi(N-n)i}\left\{\frac{3\mathrm{m}(\mathrm{N-n})^2}{[N^2-m^2(N-n)^2]}\left(e^{-i\frac{2\pi m(N-n)}{N}}-1\right)+\frac{1}{m}\left(e^{-i2\pi m\left(\frac{N-n}{N}\right)}\right.\right.$$

$$\left.\left.-1\right)\right\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \left\{\frac{3\mathrm{mN}(N-n)}{8\pi[N^2-m^2(N-n)^2]i}\left(e^{-i\frac{2\pi m(N-n)}{N}}-1\right)+\frac{N}{8\pi m(N-n)i}\left(e^{-i2\pi m\left(\frac{N-n}{N}\right)}\right.\right.$$

$$\left.\left.-1\right)\right\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{8\pi(N-n)i}\left\{\frac{N^2+2m^2(N-n)^2}{[N^2-m^2(N-n)^2]}\left(e^{i\frac{2\pi mn}{N}}-1\right)\right\}$$

So the second term is:

$$e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}B = \mathrm{e}^{-i\frac{mn\pi}{N}}B \tag{6.69}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N\mathrm{e}^{i\frac{mn\pi}{N}}}{8\pi(N-n)i} \{\frac{N^2+2m^2(N-n)^2}{[N^2-m^2(N-n)^2]}(1-e^{-i\frac{2\pi mn}{N}})\}$$

Therefore the average homonuclear dipolar interaction after XY-4 is:

$$\overline{\widetilde{H}_{homo}^{D}}([0,4\tau_r]) = \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\left[1-\mathrm{e}^{-i\frac{2\pi mn}{N}}\right]$$

$$+\sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N\mathrm{e}^{i\frac{mn\pi}{N}}}{8\pi(N-n)i} \{\frac{N^2+2m^2(N-n)^2}{[N^2-m^2(N-n)^2]}(1-e^{-i\frac{2\pi mn}{N}})\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \left(1-e^{-i\frac{2\pi mn}{N}}\right)\{\frac{N}{mn\pi i}+\frac{N\mathrm{e}^{i\frac{mn\pi}{N}}}{8\pi(N-n)i}\frac{N^2+2m^2(N-n)^2}{[N^2-m^2(N-n)^2]}\}$$

Hence we have:

$$\overline{\widetilde{H}_{homo}^{D}}([0,4\tau_r]) \tag{6.70}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \left(1-e^{-i\frac{2\pi mn}{N}}\right)\{\frac{N}{mn\pi i}+\frac{N\mathrm{e}^{i\frac{mn\pi}{N}}}{8\pi(N-n)i}\frac{N^2+2m^2(N-n)^2}{[N^2-m^2(N-n)^2]}\}$$

In Y. Ishii's paper (JCP 114, 8473-8483 (2001)), $\frac{n}{N}=\frac{2}{3}$. Plug in the n and N value, we have:

$$\overline{\widetilde{H}_{homo}^{D}}([0,4\tau_r]) \tag{6.71}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \left(1-e^{-i\frac{4\pi m}{3}}\right)\{\frac{3}{2m\pi i}+\frac{51\mathrm{e}^{i\frac{2\pi m}{3}}}{40\pi i}\}$$

In more general cases, no matter what is the ratio of the $\tau_r-\tau_p=\frac{n}{N}\tau_r$ pulse length, the average homonucler dipolar interaction due to the finite pulse effect will always be the same format as the static dipolar interaction, and the scaling factor is:

$$\kappa = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \left(1-e^{-i\frac{2\pi mn}{N}}\right)\{\frac{N}{mn\pi i} \tag{6.72}$$

$$+\frac{N\mathrm{e}^{i\frac{mn\pi}{N}}}{8\pi(N-n)i}\frac{N^2+2m^2(N-n)^2}{[N^2-m^2(N-n)^2]}\}$$

Let’s review how the spin part of final average Hamiltonian over XY-4 turns to be the same format as that the static Homonuclear dipolar interaction?

It owes to the unique phase cycles, which acts just like the selection rule in SPC5, to select out the $\mu, \nu = 0, T^2_{0,0}$ component among all tensors. As a homework, you can try to apply this XY-4 phase to heteronuclear and chemical shift/shielding recoupling, with the π only applied to one of the nucleus. You should find:

$$\overline{\widetilde{H}^{D}_{heter}}([0, 4\tau_r])$$
$$= \frac{e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}}{\tau_p}\int_0^{\tau_p} dt \sum_{\mu=-1}^{1}[\sum_{\nu=-1}^{1} T^{\mathrm{D}}_{1\nu}\, e^{i\nu\frac{\pi}{2}}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) d^1_{\nu\mu}(-\pi)$$
$$+ T^{D}_{1\mu}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right)]d^1_{\mu 0}(-\omega_r\tau_p) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega^{\mathrm{D}}_{2m}\, e^{-im\omega_r t}\}$$

As the π pulse now reverse the $T^{\mathrm{D}}_{1\nu}$ for heteronuclear dipolar interaction in every rotor period, unlike the homonuclear dipolar interaction is invariant under π pulse. Therefore, all the A terms will cancel out between adjacent rotor periods.

When $\mu = \pm 1$, $e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}} = 0$, so all cancels out for $\mu = \pm 1$.

When $\mu = 0$, $e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}} = 2$. $e^{i\nu\frac{\pi}{2}}$ will cancel out for $\nu = \pm 1$. For $\nu = 0$, $d^1_{00}(-\pi) = -1$, so $\sum_{\nu=-1}^{1} T^{\mathrm{D}}_{1\nu}\, e^{i\nu\frac{\pi}{2}}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right) d^1_{\nu\mu}(-\pi) = -2T^{\mathrm{D}}_{10}$, this cancels out again with the $T^{D}_{1\mu}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right)\Big|_{\mu=0}$.

Therefore, the heteronuclear dipolar interaction is not recoupled during the XY-4 phase by the fpRFDR.

6.7 Brief introduction of REDOR

In order to recouple heteronuclear dipolar interaction, we need to refocus T^D_{10} at the end of the rotor period by a second π pulse, applied to the same nucleus as did by the first π pulse. Alternatively, we need to apply a second π pulse to the other nucleus involved in the heteronuclear dipolar coupling. Both versions have been used by the REDOR pulse sequence. These π pulses also remove the recoupled chemical shift/shielding, as first shown by Terry Gullion and Jacob Shaeffer in their seminar paper in J. Magn. Reson. 81, 196 (1989). There are various nice reviews of

REDOR, for example, Terry Gullion's review "Rotation-Echo, Double-Resonance NMR" at Stanford website.

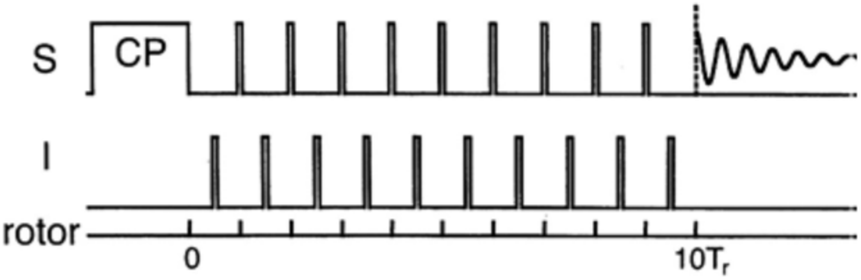


Figure 6.2. REDOR pulse sequence. Where π pulse trains are applied to both S and I spin, with XY-4 or XY-8/16 phase cycle. Adapted from T. Gullion's review "Rotation-Echo, Double-Resonance NMR".

There are various versions of REDOR application. Figure 2 shows the most popular version of the pulse sequence, where a π pulse is applied to the I spin in the middle of each rotor period, and another π pulse is applied at the end of the same rotor periods at the S spin channel that involved in the heteronuclear dipolar interaction. The phase of π pulse trains in each channel should be the same, XY-4/8/16, to compensate for pulse imperfection and resonance offset.

We can borrow our analysis for the fpRFDR above to approximate the REDOR situation, focusing on the I spin, but account for the π pulse on S spin channel by reversing the phase every other rotor period. Here we neglect the duration of π pulse on the S spin channel. We assume it instantaneously rotate the S_z in the Hamiltonian. Essentially, it means that we will have an additional minus sign in front of the T_{1v}^{D} summation from the second and fourth rotor period:

$$\overline{\widetilde{H}_{heter}^{D}}([0,4\tau_r]) \tag{6.73}$$

$$= \frac{e^{-im\omega_r\frac{1}{2}(\tau_r-\tau_p)}\sqrt{6}}{\tau_p}\int_0^{\tau_p} dt \sum_{\mu=-1}^{1}[-\sum_{\nu=-1}^{1} T_{1\nu}^{\mathrm{D}}\left(e^{-i(\mu+\nu)\frac{\pi}{2}} + e^{-i(\mu-\nu)\frac{\pi}{2}}\right) d_{\nu\mu}^{1}(-\pi)$$

$$+ T_{1\mu}^{D}\left(e^{-i\mu\frac{\pi}{2}} + e^{i\mu\frac{\pi}{2}}\right)]d_{\mu 0}^{1}(-\omega_r\tau_p) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}\}$$

Hence when $\mu, \nu = 0$, the summation over $\sum_{\nu=-1}^{1} T_{1\nu}^{\mathrm{D}}$ is no longer zero. Moreover, the A terms corresponding to the intervals in each rotor period where no pulse are applied will show up as additional contribution:

$$\overline{\widetilde{H}_{hetero}^{D}}([0,4\tau_r]) = \frac{e^{-i\frac{mn\pi}{N}}\sqrt{6}}{\tau_p}\int_0^{\tau_p} dt T_{20}^{\mathrm{D}} d_{00}^{1}(-\omega_{rf}t) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}}\, e^{-im\omega_r t}$$

$$+[1 - \mathrm{e}^{i\frac{mn\pi}{N}}]\sqrt{6}\, T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\left[1 - \exp\left(-i\frac{mn\pi}{N}\right)\right]$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{e^{-i\frac{mn\pi}{N}}}{\tau_p} \int_0^{\tau_p} dt\ \cos\omega_{rf} t\, e^{-im\omega_r t}$$

$$-\sqrt{6}\, T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\left[\mathrm{e}^{i\frac{mn\pi}{2N}} - \mathrm{e}^{-i\frac{mn\pi}{2N}}\right]^2$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{e^{-i\frac{mn\pi}{N}}}{2\tau_p} \int_0^{\tau_p} dt\ (e^{i\omega_{rf}t}+e^{-i\omega_{rf}t})e^{-im\omega_r t}$$

$$+4\sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\sin^2\frac{mn\pi}{2N}$$

Again we assume $\tau_r - \tau_p = \frac{n}{N}\tau_r$, $m\omega_r\left(\tau_r - \tau_p\right) = \frac{2mn\pi}{N}$. In addition, $\omega_{rf}\tau_p = \omega_{rf}\left(\frac{N-n}{N}\right)\tau_r = \pi = \frac{1}{2}\omega_r\tau_r$, so $\omega_{rf} = \frac{N}{2(N-n)}\omega_r$.

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{e^{-i\frac{mn\pi}{N}}}{2\tau_p} \int_0^{\tau_p} dt\ (e^{i\frac{N}{2(N-n)}\omega_r t}+e^{-i\frac{N}{2(N-n)}\omega_r t})e^{-im\omega_r t}$$

$$+4\sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\sin^2\frac{mn\pi}{2N}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{e^{-i\frac{mn\pi}{N}}}{2\omega_r\tau_p i}\{\frac{2(N-n)}{N-2m(N-n)}\left(e^{i\frac{N-2m(N-n)}{2(N-n)}\omega_r\tau_p} - 1\right)$$

$$-\frac{2(N-n)}{N+2m(N-n)}(e^{-i\frac{N+2m(N-n)}{2(N-n)}\omega_r\tau_p} - 1)\}+4\sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \frac{N}{mn\pi i}\sin^2\frac{mn\pi}{2N}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \{\frac{Ne^{-i\frac{mn\pi}{N}}}{4\pi(N-n)i}\left[\frac{2(N-n)}{N-2m(N-n)}\left(e^{i\frac{N-2m(N-n)}{N}\pi} - 1\right)\right.$$

$$\left.-\frac{2(N-n)}{N+2m(N-n)}\left(e^{-i\frac{N+2m(N-n)}{N}\pi} - 1\right)\right] + \frac{4N}{mn\pi i}\sin^2\frac{mn\pi}{2N}\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \{\frac{N}{4\pi(N-n)i}\left[-\frac{2(N-n)}{N-2m(N-n)}\left(e^{i\frac{mn}{N}\pi} + e^{-i\frac{mn\pi}{N}}\right)\right.$$

$$\left.+\frac{2(N-n)}{N+2m(N-n)}\left(e^{i\frac{mn}{N}\pi} + e^{-i\frac{mn\pi}{N}}\right)\right] + \frac{4Ni}{mn\pi}\sin^2\frac{mn\pi}{2N}\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \{\frac{-4Nm(N-n)}{\pi i[N^2-4m^2(N-n)^2]} \cos\frac{mn}{N}\pi + \frac{4N}{mn\pi i} \frac{1-\cos\frac{mn}{N}\pi}{2}\}$$

$$= \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \{\frac{2N}{mn\pi i} - \cos\frac{mn}{N}\pi\,[\frac{2N}{mn\pi i} + \frac{4Nm(N-n)}{\pi i[N^2-4m^2(N-n)^2]}]\}$$

$$\overline{\widetilde{H}_{heter}^{D}}([0,4\tau_r]) = \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} \{\frac{2N}{mn\pi i} - \cos\frac{mn}{N}\pi\,[\frac{2N}{mn\pi i} + \frac{4Nm(N-n)}{\pi i[N^2-4m^2(N-n)^2]}]\}$$

When N=2, n=1, we have:

$$\overline{\widetilde{H}_{heter}^{D}}([0,4\tau_r]) = \sqrt{6}T_{20}^{\mathrm{D}} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\mathrm{D}} [\frac{4}{m\pi i} - \cos\frac{m}{2}\pi \left[\frac{4}{m\pi i} + \frac{2m}{\pi i[1-m^2]}\right]] \tag{6.74}$$

The chemical shift/shielding anisotropy will remain zero as we still have just a single π in each rotor periods that refocuses the chemical shift/shielding.

6.8 Pithirds and phase shift associated with the time delay in a pulse train

At this stage, the advantage of the irreducible tensor representation is very clear. It does not save much computation directly. If you are a seasoned player with single spin operators, you can perfectly do just as much. Sometimes it incurs more cumbersome expressions. However, the symmetry during the rotation is explicitly manifested in the tensor representation. The insights into the symmetry can greatly enhance our ability to identify terms that lead to cancellation, which can potentially save lots of redundant computation.

Next, we can see the effect of displacement the pulses by δ in a sequence. It introduces a phase factor due to rotation of $e^{-im\omega_r\delta}$ associated with MAS. This effect is exploited in the PIRTHIRDS sequence. PITHIRDS was designed by Robert Tycko in J. Chem. Phys. 126, 064506 (2007). Basically three sets of fRDFR are concatenated head to tail, each with the XY4 phase π pulse train, but displaced by $\frac{1}{3}\tau_r$ relative to its neighboring set.

Hence, the averaged Hamiltonian of the second block is $\overline{H}(\sigma) = e^{-im\omega_r\frac{1}{3}\tau_r}\overline{\widetilde{H}_{homo}^{D}} = e^{-i\frac{2m\pi}{3}}\overline{\widetilde{H}_{homo}^{D}}$. If we have a third block with $\delta = \frac{2}{3}\tau_r$, its average Hamiltonian should be $\overline{H}(2\sigma) = e^{-i\frac{4m\pi}{3}}\overline{\widetilde{H}_{homo}^{D}}$. The average Hamiltonian of three combined blocks will be:

$$\overline{\tilde{H}_{homo}^{D}} = \bar{H}(0) + \bar{H}(\sigma) + \bar{H}(2\sigma) = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} (1 + e^{-i\frac{2m\pi}{3}} + e^{-i\frac{4m\pi}{3}}) = 0 \qquad (6.75)$$

In experiments, we can set the total number of fpRFDR blocks to be a constant N. This ensures a constant total time for the spin relaxation. In each run, set the extra $\bar{H}(0)$ to be N_0 and the complete $\bar{H}(0) + \bar{H}(\sigma) + \bar{H}(2\sigma)$ block to be N_3, so that $N_0 = 3(N - N_3)$. By varying the combination of N_0 and N_3 within a constant N, the NMR signals as a function of time by effective dipolar interaction time N_0 block, without changing the total spin relaxtion. By fitting the observed decay curve with the simulation, the distance information can be extracted. Details please read Robert Tycko's original paper at JCP 126, 064506 (2007).

One subtlety we need to pay attention is the necessity of rotor synchronization for PITHIRDS. The recoupled Hamiltonian of fpRFDR depends on the γ angle, as shown in 6.70. Therefore, the amplitude of the recoupled dipolar interaction depends on the orientation of the molecule in the powder distribution. When multiple scans are accumulated to enhance signal to noise, the summation of signals acquired without rotor synchronization can be scrambled and lead to the destructive interference effect between physical rotation and spin rotation. This may not be a big deal if we simply want crosspeaks to identify correlation between sites. However, for accurate distance measurements, it is undesirable. Therefore, it is very critical PITHIRDS experiments are to be performed with stable spinning and accurate rotor synchronization. Following the same reasoning, REDOR should be performed with rotor synchronization as well.

Chapter 7 Decoupling of interactions under magic under spinning

Decoupling of interactions is a common and essential practice in protein NMR work. Detection of high-resolution $^{13}C/^{15}N$ spectra demands efficient heteronuclear decoupling of the spins from ^{1}H. Proton homonuclear decoupling is also necessary for minimization of proton spin diffusion measurements or proton detection at high MAS or with deuterated proteins. However, it is more complicated to understand than the recoupling physics, due to the strong dipolar network among protons.

We will start our discussion with a qualitative description how the spectral resolution and relaxation are affected by the inhomogeneous and homogeneous interactions. A simple derivation based on our knowledge of the Wigner rotation matrix will show how Lee-Goldberg decoupling works. Then we will explain the decoupling effects by MAS and RF irradiation separately. We will first show how the spectral linewidth narrows inversely proportional to MAS speed ω_r by AHT (AHT). Then using perturbation theory, we will derive how RF irradiation alone helps reduce NMR linewidth in isolated spin systems (or systems without strong proton dipolar network, such as in solution NMR). When a system is exposed to simultaneous MAS and RF irradiation, the situation becomes very challenging for AHT. Analytical solutions can still be obtained for various rotary resonance conditions (including the cross polarization which was explained in Sect. 4.12), or more generally, when the ratio of MAS and RF irradiation strength is multiples of integer. When the RF irradiation and MAS strength are not commensurate, it is not possible to derive analytical solution by AHT. To get insights into such systems, which is common in our daily practice, we will introduce the Floquet theory. It transforms the periodic MAS and RF irradiation into respective frequency dependent functions. The multilayer integrations that limit AHT are then replaced by respective frequency summation series. Our introduction will focus on how the framework of the Floquet theory is established, so we know not only how it works, but why it works and where it may fail. The actual application of the Floquet theory will be your homework, which should simply be a plug-and-play practice.

7.1 Overview of correlation between the spectral resolution and interactions

After we become familiar with recoupling, it is natural to consider decoupling. These two topics are intimately related. If not analyzed jointly, a pulse sequence may not achieve its desired purpose.

In liquids, Brownian motion makes molecules translate and rotate with their directions alternating at high frequencies. The frequencies of these fast motions are much higher than dipolar or chemical shift anisotropy (csa), and thus averages out the anisotropic interactions. Things become much messier in solids, due to the absence of Brownian motion. Anisotropic interactions are present, which lead to broadened NMR resonances. That is why MAS was introduced, so the effect of anisotropy is attenuated for better resolution.

Exactly how and why NMR linewidth is related to these anisotropic interactions? This can be appreciated qualitatively by the following reasoning.

As we introduced in Eq. 4.66 in Sec.t 4.5, the spectrum line shape in solids can be approximated by a Gaussian function:

$$f(\omega) \propto \exp\left(-\frac{\omega^2}{2\sigma^2}\right)$$

The FWHM of such a resonance was shown by Eq. 4.67 as:

$$\Delta\omega = 2\sqrt{2\ln(2)}\,\sigma = 2.355\sigma$$

If we define T_2 as the time for NMR signal to decay to 1/e of the initial FID amplitude, then we can show

$$T_2 = \frac{\sqrt{2}}{\sigma} = \frac{4\sqrt{\ln(2)}}{\Delta\omega} = \frac{3.33}{\Delta\omega}$$

Therefore, we can see the linewidth is inversely proportional to the relaxation time. Likewise, you can show for a spectrum with a Lorentzian line shape (typical in solution NMR):

$$T_2 = \frac{2}{\Delta\omega}$$

Recall that the relaxation mechanisms we introduced at the end of Chapter 3, $1/T_2$ is directly proportional to the square of the strength of respective interactions. Hence, NMR linewidth is a directly a manifestation of the relaxation. For more detailed analysis, you can read over the chapters of relaxation and linewidth in C. P. Slichter or A. Abragam's classical textbooks, but be prepared with some serious quantum mechanics.

The other perspective is the definition of linewidth: it is the convolution of all the different NMR transition frequencies between spin up and down states of a specific nuclear site in a specific chemical position. In simple words, NMR linewidth reflects the range of variations of NMR transition energy.

We can divide the contribution into two categories by the source of variations: the variation due to the structurally distinct molecules, and due to the variations of local interactions for molecules of the same conformation.

To differentiate these sources, we may ask one question: can the differences of molecules be minimized or removed by physical re-orientation of the entire molecule as a rigid body, without changing the relative orientations of the components in each molecule or the structure of the supramolecular complex?

If the answer is Yes, then the line broadening is of the second kind, and can reduced by NMR techniques. If the answer is No, then most likely, NMR techniques can't do the magic, and you have to refine the sample preparation to improve the structural uniformity. A good example is the protein in a crystalline sample in contrast to the same protein in a disordered sample obtained by rapid cooling. NMR spectral linewidth of the formal is very sharp, but the later produces broad lines that will not be saved by high MAS and decoupling.

Our decoupling discussion will focus on the minimization of linebroadening due to variations of local interactions associated with variations of molecular orientations in solids. The linewidth then will greatly benefit from a thorough decoupling the spins of observation channel from protons.

In the absence of local interactions, interactions of a specific site in molecules at different orientations are identical, due to the Zeeman interaction. The transition energy between different spin levels is entirely determined by the external magnetic field, and the gyromagnetic ratio of the nucleus. Therefore, all nuclei of the same gyromagnetic ratio will have exactly the same transition frequency, and produce a single NMR line as a δ function. This will make NMR spectra easy to assign. At the same time, NMR results are nearly useless except to identify different nuclear species.

When we have the same nucleus in the different chemical bonds, they will produce different NMR resonances due to different chemical shifts. This difference renders us to resolve the same nucleus in different chemical environments. If all molecules are aligned perfectly as in a single crystal, the NMR spectrum will be consisted of multiple δ functions, each corresponding to its specific chemical shielding strength at that specific alignment angle $H_{cs}(\alpha, \beta)$, as we derived in Eq. 5.63:

$$H_{cs}(\alpha,\beta) = \omega_0\left\{\delta_{iso} + \sqrt{\frac{3}{2}}\delta_{aniso}\left[\frac{(3\cos^2\beta - 1)}{2} - \frac{\eta}{2}\cos 2\alpha\sin^2\beta\right]\right\}I_z$$

In solution, fast brownian motions will remove the angular dependent part in Eq. 5.63, and produce single sharp transitions at corresponding isotropic chemical shift positions. Additional isotropic J coupling will split each chemical shift into multiplets, though still sharp.

When molecules lose fast motions as in gel or solids, anisotropy shows up. This means that the nucleus in the same chemical bonding environments can assume different physical orientations with respect to the external magnetic field. This orientation difference doesn't change the molecular structure or the assembly suprastructure. However, as shown by the anisotropy part in Eq. 5.63, it will render nuclei at the same chemical site to adopt slightly different transition energies between spin states due to the orientational dependence of local interactions. Besides chemical shielding, such variations of local interactions include homo and heternuclear dipolar interactions. This is clearly illustrated in the powder distribution spectra for csa and dipolar interaction in Fig. 5.4. The Hamiltonians of these interactions have explicit orientation dependent spatial parameter parts. The magnitude of these interactions, large or small, are all small compared to Zeeman interaction (Larmor frequency), so they are just local perturbations. As indicated by the orientation dependence, as long as we have a continuously variation of the molecular orientation, the perturbations due to these anisotropic interactions are also continuous. This is manifested by the transformation of the spatial part of the Hamiltonians from the principal axis frame of these anisotropic interactions to the lab frame:

$$R_{20}^{L} = \sum_{m=-2}^{2} R_{22}^{P} D_{2m}^{2}(\alpha,\beta,\gamma) + \sum_{m=-2}^{2} R_{2,-2}^{P} D_{-2,m}^{2}(\alpha,\beta,\gamma) \tag{7.1}$$

The Wigner-rotation matrices in the summation carry the orientation dependent terms, which will give a complete [-1, 1] range of variations to the $R_{2,\pm 2}^{P}$ terms, the spatial part of the Hamiltonians in the principal axis frame. In spectral, it means that all frequency values in the range $[R_{2-2}^{P}, R_{2,2}^{P}]$ around the isotropic chemical shifts (plus splitting of multiplets by J couplings) become the NMR transition frequencies of certain nuclei in the same chemical site of some molecules at a particular orientation. Hence, our original δ function style NMR lines spread into a broad peak, at attenuated intensity. NMR techniques, such as MAS or decoupling sequences, help reduce or suppress the broadening associated with such variations of interactions by turning the orientation dependent term in Eq. 5.63 into time-dependent periodic oscillation terms, shown in Eq. 5.62 and 5.64, which becomes individual spinning side-bands and central line at the isotropic chemical shift position.

But the line broadening contribution does not end here. The Hamiltonians of homonuclear dipolar and J couplings are particularly nasty. Their Hamiltonians don't commute with those of other interactions, or themselves. This incommutable effect further introduces variations of even smaller variations of transition energies for the time-dependent Hamiltonian under MAS. In analogy, these nonzero commutators are perturbations to the original interactions, just as these interactions are perturbations to the original Zeeman interactions. It is in a sense like a chain reaction in the A-bomb.

Therefore, by analyzing the strength of all anisotropic interactions and their nonzero commutator terms modulated by pulse sequences and MAS, we can see how our NMR linewidth is narrowed and the relaxation is extended, or so called decoupling. Essentially, we can also say that this strategy is the same as our analysis of recoupling. But we will see a different theoretical approach can help simplify the analysis and help bring out the physics picture.

By the hand-waving statements, we can see that even those originally clean interactions that won't broaden NMR lines by themselves under MAS (or so called inhomogeneous interactions by Marciq and Waugh), get "contaminated" by the homogeneous dipolar and J coupling, also contribute to line broadenings. For example, the scalar/isotropic interactions such as isotropic chemical shift or heteronuclear J coupling, originally they just shift or split lines into multiple δ function style NMR lines. Now, due to their nonzero commutators with homonuclear dipolar and J couplings, the same site in molecules of different orientations thus also contribute different perturbative transition energies, so called cross terms. Such cross terms, in addition to broaden NMR lines, also speed up the relaxations, as now motions originally outside the δ function style NMR lines that do not contribute to relaxation, are now overlapping with NMR transitions, and can cause additional transitions to accelerate the decoherence process. We will see in this chapter how such effects come by in explicit physical terms, and how NMR decoupling techniques suppress these contributions.

In summary, to understand a decoupling technique, all we need to do is to show how it modulates various interactions, since the magnitude of orientation dependent interactions and their cross terms are the direct measure of NMR linewidth. As the linewidth is inversely proportional to the intensity, the effect of the pulse sequence on signal noise is obvious to see at the same time.

7.2 Lee-Goldberg experiments to decouple homonuclear dipolar interaction.

M. Lee and W.I. Goldberg discovered the combined effect of resonance offset and RF irradiation in the transverse plane can decouple homonuclear dipolar interactions in their seminar paper PRL 11, 255 (1963). It consists of a continuous RF irradiation applied along a fixed axis in the rotating frame $H_1 = -\omega_1 I_x$. If the strength of this field and the resonance offset $H_{offset} = -\delta\omega_0 I_z$ satisfy:

$$\tan\theta = \frac{\omega_1}{\delta\omega_0} = \sqrt{2} \tag{7.2}$$

the NMR linewidth corresponding to the irradiated nucleus is reduced significantly. Since then, various variants of Lee-Goldberg (LG) pulse sequence have been developed and applied to decouple homonuclear interactions. For example, in various sequences from Mei Hong and Tim Cross's groups to probe water conduction in the membrane peptides.

The mechanism of LG can be analyzed in the classical transformation of reference frame in various literature. It can also be easily understood with the Wigner rotation matrix. Without losing generality, we recall Eq. 5.64, the Hamiltonian of dipolar interactions with MAS is:

$$H_D = \sqrt{6}T_{20}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2,m}^{D}\,exp(im\omega_r t) = \omega_D(t)T_{20}$$

Where $T_{20} = \frac{2}{\sqrt{6}}I_z S_z$ for heteronuclear dipolar interaction, and $T_{20} = \frac{1}{\sqrt{6}}(3I_{z1}I_{z2} - I_1\cdot I_2)$ for homonuclear dipolar interaction:

$$\omega_D(t) = \sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2,m}^{D}\,exp(im\omega_r t)$$

$$\omega_{20}^{D} = b_{IS}\frac{(3\cos^2\beta - 1)}{2}\frac{(3\cos^2\theta_M - 1)}{2} = 0$$

$$\omega_{2,\pm 1}^{D} = -\frac{b_{IS}}{2\sqrt{2}}\sin 2\beta\, exp(\pm i\gamma)$$

$$\omega_{2,\pm 2}^{D} = \frac{b_{IS}}{4}\sin^2\beta\, exp(\pm i2\gamma)$$

$$b_{IS} = -\frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S}{r_{IS}^3}\ (rad/s)$$

The situation without MAS can be analyzed as a special case where $\omega_r = 0$. Likewise, any arbitrary orientation of sample position can be retrieved by setting θ_M to the corresponding value.

Therefore, to see how the spin part of Hamiltonian is affected by LG, we just need to apply the transformation to the interaction frame of LG condition's resonance offset and RF irradiation:

$$H_{LG} = -\delta\omega_0 I_z - \omega_1 I_x \tag{7.3}$$

$$\widetilde{H_D} = U^{-1}H_D U$$

$$U = \exp(-i\int_0^t H_{LG}dt') = \exp[-i\int_0^t(-\delta\omega_0 I_z - \omega_1 I_x)dt']$$

Recall Eq. 5.2:

$$\exp(-i\beta n\cdot J) = \exp\left[-i\beta\left(I_x\sin\theta\cos\varphi + I_y\sin\theta\sin\varphi + I_z\cos\theta\right)\right]$$
$$= \exp(i\varphi I_z)\left[\exp\left(-i\theta I_y\right)\exp(-i\beta I_z)\exp\left(i\theta I_y\right)\right]\exp(-i\varphi I_z)$$

So we can rearrange Eq. 7.2:

$$H_{LG} = -\delta\omega_0 I_z - \omega_1 I_x = -H_{eff}(I_z\cos\theta + I_x\sin\theta) \tag{7.4}$$

Where

$$H_{eff} = \sqrt{(\delta\omega_0)^2 + (\omega_1)^2}$$
$$\cos\theta = \frac{\delta\omega_0}{H_{eff}}, \sin\theta = \frac{\omega_1}{H_{eff}}$$

So just like what we did in the analysis of the system under SPC5's double quantum interaction Hamiltonian, where we converted Eq. 6.18 to 6.20, we can convert the resonance offset and the RF irradiation into one effective field:

$$U = \exp\left(-i\theta I_y\right)\exp\left(-i\int_0^t -H_{eff}I_z dt'\right)\exp\left(i\theta I_y\right) \tag{7.5}$$

The resonance offset and RF irradiation, will affect the spin part of Hamiltonian, but won't affect the physical parameter parts in $\omega_D(t)$**.** Thus we can leave them out in our analysis. Let's focus on the effect on T_{20}:

$$\widetilde{H_D} = U^{-1}H_D U \tag{7.6}$$

$$= \exp\left(-i\theta I_y\right)\exp\left(-i\int_0^t H_{eff} I_z dt^{'}\right)\exp\left(i\theta I_y\right) T_{20}\exp\left(-i\theta I_y\right)\exp\left(-i\int_0^t -H_{eff} I_z dt^{'}\right)\exp\left(i\theta I_y\right)$$

$$= \exp\left(-i\theta I_y\right)\exp\left(-i\int_0^t H_{eff} I_z dt^{'}\right)\sum_{\mu=-2}^{2} T_{2\mu}\, d^2_{\mu 0}(\theta)\exp\left(-i\int_0^t -H_{eff} I_z dt^{'}\right)\exp\left(i\theta I_y\right)$$

We know that among $T_{2\mu}$ with different μ, T_{20} is the zero order effect which survives the high field truncation. So to the zeroth order, we have:

$$\widetilde{H_D^{(0)}} = \exp\left(-i\theta I_y\right)\exp\left(-i\int_0^t H_{eff} I_z dt'\right) T_{20} d^2_{00}(\theta)\exp\left(-i\int_0^t -H_{eff} I_z dt'\right)\exp\left(i\theta I_y\right) \tag{7.7}$$

Where $d^2_{00}(\theta) = \frac{1}{2}(3\cos^2\theta - 1)$.

Hence when $\cos^2\theta = \frac{1}{3}$, $d^2_{00}(\theta) = 0$, we will have $\widetilde{H_D^{(0)}} = 0$.

The reason we still see nonzero linewidth with the application of LG, can be attributed to the difficulty to simultaneously satisfy this condition $Eq. 7.2$ for multiple nuclei with different $\delta\omega_0$. In addition, there is still higher order contribution from $T_{2\mu}$ with $\mu \neq 0$:

$$\sqrt{6}T_{2,\pm 2}\sqrt{\frac{3}{8}}\sin^2\theta = I_i^{\pm} I_j^{\pm}\sqrt{6}\times\sqrt{\frac{3}{8}}\times\frac{2}{3} = \frac{1}{\sqrt{2}} I_i^{\pm} I_j^{\pm} = T_{2,\pm 2} = 0.707 T_{2,\pm 2}$$

$$\sqrt{6}T_{2,\pm 1}\left(\pm\sqrt{\frac{3}{8}}\sin 2\theta\right) = T_{2,\pm 1}\sqrt{6}\times\sqrt{\frac{3}{8}}\times\frac{2\sqrt{2}}{3} = T_{2,\pm 1}$$

Compared to the non-irradiated case, at least the $T_{2,\pm 2}$ contribution is also scaled down.

Alternatively, the resonance offset and RF irradiation is equivalent to transform the spin part of Hamiltonian to a new frame of reference with the z axis along the effective field direction $\tan\theta = \frac{\omega_1}{\delta\omega_0}$ in the old rotating frame. This is just like our treatment of MAS in Chapter 5 by transforming the physical part of Hamiltonian between different reference frames, but mind you the angle of rotation should be reversed, since it is the perspective of observation that is rotated, not the actual tensors as remarked by L. Mueller in his paper Concepts in Magnetic Resonance Part A, 38A(5), 221-235 (2011) . You can do this treatment by applying the transformation using Wigner-rotation matrix with $\theta = -\tanh^{-1}(\frac{\omega_1}{\delta\omega_0})$. I will leave this as a homework for you.

7.3 Effect of homogenous homonuclear dipolar interactions on linewidth under MAS.

In Chapter 5, we briefly mentioned that if all interactions are commutable with each other and with themselves, the linewidth in the presence of MAS will be zero in theory, if there were no structurally inequivalent molecules in the sample. This is now easy to see: since all interactions are commutable with Zeeman interaction, the strength of these interactions is a constant in the eigenstates of I_z/S_z, except the

MAS part $\exp(im\omega_r t)$. Thus they can be treated rigorously by their average over a rotation period. Since the Hamiltonian of all interactions are in the form described by Eq. 5.69:

$$\sum_{\Lambda} H_{\Lambda} = \omega_0 \delta_{\text{iso}} I_z + \sum_{\Lambda} T_{\lambda 0}^{\Lambda} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda} \exp(-im\omega_r t)$$

The average over a rotor period will be zero, except the isotropic chemical shift $\omega_0 \delta_{\text{iso}} I_z$.Thus we will have just δ function-style linewidth at respective isotropic chemical shift positions δ_{iso} as the central transitions, plus spinning side-bands associated with MAS due to the dynamic phase as we derived in Eq. 5.86:

$$\langle A \rangle = \exp(-i\omega_0 \delta_{\text{iso}} \mathrm{t}) \prod_{\Lambda} \exp\{-\frac{Z_r - Z_s}{\omega_r} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \frac{\omega_{2m}^{\Lambda}}{m} [\exp(im\omega_r t) - 1]\}$$

However, this is not exactly what we observe for most protein samples. The reason is the homogeneous interactions with Hamiltonians that do not commute with others and even with themselves at different time points. Specifically, the mononuclear dipolar interactions and J couplings are such culprits.

The effect of these so called homogeneous interactions coined by A. M. Portis in Phys. Rev. 91, 1971 (1953), is to cause additional higher order perturbations to originally energy levels, which broaden NMR transition energy. The physical picture behind it was explained very clearly by C. P. Slichter in his book in the section regarding MAS.

To re-iterate, MAS works because it averages the internal magnetic fields from the interactions by rotating the spatial part of the interactions in a periodic fashion, while the rest spin part of the Hamiltonian is not affected. Hence, if the spin part of the Hamiltonian remains a constant during the process, the Hamiltonian of the interaction simply follows the sinusoidal modulation of the spatial part and adds to zero over one complete rotor period.

However, we cannot treat the spin part of the Hamiltonians as time-independent in this process, if they don't commute at different point in time. For example, the spin part of homonuclear dipolar interactions of I_i and I_j doesn't commute with that of homonuclear dipolar interactions of I_i and I_k, shown in Eq. 5.77. This leads to $I_i^{\pm}$ terms. Such spin flip-flop terms will cause flip-flop of states on I_i, I_j and I_k. They will activate spin diffusion process to re-distribute the populations between spin up and spin down states of all involved nuclei, and change their respective polarizations. Therefore, the magnetic fields experienced by other spins around them become different before and after the spin flipping, which will interfere with the spatial part averaging by MAS. If the frequency of such spin flipping is faster than or comparable to the MAS speed, they introduce strong fluctuations of magnetic fields on all involved spins, which interferes with the sinusoidal modulation by MAS and invalidates the perfect cancellation of interactions over the MAS rotation period. Thus to make MAS work, we need to spin faster than the frequency of such flip-flop actions from incommutable Hamiltonians: $\omega_r \gg |H|$, so that less chance and effect of such terms can interfere with MAS.

Now let's see how such interactions produce nonzero commutations. For the moment, let's focus on the spin part commutation first. Once we understand the commutation, we will analyze how this couples to the MAS rotation and spatial part of Hamiltonians. It becomes complicated as we may have different regimes depending on the relative strength of relevant parameters: the MAS speed and the RF irradiation strength, for example.

a. For homonuclear dipolar interactions, they do not commute with themselves. If a nucleus I_i is involved in homonuclear dipolar interactions with two different sites I_j and I_k, we can show that they don't commute, as we showed in Eq. 5.77:

$$\left[H_{D_{II}}^{ij}, H_{D_{II}}^{ik}\right] = [3I_{zi}I_{zj} - I_i \cdot I_j, 3I_{zi}I_{zk} - I_i \cdot I_k] \tag{7.8}$$

$$= 4iI_{xi}\left(I_{yj}I_{zk} - I_{zj}I_{yk}\right) + 4iI_{yi}\left(I_{zj}I_{xk} - I_{xj}I_{zk}\right) + iI_{zi}\left(I_{xj}I_{yk} - I_{yj}I_{xk}\right)$$

$$= -(I_i^+ I_k^- - I_k^+ I_i^-)I_{zj} + \left(I_i^+ I_j^- - I_j^+ I_i^-\right)I_{zk} - \frac{1}{2}\left(I_j^+ I_k^- - I_k^+ I_j^-\right)I_{zi}$$

$$= -2iI_0^{yik}I_{zj} + 2iI_0^{yij}I_{zk} - iI_0^{yjk}I_{zi} \neq 0$$

Here we use $H_{D_{II}}^{ij}$ to stand for the homodipolar interaction between spin I_i and I_j. I_0^{yij} stands for the fictitious spin y component formed by spin I_i and I_j.

Eq. 7.8 can be proved as follows:

$$\left[I_{zi}, 3I_{zi}I_{zj} - I_i \cdot I_j\right] = [I_{zi}, 3I_{zi}I_{zj}] - [I_{zi}, I_i \cdot I_j]$$

Note $\left[I_{zi}, 3I_{zi}I_{zj}\right] = 0$, as I_{zi} commutes with itself, and it commutes with operators of a different spin I_j. So we just have to compute:

$$\left[I_{zi}, I_i \cdot I_j\right] = [I_{zi}, I_i] \cdot I_j = \left[I_{zi}, I_{xi}I_{xj} + I_{yi}I_{yj} + I_{zi}I_{zj}\right] = \left[I_{zi}, I_{xi}I_{xj}\right] + \left[I_{zi}, I_{yi}I_{yj}\right]$$

$$= [I_{zi}, I_{xi}]I_{xj} + \left[I_{zi}, I_{yi}\right]I_{yj} = iI_{yi}I_{xj} - iI_{xi}I_{yj} = \frac{i}{2i}\left(I_i^+ I_j^- - I_j^+ I_i^-\right)$$

Recall that $I_0^y = \frac{1}{2i}(I^+S^- - I^-S^+) = I_yS_x - I_xS_y$; $I_0^x = \frac{1}{2}(I^+S^- + I^-S^+) = I_xS_x + I_yS_y$

$$\left[I_{zi}, I_i \cdot I_j\right] = \left[I_{zi}, I_{xi}I_{xj} + I_{yi}I_{yj} + I_{zi}I_{zj}\right] = \left[I_{zi}, I_0^{xij} + I_{zi}I_{zj}\right] = iI_0^{yij} \tag{7.9}$$

Therefore, we have:

$$\left[I_{zi}, 3I_{zi}I_{zj} - I_i \cdot I_j\right] = -iI_{yi}I_{xj} + iI_{xi}I_{yj} = -\frac{1}{2}\left(I_i^+ I_j^- - I_j^+ I_i^-\right) = -iI_0^{yij} \neq 0 \tag{7.10}$$

In addition, we can evaluate $\left[I_i \cdot I_j, I_i \cdot I_k\right] = \left[I_{xi}I_{xj} + I_{yi}I_{yj} + I_{zi}I_{zj}, I_{xi}I_{xk} + I_{yi}I_{yk} + I_{zi}I_{zk}\right] =$

$$\left[I_{xi}I_{xj}, I_{yi}I_{yk}\right] + \left[I_{xi}I_{xj}, I_{zi}I_{zk}\right] + \left[I_{yi}I_{yj}, I_{xi}I_{xk}\right] + \left[I_{yi}I_{yj}, I_{zi}I_{zk}\right] + \left[I_{zi}I_{zj}, I_{xi}I_{xk}\right] + \left[I_{zi}I_{zj}, I_{yi}I_{yk}\right]$$

$$= iI_{zi}I_{xj}I_{yk} - iI_{yi}I_{xj}I_{zk} - iI_{zi}I_{yj}I_{xk} + iI_{xi}I_{yj}I_{zk} + iI_{yi}I_{zj}I_{xk} - iI_{xi}I_{zj}I_{yk}$$

$$= iI_{xi}\left(I_{yj}I_{zk} - I_{zj}I_{yk}\right) + iI_{yi}\left(I_{zj}I_{xk} - I_{xj}I_{zk}\right) + iI_{zi}\left(I_{xj}I_{yk} - I_{yj}I_{xk}\right)$$

$$= -i\left(I_{yi}I_{xj} - I_{xi}I_{yj}\right)I_{zk} + i\left(I_{yi}I_{xk} - I_{yi}I_{xk}\right)I_{zj} - i\left(I_{yj}I_{xk} - I_{xj}I_{yk}\right)I_{zi}$$

$$= -\frac{1}{2}\left(I_i^+ I_j^- - I_j^+ I_i^-\right)I_{zk} + \frac{1}{2}(I_i^+ I_k^- - I_k^+ I_i^-)I_{zj} - \frac{1}{2}\left(I_j^+ I_k^- - I_k^+ I_j^-\right)I_{zi}$$

Or equivalently, we have:

$$\begin{aligned}\left[I_i\cdot I_j, I_i\cdot I_k\right] &= \left[I_0^{xij}+I_{zi}I_{zj}, I_0^{xik}+I_{zi}I_{zk}\right]\\ &= -iI_0^{yij}I_{zk}+iI_0^{yik}I_{zj}-iI_0^{yjk}I_{zi}\end{aligned} \tag{7.11}$$

This can be expressed using Eq. 7.9 as:

$$= \left[I_0^{xij}, I_{zi}I_{zk}\right]+\left[I_{zi}I_{zj}, I_0^{xik}\right]+\left[I_0^{xij}, I_0^{xik}\right]$$

$$= -iI_0^{yij}I_{zj}+iI_0^{yik}I_{zj}+\left[I_0^{xij}, I_0^{xik}\right]$$

So we get a new relation:

$$\left[I_0^{xij}, I_0^{xik}\right] = iI_0^{yjk}I_{zi} \tag{7.12}$$

Hence

$$[3I_{zi}I_{zj}-I_i\cdot I_j, 3I_{zi}I_{zk}-I_i\cdot I_k] = -3I_{zj}[I_{zi}, I_i\cdot I_k]+3I_{zk}[I_{zi}, I_i\cdot I_j]+[I_i\cdot I_j, I_i\cdot I_k]$$

$$= -3I_{zj}\left(-iI_{yi}I_{xk}+iI_{xi}I_{yk}\right)+3I_{zk}\left(-iI_{yi}I_{xj}+iI_{xi}I_{yj}\right)+iI_{xi}\left(I_{yj}I_{zk}-I_{zj}I_{yk}\right)+iI_{yi}\left(I_{zj}I_{xk}-I_{xj}I_{zk}\right)$$

$$+iI_{zi}\left(I_{xj}I_{yk}-I_{yj}I_{xk}\right)$$

$$= 4iI_{xi}\left(I_{yj}I_{zk}-I_{zj}I_{yk}\right)+4iI_{yi}\left(I_{zj}I_{xk}-I_{xj}I_{zk}\right)+iI_{zi}\left(I_{xj}I_{yk}-I_{yj}I_{xk}\right)$$

Or in the raising and lowing operators of each spins:

$$[3I_{zi}I_{zj}-I_i\cdot I_j, 3I_{zi}I_{zk}-I_i\cdot I_k] = -3I_{zj}[I_{zi}, I_i\cdot I_k]+3I_{zk}[I_{zi}, I_i\cdot I_j]+[I_i\cdot I_j, I_i\cdot I_k]$$

$$= -3I_{zj}\frac{1}{2}(I_i^+I_k^- - I_k^+I_i^-)+3I_{zk}\frac{1}{2}\left(I_i^+I_j^- - I_j^+I_i^-\right)-\frac{1}{2}\left(I_i^+I_j^- - I_j^+I_i^-\right)I_{zk}+\frac{1}{2}(I_i^+I_k^- - I_k^+I_i^-)I_{zj}$$

$$-\frac{1}{2}\left(I_j^+I_k^- - I_k^+I_j^-\right)I_{zi}$$

$$\begin{aligned}\left[H_{homo}^D(ij), H_{homo}^D(ik)\right] &= \left[3I_{zi}I_{zj}-I_i\cdot I_j, 3I_{zi}I_{zk}-I_i\cdot I_k\right]\\ &= -(I_i^+I_k^- - I_k^+I_i^-)I_{zj}+\left(I_i^+I_j^- - I_j^+I_i^-\right)I_{zk}-\frac{1}{2}\left(I_j^+I_k^- - I_k^+I_j^-\right)I_{zi}\end{aligned} \tag{7.13}$$

Or this can be written in terms of fictitious spin operators in a more concise form:

$$\left[H_{D_{II}}^{ij}, H_{D_{II}}^{ik}\right] = [3I_{zi}I_{zj}-I_i\cdot I_j, 3I_{zi}I_{zk}-I_i\cdot I_k] = [2I_{zi}I_{zj}-I_0^{xij}, 2I_{zi}I_{zk}-I_0^{xik}]$$

$$= -2iI_0^{yik}I_{zj}+2iI_0^{yij}I_{zk}-iI_0^{yjk}I_{zi}$$

If we including the spatial part of the Hamiltonian, we have:

$$\begin{gathered}\left[H_{D_{II}}^{ij}, H_{D_{II}}^{ik}\right]\\ = \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij)\,\omega_{2n}^{D_{II}}(ik)e^{im\omega_r t_2}e^{in\omega_r t_1}\left(-2iI_0^{yik}I_{zj}+2iI_0^{yij}I_{zk}-iI_0^{yjk}I_{zi}\right)\end{gathered} \tag{7.14}$$

Here you noticed I differentiate the time-dependent MAS oscillation argument as $e^{im\omega_r t_2}$ and $e^{in\omega_r t_1}$. The intention of this is for AHT computation later which uses the Magnus expansion. As we show in Eq. 5.45, its first order expansion involves this commutator with different arguments:

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega}} dt_2 \int_0^{t_2} [H(t_2), H(t_1)]dt_1$$

In our computation of the commutations, we intentionally tag the first term in Hamiltonian with t_2, and the second term with t_1, so our later computation by AHT can directly utilize these results.

b. It is easy now to see the commutations of the homonuclear dipolar interaction with chemical shielding, isotropic chemical shift, heteronuclear dipolar interaction and heteronuclear J coupling $H_J^{IS} = 2\pi J_{ij}^{IS} I_{iz}S_{jz}$are not zero, as long as they share one common spin in their spin parts of Hamiltonian. This is actually the same as the relation derived in Eq. 7.10:

$$[H_\Lambda(i), H_{D_{II}}^{ij}] = [I_{zi}, 3I_{zi}I_{zj} - I_i\cdot I_j] = [I_{zi}, 2I_{zi}I_{zj} - I_0^{xij}] = -iI_{yi}I_{xj} + iI_{xi}I_{yj}$$
$$= -\frac{1}{2}\left(I_i^+I_j^- - I_j^+I_i^-\right) = -iI_0^{yij} \neq 0$$

Or directly apply our newly derived commutator for fictitious spin 0 and spin ½ in Eq. 7.9:

$$[I_{zi}, 2I_{zi}I_{zj} - I_0^{xij}] = -[I_{zi}, I_0^{xij}] = -iI_0^{yij}$$

This means:

$$[H_{D_{II}}^{ij}, H_{D_{IS}}^{i}] \tag{7.15}$$
$$= \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2n}^{D_{IS}}(i)\omega_{2m}^{D_{II}}(ij)e^{im\omega_r t_2}e^{in\omega_r t_1}\, S_z\left(iI_{yi}I_{xj} - iI_{xi}I_{yj}\right)$$
$$= \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2n}^{D_{IS}}(i)\omega_{2m}^{D_{II}}(ij)e^{im\omega_r t_2}e^{in\omega_r t_1}\, iS_z I_0^{yij}$$

Here $H_{D_{IS}}^{i}$ stands for heteronuclear dipolar interaction between spin I_i and S.

$$[H_{D_{II}}^{ij}, H_{csa}^{i}] \tag{7.16}$$
$$= \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2n}^{csa}(i)\omega_{2m}^{D_{II}}(ij)e^{im\omega_r t_2}e^{in\omega_r t_1}\left(iI_{yi}I_{xj} - iI_{xi}I_{yj}\right)$$
$$= \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2n}^{csa}(i)\omega_{2m}^{D_{II}}(ij)e^{im\omega_r t_2}e^{in\omega_r t_1}\, iI_0^{yij}$$

Here H_{csa}^{i} stands for the csa of spin I_i.

$$[H_{D_{II}}^{ij}, H_{cs}^{i}] \tag{7.17}$$

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{iso} e^{im\omega_r t_2} \left(iI_{yi}I_{xj} - iI_{xi}I_{yj}\right) = \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{iso} e^{im\omega_r t_2}\, iI_0^{yij}$$

Here H_{cs}^{i} stands for the isotropic chemical shift of spin I_i.

$$\left[H_{D_{II}}^{ij}, H_J^{IS}\right] \tag{7.18}$$

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} 2\pi J_i^{IS} e^{im\omega_r t_2}\, S_z\left(iI_{yi}I_{xj} - iI_{xi}I_{yj}\right) = \sum_{\substack{m=-2\\ m\neq 0}}^{2} 2\pi J_{ij}^{IS} e^{im\omega_r t_2}\, iS_z I_0^{yij}$$

Here H_J^{IS} stands for the heteronuclear J coupling between spin I_i and S.

c. For homonuclear J coupling $H_{Homo}^{J} = 2\pi J^{II} I_i \cdot I_j$, its commutation with another homonuclear J coupling pair sharing one common spin is not zero. The proof is actually part of the proof above in Eq. 7.11 for homonuclear dipolar interactions:

$$\left[H_{J_{II}}^{ij}, H_{J_{II}}^{ik}\right] = \left[I_i \cdot I_j, I_i \cdot I_k\right] = i\left(-I_0^{yij} + I_0^{yik} - I_0^{yjk}\right) \tag{7.19}$$

With the spatial part of Hamiltonian, we have:

$$\left[H_{J_{II}}^{ij}, H_{J_{II}}^{ik}\right] = 4\pi^2 J_{II}^{ij} J_{II}^{ik}\, i\left(-I_0^{yij} + I_0^{yik} - I_0^{yjk}\right) \tag{7.20}$$

d. Following Eq. 7.9, it is also easy to see the commutation of homonuclear J couplings with chemical shielding, isotropic chemical shift, heteronuclear dipolar interaction and J coupling are not zero, if they share a common spin I_i:

$$\left[H_\Lambda(i), H_{J_{II}}^{ij}\right] = \left[I_{zi}, I_i \cdot I_j\right] = \left[I_{zi}, I_0^{xij} + I_{zi}I_{zj}\right] = iI_0^{yij}$$

So this means:

$$\left[H_{cs}^{i}, H_{J_{II}}^{ij}\right] = 2\pi J_{II}^{ij} \omega_{iso}\left[I_{zi}, I_i \cdot I_j\right] = \left[I_{zi}, I_0^{xij} + I_{zi}I_{zj}\right] = i2\pi J_{II}^{ij} \omega_{iso} I_0^{yij} \tag{7.21}$$

$$\left[H_{csa}^{i}, H_{J_{II}}^{ij}\right] = \sum_{\substack{m=-2\\ m\neq 0}}^{2} 2\pi J_{II}^{ij} \omega_{2m}^{csa}(i) e^{im\omega_r t_2}\, iI_0^{yij} \tag{7.22}$$

$$\left[H_{J_{IS}}^{i}, H_{J_{II}}^{ij}\right] = 4\pi^2 J_{IS}^{i} J_{II}^{ij}\, iS_z I_0^{yij} \tag{7.23}$$

$$\left[H_{D_{IS}}^{i}, H_{J_{II}}^{ij}\right] = \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{D_{IS}} e^{im\omega_r t_2}\, S_z iI_0^{yij} \tag{7.24}$$

e. Homonuclear J coupling obviously doesn't commute with homonulcear dipolar interaction, if they share a common spin I_i:

$$[H_{J_{II}}^{ij}, H_{D_{II}}^{ik}] = [I_i \cdot I_j, 3I_{zi}I_{zk} - I_i \cdot I_k] = -3I_{zk}[I_{zi}, I_i \cdot I_j] - [I_i \cdot I_j, I_i \cdot I_k] \tag{7.25}$$

$$= -3I_{zk}(iI_{yi}I_{xj} - iI_{xi}I_{yj})$$

$$-[iI_{xi}(I_{yj}I_{zk} - I_{zj}I_{yk}) + iI_{yi}(I_{zj}I_{xk} - I_{xj}I_{zk}) + iI_{zi}(I_{xj}I_{yk} - I_{yj}I_{xk})]$$

$$= iI_{xi}(2I_{yj}I_{zk} + I_{zj}I_{yk}) - iI_{yi}(I_{zj}I_{xk} + 2I_{xj}I_{zk}) - iI_{zi}(I_{xj}I_{yk} - I_{yj}I_{xk})$$

$$= -3I_{zk}\frac{1}{2}(I_i^+I_j^- - I_j^+I_i^-) + \frac{1}{2}(I_i^+I_j^- - I_j^+I_i^-)I_{zk} - \frac{1}{2}(I_i^+I_k^- - I_k^+I_i^-)I_{zj} + \frac{1}{2}(I_j^+I_k^- - I_k^+I_j^-)I_{zi}$$

$$= -(I_i^+I_j^- - I_j^+I_i^-)I_{zk} - \frac{1}{2}(I_i^+I_k^- - I_k^+I_i^-)I_{zj} + \frac{1}{2}(I_j^+I_k^- - I_k^+I_j^-)I_{zi}$$

$$= -2iI_0^{yij}I_{zk} - iI_0^{yik}I_{zj} + iI_0^{yjk}I_{zi}$$

Or if we apply our newly derived spin ½ and spin 0 commutation relationship:

$$[I_i \cdot I_j, 3I_{zi}I_{zk} - I_i \cdot I_k] = [I_{zi}I_{zj} + I_0^{xij}, 2I_{zi}I_{zk} - I_0^{xik}] = -[I_{zi}, I_0^{xik}]I_{zj} - 2[I_{zi}, I_0^{xij}]I_{zk} + [I_0^{xij}, I_0^{xik}]$$

$$= -2iI_0^{yij}I_{zk} - iI_0^{yik}I_{zj} + iI_0^{yjk}I_{zi}$$

With the spatial part of Hamiltonians, we have:

$$[H_{J_{II}}^{ij}, H_{D_{II}}^{ik}] \tag{7.26}$$

$$= \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{D_{IS}} e^{im\omega_r t_1} (-2iI_0^{yij}I_{zk} - iI_0^{yik}I_{zj} + iI_0^{yjk}I_{zi})$$

f. Note that homonuclear J coupling commutes with homonulcear dipolar interaction of the same pair of nuclei:

$$[H_{J_{II}}^{ij}, H_{D_{II}}^{ij}] = [I_i \cdot I_j, 3I_{zi}I_{zj} - I_i \cdot I_j] = [I_i \cdot I_j, 3I_{zi}I_{zj}] = [I_0^{xij} + I_{zi}I_{zj}, 3I_{zi}I_{zj}]$$

$$= 3[I_{xi}I_{xj}, I_{zi}I_{zj}] + 3[I_{yi}I_{yj}, I_{zi}I_{zj}] = 3I_{xi}I_{xj}I_{zi}I_{zj} - 3I_{zi}I_{zj}I_{xi}I_{xj} + 3I_{yi}I_{yj}I_{zi}I_{zj} - 3I_{zi}I_{zj}I_{yi}I_{yj}$$

Recall $I_iI_j = \frac{i}{2}\hbar\varepsilon_{ijk}I_k$ (Here subscript means spin components $i, j, k = x, y, z$, not different spin i, j, k),

$$= -\frac{3}{4}I_{yi}I_{yj} + \frac{3}{4}I_{yi}I_{yj} - \frac{3}{4}I_{xi}I_{xj} + \frac{3}{4}I_{xi}I_{xj} = 0$$

So this implies

$$[I_0^{xij}, I_{zi}I_{zj}] = 0 \tag{7.27}$$

In the above derivations, the components and the nucleus index of fictitious spin operators are in superscript positions, opposite to the single spin ½ nuclei, please note that.

What do these cross terms imply?

They all give rise to “new” recoupled interactions: the spatial part are the product of the spartial part of interactions involved in the cross terms, and the spin parts are all spin 0(zero quantum coherence) operators of involved nuclei, plus some spin z of the third spin involved, if there is.

Secondly, all incomputable cross terms all involve a term I_0^{yij}. It is a spin flip-flop interaction between spin pair I_i and I_j. It corresponds to transitions between spin up and down states at I_i and I_j pair simultaneously, thus to change the polarization (which is the magnetic moment, and local field produced by the spins), and forfeits the perfect cancellation of magnetic field by MAS. At the same time, it activates the decoherence process for relaxation.

Well, you may say, hold on, hold on! Yeah, there is an I_i spin flip up coupled with I_j flop down, but the I_0^{yij} also has its complex conjugate term, the I_i spin flop down and I_j spin flip up, which should return the states back to the original situation at the same time. So these two terms cancel each other.

If there is the case, how would this change the local polarization and activates spin diffusion?

Yeah, you are right about the cross term. But here are two subtleties not stated explicitly.

First of all, all these actions have their corresponding probability. In computation, we have to account this probability by statistics, which in the sense of density matrix theory, is to couple the commutator with the corresponding availability of states: the product of the spins in the initial states and available positions in the finial states. For instance, to transitions from a spin down to spin up, we need to multiply the populations in spin down states with the available positions in spin up states. Making sense, right? So naturally with a polarized spin, we will have higher chance to reverse the polarization, thus the tendency of decreasing the polarization is higher than enhancing the polarization, thus the relaxation process is normally activated by this process.

Secondly, yeah, we do have the complex conjugate term that seems to cancel the effect. In addition to the weight factor of initial and final states, there should be an implicit concept of time here. But what is time? Is there a true simultaneousness?

The following statements are just my own personal understanding, since I am no expert on quantum mechanics, it could be very absurd or wrong, so please read it with a grain of salt. In quantum mechanics, I don't think there is a true sense of time here. Time is a conjugate parameter to energy in quantum mechanics, just like position to momentum in the uncertainty principle. However, unlike position, momentum and energy which have their corresponding quantum mechanical operators, time does not have a defined quantum mechanical operator. This means time is not quantized (well, you may argue that the finest time is correlated to the Plank constant, which reflects the initial big bang state of the universe)! Time is not clearly defined! And time cannot be accurately measured!

What? You can't say that! You tell me my 100 k Swiss watch cannot tell me what time it is? You must be out of your mind!

Well, time is still a classical parameter in quantum mechanics (a bug, maybe?) How can we say two things happen simultaneously? How can you define two actions take place SIMULTANEOUSLY? I don't think there is a true sense of simultaneous action. For example, think about photo electric effect, does the absorption of photon and the release of electron take place simultaneous? There must be a differentiation of action sequence in time, but that is not encoded in our cross terms. So what I want to say is, at a second layer of understanding, in addition to the unequal probability of a spin to flip than flop as indicated by the I_0^{yij} operator, there is also an difference in their order of action. Combined together, they randomize the local polarization/magnetization, forfeits the perfect cancellation of magnetic field by MAS, and activate the spin/polarization diffusion process.

I hope this long paragraph of rambling helps to clarify the physics picture behind the theoretical derivation. It is very important to know the derivation, if you can. But it is more important to establish the correct physical picture. The physical picture is the motivation for our derivation, so we understand thoroughly the mechanism of the process by the rigorous mathematical logics. But we could easily get lost in these lengthy derivation and formula if we don't use it to light up our physical picture.

Therefore, if there is no RF irradiation/decoupling and only MAS is present, these non-vanishing cross terms will produce non-zero first order average over a complete MAS rotation period. Their effect can be approximated by the Magnus expansion in Eq. 5.45, to be represented by time-independent terms at different orders of approximation:

$$H(t) = H^0 + H^1 + H^2 + \cdots$$

$$H^0 = \frac{\omega}{2\pi}\int_0^{t=\frac{2\pi}{\omega}} H(t)dt$$

$$H^1 = -\frac{i}{2t\hbar}\int_0^{t=\frac{2\pi}{\omega}} dt_2 \int_0^{t_2} dt_1 [H(t_2), H(t_1)]$$

$$H^2 = \frac{1}{6t\hbar^2}\int_0^{t=\frac{2\pi}{\omega}} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \, \{[H(t_3),[H(t_2),H(t_1)]] + [H(t_1),[H(t_2),H(t_3)]]\}$$

For those individual interactions with Hamiltonians commutable with themselves and with others, it is easy to see their average over different orders are zero, in the presence of MAS, and thus won't contribute to linewidth, since linewidth is proportional to the convolution of H^i.

For homonuclear dipolar interaction, we can see the $H^0 = 0$ since the MAS gives rise to the spatial part $\exp(im\omega_r t)$. However, H^1 and higher orders are no longer zero. We already derived the spin part of the commutator. The complete commutator should be as shown in Eq. 7.14:

$$\left[H_{D_{II}}^{ij}(t_2), H_{D_{II}}^{ik}(t_1)\right] \tag{7.29}$$

$$= \left[\left(3I_{zi}I_{zj} - I_i \cdot I_j\right) \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2,m}^{D_{ij}}\, exp(im\omega_r t_2), \left(3I_{zi}I_{zk} - I_i \cdot I_k\right) \sum_{\substack{n=-2 \\ n\neq 0}}^{2} \omega_{2,n}^{D_{ik}}\, exp(in\omega_r t_1)\right]$$

$$= \sum_{\substack{m,n=-2 \\ m,n\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_{2,m}^{D_{ij}} \exp[i(m\omega_r t_2 + n\omega_r t_1)] \left[3I_{zi}I_{zj} - I_i \cdot I_j, 3I_{zi}I_{zk} - I_i \cdot I_k\right]$$

$$= [H_{homo}, H_{homo}] \sum_{\substack{m,n=-2 \\ m,n\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_{2,m}^{D_{ij}} \exp[i(mt_2 + nt_1)\omega_r]$$

Here we use

$$[H_{homo}, H_{homo}] = \left[3I_{zi}I_{zj} - I_i \cdot I_j, 3I_{zi}I_{zk} - I_i \cdot I_k\right]$$

All parts are not time-dependent, except the $\exp[i(mt_2 + nt_1)\omega_r]$, so we can evaluate just the time-dependent $\exp[i(mt_2 + nt_1)\omega_r]$ in the first order Magnus expansion:

$$-\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \int_0^{t_2} dt_1 \exp[i(mt_2 + nt_1)\omega_r]$$

$$= -\frac{i}{2t}\frac{1}{in\omega_r}\int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \{\exp[i(m+n)\omega_r t_2] - \exp[im\omega_r t_2]\}$$

$$= \frac{i\omega_r}{4\pi n(m+n)\omega_r^2}\{\exp\left[i(m+n)\omega_r\frac{2\pi}{\omega_r}\right]-1\}$$

Only when $m+n=0$ will the integral be nonzero. At $n=-m$, we apply the L'Hopital Rule:

$$= \frac{1}{2m\omega_r}$$

So:

$$H^1\{[H_{D_{II}}^{ij}(t_2), H_{D_{II}}^{ik}(t_1)]\} = [H_{homo}, H_{homo}]\frac{1}{\omega_r}\sum_{\substack{m=-2\\m\neq 0}}^{2}\omega_{2,-m}^{D_{ik}}\omega_{2,m}^{D_{ij}}\frac{1}{2m} \tag{7.30}$$

Here we can see that the magnitude of the commutator H^1 is inversely proportional to the MAS speed ω_r. So the linewidth $\sim\frac{1}{\omega_r}$ with MAS in the absence of RF decoupling.

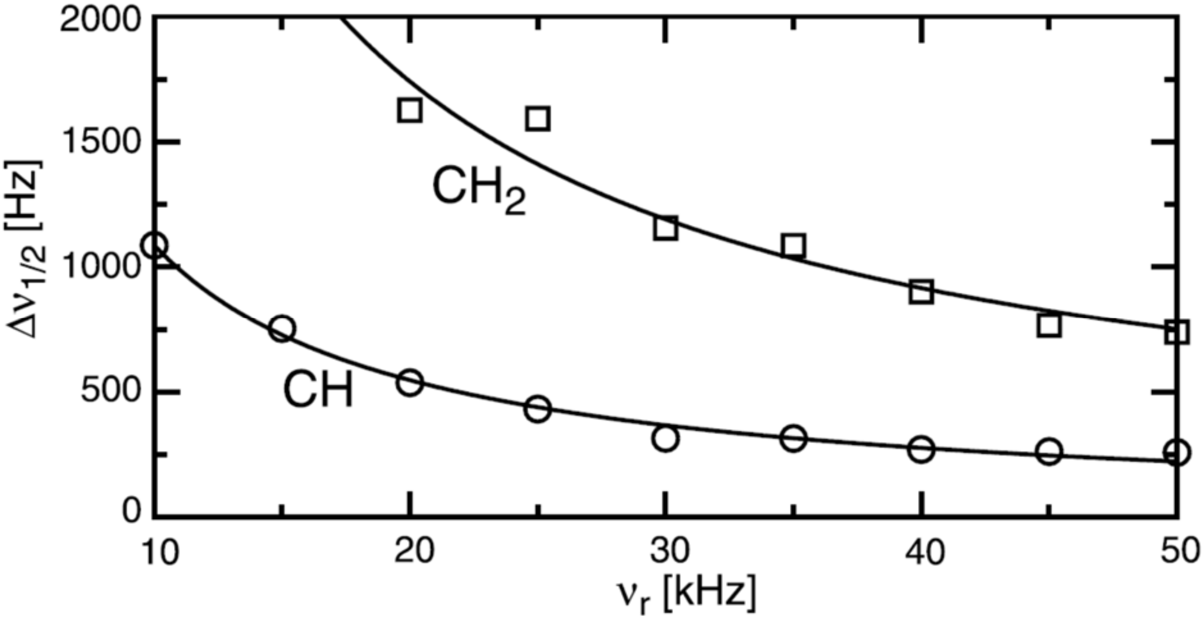


Figure 7.1. Linewidth (FWHM) of the CH2 group of the selective 2-13C labeled glycine and the CH group of selective 2-13C labeled analine vs. MAS spinning speed. Adapted from reference M. Ernst, A. Samoson, B.H. Meier, Chem. Phys. Lett. 348, 293 (2001).

For the cross terms between interactions with a Hamiltonian involving one common I_{zi} spin operator with the homonuclear dipolar interaction, such as chemical shielding tensor, heteronuclear dipolar interaction, they have similar characters in the format of their Hamiltonian. We will just take the chemical shielding as an example:

$$\left[H_{csa}^{i}(t_2), H_{D_{II}}^{ik}(t_1)\right] = \left[(I_{zi}) \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2,m}^{cs_i}\, exp(im\omega_r t_2), (3I_{zi}I_{zk} - I_i \cdot I_k) \sum_{\substack{n=-2\\ n\neq 0}}^{2} \omega_{2,n}^{D_{ik}}\, exp(in\omega_r t_1)\right]$$

$$= \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_{2,m}^{cs_i} \exp[i(m\omega_r t_2 + n\omega_r t_1)]\, [I_{zi}, 3I_{zi}I_{zk} - I_i \cdot I_k]$$

$$= [H_{csa}, H_{homo}] \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_{2,m}^{cs_i} \exp[i(mt_2 + nt_1)\omega_r]$$

Here we use:

$$[H_{csa}, H_{homo}] = [I_{zi}, 3I_{zi}I_{zk} - I_i \cdot I_k]$$

At this step, we can repeat the remaining derivation of averaging over the period of rotation just like our derivation for the homonuclear-homonuclear crossing term above. If you go through the integration, you will also find:

$$H^1\{\left[H_{csa}^{i}(t_2), H_{D_{II}}^{ik}(t_1)\right]\} = [H_{cs}H_{homo}] \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_{2,m}^{cs_i} \frac{1}{2n\omega_r} \tag{7.31}$$

Homework: note that for the cross terms with isotropic chemical shift, isotropic parts of hetero and homonuclear J couplings, we will not have the time-dependent terms $\omega_{2,m}^{\Lambda_1}$. In stead, we have:

$$H^1\{\left[H_{J}^{i}(t_2), H_{D_{II}}^{ik}(t_1)\right]\} = \left[H_J, H_{homo}\right] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2,n}^{D_{ik}} 2\pi J \left\{-\frac{i\omega_r}{4\pi} \int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \int_0^{t_2} dt_1 \exp[in\omega_r t_1]\right\}$$

$$H^1\{\left[H_{cs}^{i}(t_2), H_{D_{II}}^{ik}(t_1)\right]\} = [H_{cs}, H_{homo}] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_0 \delta_{iso} \left\{-\frac{i\omega_r}{4\pi} \int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \int_0^{t_2} dt_1 \exp[in\omega_r t_1]\right\}$$

After integration, you can show that

$$H^1\{\left[H_{J}^{i}(t_2), H_{D_{II}}^{ik}(t_1)\right]\} = \left[H_J H_{homo}\right] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2,n}^{D_{ik}} 2\pi J \left[-\frac{1}{m\omega_r}\right] \tag{7.32}$$

$$H^1\{\left[H_{cs}^{i}(t_2), H_{D_{II}}^{ik}(t_1)\right]\} = \left[H_{cs^{iso}} H_{homo}\right] \sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2,n}^{D_{ik}} \omega_0 \delta_{iso} \left[-\frac{1}{m\omega_r}\right] \tag{7.33}$$

I will leave the detailed computation as a homework.

There is a negative sign relative to cross terms of homonuclear dipolar interaction with any interactions exhibiting explicit time dependence on MAS, carrying their own $\exp[im\omega_r t]$ in their Hamiltonians.

We note the common terms in all cross terms $\frac{1}{m\omega_r}$. As we will show later in Floquet theory, this corresponds to a common term $\frac{1}{(m_{u0}-n_{v0})\omega_r}$, where $m_{u0}\ and\ n_{v0}$ are the respective index of the exponential frequency dependent terms.

Combine all terms we have:

$$H^1 = \frac{1}{\omega_r}\sum_{\substack{m=-2\\ m\neq 0}}^{2}\frac{\pi}{m}\sum_{\Lambda_1,\Lambda_2}\omega_{2,m}^{\Lambda_1}\{\omega_{2,-m}^{\Lambda_1}\left[H_{\Lambda_1}H_{\Lambda_2}\right] - 2J\,[H_J H_{\Lambda_1}]\} \tag{7.34}$$

Combined, our derivation just illustrates that all the non-zero commutator scales with $\frac{1}{\omega_r}$, and the linewidth should decrease proportional to $\frac{1}{\omega_r}$ when we perform MAS. This was shown experimentally by Ernst and others, in Fig. 7.1.

Note that for the Magus expansion approximation to be true (convergence condition), we have to limit the integration over small intervals, such that the multiplication of the time integral with the magnitude of the crossing terms is smaller than π.

So a natural follow-up question is, how could we say these cross terms are just perturbations?

Let's we take the CH group in 2-^{13}C labeled Alanine (Fig. 7.1) as an example, the chemical shielding of the C-apha is 50.9 ppm (Chaohui Ye et al. Magnetic Resonance in Chemistry 31, 699-704 (1993)), which scales with magnetic field. At 600 MHz field, it can be about 7.635 kHz. However, the ^{13}C-^{13}C homonulcear dipolar interaction between nearest ^{13}C-alpha sites in neighboring molecule would be very small, so the contribution to linewidth from them will be negligible. Meanwhile, the heteronuclear dipolar interaction between ^{1}H-alpha and ^{13}C-alpha is about 21.5 kHz as we computed earlier in Sect. 3.4. Homonuclear J coupling can be as strong as 150 Hz. The ^{1}H-alpha to its closest proton neighbor in the methyl group is about 2.5 Å. So the ^{1}H-^{1}H dipolar interaction is ~ 7.686 kHz. So the dominant cross terms to ^{13}C linewidth should be the ^{1}H-^{1}H homonuclear dipolar interactions and ^{1}H-^{13}C heteronuclear dipolar interaction.

According to the Magnus expansion:

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega}} dt_2\int_0^{t_2}[H(t_2), H(t_1)]dt_1$$

Here we can insert the cross terms computed above in Eq. 7.15:

$$\left[H_{D_{II}}^{ij}, H_{D_{IS}}^{i}\right] = \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2}\omega_{2n}^{D_{IS}}(ij)\,\omega_{2m}^{D_{II}}(ij)\,e^{im\omega_r t_2}e^{in\omega_r t_1}\, iS_z I_0^{yij}$$

To evaluate the size of the spin part of the cross terms, we need to transform into the rotating frame:

$$\begin{aligned} &e^{i\omega_j I_{zj}t}e^{i\omega_i I_{zi}t}I_0^{yij}e^{-i\omega_i I_{zi}t}e^{-i\omega_j I_{zj}t}\\ &=\frac{1}{2i}e^{i\omega_j I_{zj}t}e^{i\omega_i I_{zi}t}(I_i^+I_j^- - I_j^+I_i^-)e^{-i\omega_i I_{zi}t}e^{-i\omega_j I_{zj}t}\end{aligned} \tag{7.35}$$

Recall the relation in Eq. 4.60:

$$\exp(-i\phi I_z)\, I^{\pm} \exp(i\phi I_z) = \exp(\mp i\phi) I^{\pm}$$

We have:

$$= \frac{1}{2i}\left(e^{-i(\omega_i-\omega_j)t} I_i^+ I_j^- - e^{i(\omega_i-\omega_j)t} I_j^+ I_i^-\right) \tag{7.36}$$

It produce no diagonal terms in the eigenstates of I_{zi} or I_{zj}. According to the second order perturbation theory,

$$\langle I_i^+ I_j^- \rangle = \sum_{k\neq n} \frac{\langle k|I_i^+ I_j^-|n\rangle\langle n|I_i^+ I_j^-|k\rangle}{E_n - E_k} \tag{7.37}$$

Here $|k\rangle = \beta_i\alpha_j$ and $|n\rangle = \alpha_i\beta_j$, where α and β are the spin up and down states of two dipolar coupled protons, since now we work with two coupled ^{1}H (nearest methyl group and ^{1}H –alpha) and ^{13}C-alpha system. Therefore,

$$E_n - E_k = \omega_{iso}^i - \omega_{iso}^j;\ \langle I_i^+ I_j^- \rangle = \frac{1}{\omega_{iso}^i - \omega_{iso}^j}$$

$$\exp(-i\phi I_z)\, I^{\pm} \exp(i\phi I_z) = \exp(\mp i\phi)\, I^{\pm} = \frac{1}{2i} \times \frac{1}{\omega_{iso}^i - \omega_{iso}^j}\left[e^{-i(\omega_i-\omega_j)t} + e^{i(\omega_i-\omega_j)t}\right]$$

$$= \frac{-i}{\omega_{iso}^i - \omega_{iso}^j}\cos\left(\omega_i - \omega_j\right)t \tag{7.38}$$

Here the chemical shifts ω_i and ω_j are for H-alpha and H-beta in Alanine are 4.32 and 1.39 ppm, respectively (D.S. Wishart. J. Biomol. NMR 5, 67-81 (1995)). At 600 MHz, $\omega_i - \omega_j = 1.758$ kHz. Compared to MAS period, we can approximate $\cos\left(\omega_i - \omega_j\right)t \sim 1$

Alternatively, we can use the perturbation theory for degenerate system: as now the unperturbed states affected by the $I_i^+ I_j^-$ and $I_j^+ I_i^-$ have the nearly energy (degeneracy) of the eigenstates formed by two spins I and J. The system Hamiltonian is:

$$H(t) = -\omega_{iso}^i I_{zi} - \omega_{iso}^j I_{zj} + \Delta I_i^+ I_j^- + \Delta^* I_j^+ I_i^- U \tag{7.39}$$

In the eigenstates of two coupled spins:

$$H(t) = \begin{array}{c|cccc} & \alpha_i\alpha_j & \alpha_i\beta_j & \beta_i\alpha_j & \beta_i\beta_j \\ \hline \alpha_i\alpha_j & -A-B & 0 & 0 & 0 \\ \alpha_i\beta_j & 0 & -A+B & \Delta^* & 0 \\ \beta_i\alpha_j & 0 & \Delta & A-B & 0 \\ \beta_i\beta_j & 0 & 0 & 0 & A+B \end{array} \tag{7.40}$$

Here $A = \omega_{iso}^i, B = \omega_{iso}^j$, Δ is the coefficient of our commutator. To see the effect of the commutator, we have to compute the perturbation to the eigenvalues by the commutator. Although this is the 4x4 matrix, the perturbation only affects the two states it connect, so practically we just need to diagonalize the subspace spanned by the $\alpha_i\beta_j$ and $\beta_i\alpha_j$, which is the determinant calculation:

$$\begin{array}{c|cc} & \alpha_i\beta_j & \beta_i\alpha_j \\ \hline \alpha_i\beta_j & -A+B-\lambda & \Delta^* \\ \beta_i\alpha_j & \Delta & -B-\lambda \end{array}$$

So we have:

$$(-A+B-\lambda)(A-B-\lambda)-\Delta\Delta^*=0 \qquad (7.41)$$

For simplicity, we assume Δ is real:

$$\lambda^2-(B-A)^2-\Delta^2=0$$
$$\lambda_{1,2}=\pm\sqrt{(B-A)^2+\Delta^2} \qquad (7.42)$$
$$\sim\pm|B-A|(1+\frac{1}{2}\frac{\Delta^2}{(B-A)^2})$$

So we see that the energy levels of the original system will be shifted by the magnitude of the commutator, scaled down by $\frac{1}{|B-A|}$. Recall that $A=\omega_{iso}^{i}, B=\omega_{iso}^{j}$, this means the effect of perturbation will be scaled down by the difference of the isotropic chemical shifts of two sites. This agrees with our earlier computation according to second order perturbation theory. We will see a similar scaling factor in Floquet theory as well.

In addition, Eq. 7.15 also has the time-dependent $e^{im\omega_r t_2}e^{in\omega_r t_1}$ for integration:

$$-\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega}}dt_2\int_0^{t_2}dt_1\, e^{im\omega_r t_2}e^{in\omega_r t_1}=\frac{i}{2t(n+m)\omega_r n\omega_r}(e^{i(m+n)\omega_r t}-1)$$

Apply L'Hopital Rule, when $(n+m)=0$:

$$=\frac{i}{2\omega_r t n\omega_r}(i\omega_r t)=-\frac{1}{2n\omega_r}$$
$$\Delta\sim H^1=\frac{1}{2}\times\frac{1}{2n\omega_r}=\frac{1}{4n\omega_r}[\omega_{2n}^{D_{IS}}(ij)\omega_{-2n}^{D_{II}}(ij)] \qquad (7.43)$$

Assume we are spinning at 20 kHz,

$$\Delta=\frac{(21.5\times 7.686)(kHz)^2}{4\times 20kHz}=4.1312\ kHz$$

Here the chemical shifts for H-alpha and H-beta in Alanine are 4.32 and 1.39 ppm, respectively (D.S. Wishart. J. Biomol. NMR 5, 67-81 (1995)). So, the perturbation to the original energy level is:

$$\Delta E \qquad (7.44)$$
$$=\sqrt{4.1312^2kHz^2+[(4.32-1.39)ppm\times 0.6kHz/ppm]^2}-(4.32-1.39)ppm\times\frac{0.6kHz}{ppm}$$

$$\Delta E = 1.98\ kHz$$

This rough estimation qualitatively agrees with the experimental reported value of ~ 0.75 kHz by Ernst et al. in Chem. Phys. Lett. 348, 293 (2001), shown in Fig. 7.1.

One possible reason for the larger deviation of our estimation could be due to over estimation of the ^{1}H-^{1}H dipolar interaction. The methyl group normally experiences some fast rotation motion, which should attenuate the actual dipolar interaction, and reduce the Δ accordingly. Reversely, we can compare the computed linewidth using the rigid limit dipolar interaction to the observed linewidth to deduce the motion of methyl group (or similar functional motions). Experimentally, recoupled dipolar interaction have been used to measure amide proton and nitrogen tensor to calibrate the ^{1}H-^{15}N motion.

The above estimation also shows that the cross terms are indeed much smaller than the Zeeman interaction, and also justifies as higher order compared with the 21.5 kHz ^{1}H-alpha and ^{13}C-alpha heteronuclear dipolar interaction or ~ 7.686 kHz ^{1}H-^{1}H dipolar interaction, if the MAS speed is faster than the strength of the largest interaction present in the cross terms.

From Fig. 7.1 we also see that the ^{13}C linewidth is still quite broad (~ 250 Hz at 50 kHz MAS) even at very fast MAS. So we need more than just MAS. Next, we would like to understand how RF decoupling pulses modulate linewidth.

7.4 Effect of RF irradiation on linewidth in isolated spin systems.

On this topic, there are a large number of rigorous and thorough discussions in literature from various groups. The following discussion is what I learned from a series of papers by M. Ernst et al.'s: J. Chem. Phys. 105, 3387 (1996), JMR 162, 1-34 (2003), J. Chem. Phys. 130, 114510 (2009), and J. Chem. Phys. 145, 094201 (2016). Here I will try to reiterate some of the essential concepts in detailed steps.

There are two different decoupling situations. One is the strongly coupled system, and the other is the isolated spin system. An example of the first category will be the normal uniformly ^{13}C, ^{15}N labeled protein with all protons. The strong proton dipolar interactions can interfere with our efforts to decouple the ^{1}H-^{13}C heteronuclear interaction due to the interference effect from the cross terms of ^{1}H-^{1}H homonuclear interactions with other interactions. It is one of the major challenge in ssNMR to obtain high-resolution NMR spectrum, and also difficult to analyze by theoretical approach.

In contrast, it is significantly simpler to decouple isolated protons from carbons in real practice, and also easier to analyze in theory, since we don't have to account for the homonuclear dipolar interaction between protons. In solution, the Brownian motion naturally decouples the proton homonuclear dipolar interactions. In solids, we can dilute protons by deuterium labeling. By diluting the protons in the proteins, we attenuate the strong proton homonuclear dipolar coupling network. It helps to achieve more efficient decoupling for resolution and extend relaxation time. The ^{13}C labeling in protein can also be diluted, for example, we can use 1,3/2-^{13}C glycerol or selectively labeled glucose as carbon source for recombinant expression.

Let's look at the system with isolated spins first. We will use perturbation theory to show the mechanism of decoupling in such a system.

We will use spin I to represent proton and spin S to represent carbon/nitrogen. Then the Hamiltonian of the system is:

$$H(t) = H_S^{cs} + H_I^{cs} + H_{Is}^{J} + H_S^{CSA}(t) + H_I^{CSA}(t) + H_{IS}^{D}(t) + H_I^{rf} \qquad (7.45)$$

$$= \omega_S^{iso} S_z + \omega_I^{iso} I_z + 2\pi J S_z I_z + \omega_S^{cs}(t) S_z + \omega_I^{cs}(t) I_z + \omega_{IS}^{D}(t) 2 S_z I_z + \omega_1 I_x$$

Essentially the Hamiltonian exhibits the typical chemical shifts of spin I and spin S, with their respective CSA, the heteronuclear J and dipolar couplings and RF irradiation applied to the I spins.

Again, the dominant interactions are the Zeeman interactions for spin I and spin S. As we are treating the system with the coupling between spin I and spin S, we can use the outer product of the eigenstates of spin I and spin S as the basis.

$$H(t) = \frac{1}{2} \begin{array}{c|cccc} & \alpha_S\alpha_I & \alpha_S\beta_I & \beta_S\alpha_I & \beta_S\beta_I \\ \hline \alpha_S\alpha_I & A+B+C & \omega_1 & 0 & 0 \\ \alpha_S\beta_I & \omega_1 & A-B-C & 0 & 0 \\ \beta_S\alpha_I & 0 & 0 & -A-B+C & \omega_1 \\ \beta_S\beta_I & 0 & 0 & \omega_1 & -A+B-C \end{array} \tag{7.46}$$

We put $\frac{1}{2}$ in front of the matrix as it is the co-factor of eigenvalues I_z or S_z. Note if we are to account for homonuclear dipolar interaction between protons, we can do so, but this will at least expand the corresponding matrix from 4 by 4 to 8 by 8.

Here I laid out the spin states for two nuclei explicitly along the top and left of the matrix, so we can follow the physical meaning of various terms in Hamiltonian. $C = \omega_I^{iso} + \omega_I^{cs}(t)$, $B = 2\pi J + 2\omega_{IS}^{D}(t)$, $\mathrm{A} = \omega_S^{iso} + \omega_S^{cs}(t)$.

Now we just have to diagonalize the matrix to find out the eigenstates and eigen-energies, which should manifest how the Zeeman levels of the original isolated two-spin system are affected by various interactions between the spins and RF irradiations. So now the problem becomes a simple linear algebra procedure to find eigenvalues and eigenstates:

$$det \begin{pmatrix} A+B+C-2\lambda & \omega_1 & 0 & 0 \\ \omega_1 & A-B-C-2\lambda & 0 & 0 \\ 0 & 0 & -A-B+C-2\lambda & \omega_1 \\ 0 & 0 & \omega_1 & -A+B-C-2\lambda \end{pmatrix} = 0 \tag{7.47}$$

We get the determinant of this 4x4 matrix to be:

$$(A+B+C-2\lambda)(A-B-C-2\lambda)[(-A-B+C-2\lambda)(-A+B-C-2\lambda) - \omega_1^2] \\ -\omega_1^2[(-A-B+C-2\lambda)(-A+B-C-2\lambda) - \omega_1^2] = 0 \tag{7.48}$$

$$[(A+B+C-2\lambda)(A-B-C-2\lambda) - \omega_1^2][(-A-B+C-2\lambda)(-A+B-C-2\lambda) - \omega_1^2] = 0$$

$$[(A-2\lambda)^2 - (B+C)^2 - \omega_1^2][(-A-2\lambda)^2 - (B-C)^2 - \omega_1^2] = 0$$

Solve this and we get four energy levels:

$$\lambda_{1,2} = \frac{1}{2}A \pm \frac{1}{2}\sqrt{(B+C)^2 + \omega_1^2} \tag{7.49}$$

$$= \frac{1}{2}[\omega_S^{iso} + \omega_S^{cs}(t)] \pm \frac{1}{2}\sqrt{\{[2\pi J + 2\omega_{IS}^{D}(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]\}^2 + \omega_1^2}$$

$$= \frac{1}{2}[\omega_S^{iso} + \omega_S^{cs}(t)] \pm \frac{\omega_1}{2}\sqrt{\{\frac{[2\pi J + 2\omega_{IS}^{D}(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1}$$

$$\lambda_{3,4} = -\frac{1}{2}A \pm \frac{1}{2}\sqrt{(B - C)^2 + \omega_1^2} \tag{7.50}$$

$$= -\frac{1}{2}[\omega_S^{iso} + \omega_S^{cs}(t)] \pm \frac{1}{2}\sqrt{\{[2\pi J + 2\omega_{IS}^{D}(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]\}^2 + \omega_1^2}$$

$$= -\frac{1}{2}[\omega_S^{iso} + \omega_S^{cs}(t)] \pm \frac{\omega_1}{2}\sqrt{\{\frac{[2\pi J + 2\omega_{IS}^{D}(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1}$$

We can also plug in the eigenvalues back into the matrix to get eigenstates:

$$\begin{array}{cccc} \alpha_S\alpha_I & \alpha_S\beta_I & \beta_S\alpha_I & \beta_S\beta_I \\ \end{array}$$
$$\begin{pmatrix} A + B + C - \lambda & \omega_1 & 0 & 0 \\ \omega_1 & A - B - C - \lambda & 0 & 0 \\ 0 & 0 & -A - B + C - \lambda & \omega_1 \\ 0 & 0 & \omega_1 & -A + B - C - \lambda \end{pmatrix}\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = 0 \tag{7.51}$$

You will have:

$$(A + B + C - \lambda)a + b\omega_1 = 0$$

$$(A - B - C - \lambda)b + a\omega_1 = 0$$

$$(-A - B + C - \lambda)c + d\omega_1 = 0$$

$$(-A + B - C - \lambda)d + c\omega_1 = 0$$

Solve these simultaneous equations, we have:

$$\begin{gathered} a = [\omega_1^2 - (A - \lambda)^2 + (B + C)^2](-A + B + C + \lambda)/\omega_1 \\ b = \omega_1^2 - (A - \lambda)^2 + (B + C)^2 \\ c = [\omega_1^2 - (A + \lambda)^2 + (B + C)^2](A - B + C + \lambda)/\omega_1 \\ d = \omega_1^2 - (A + \lambda)^2 + (B + C)^2 \end{gathered} \tag{7.52}$$

You can plug in each λ value, and obtain corresponding eigenstate (a, b, c, d). Find their norm and compute relative weight to each other. It will give us the respective intensity of the transition. I will leave this as a homework for you to complete:

$$I_{1,2} = \frac{1}{4} - \frac{1}{4}\{1 + \frac{4[2\pi J + 2\omega_{IS}^{D}(t)]\omega_1^2}{([2\pi J + 2\omega_{IS}^{D}(t)]^2 + \left[\omega_I^{iso} + \omega_I^{cs}(t)\right]^2 + \omega_1^2)^2}\}^{-1/2} \tag{7.53}$$

$$I_{3,4} = \frac{1}{4} + \frac{1}{4}\{1 + \frac{4[2\pi J + 2\omega_{IS}^{D}(t)]\omega_1^2}{([2\pi J + 2\omega_{IS}^{D}(t)]^2 + \left[\omega_I^{iso} + \omega_I^{cs}(t)\right]^2 + \omega_1^2)^2}\}^{-1/2} \tag{7.54}$$

Hence combining Eq. 7.49 and 7.50, we can get the transition frequencies by $\lambda_{1,2} - \lambda_{3,4}$. This gives us four symmetric transitions about the carbon resonance frequency $\omega_S^{iso} + \omega_S^{cs}(t)$:

$$\omega^{1,2}(t) = [\omega_S^{iso} + \omega_S^{cs}(t)] \pm \tag{7.55}$$

$$\frac{\omega_1}{2}[\sqrt{\{\frac{[2\pi J + 2\omega_{IS}^D(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1} + \sqrt{\{\frac{[2\pi J + 2\omega_{IS}^D(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1}]$$

And:

$$\omega^{3,4}(t) = [\omega_S^{iso} + \omega_S^{cs}(t)] \pm \tag{7.56}$$

$$\frac{\omega_1}{2}[\sqrt{\{\frac{[2\pi J + 2\omega_{IS}^D(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1} - \sqrt{\{\frac{[2\pi J + 2\omega_{IS}^D(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1}]$$

We can plug in typical values in protein to get some idea what these solutions mean. Typically, $J_{IS} \sim 150\ Hz$, $\omega_{IS}^D \sim b_{IS} = -\frac{\mu_0}{4\pi}\frac{\gamma_I \gamma_S}{r_{IS}^3} \sim 21.5\ kHz$, $\omega_I^{iso} \sim \omega_I^{cs} \sim$ 10 ppm for amide proton, which is about 6 kHz in 600 MHz field. So when continuous RF irradiation is at 60 kHz or higher, we have $\omega_1 > [2\pi J + 2\omega_{IS}^D(t)] \pm [\omega_I^{iso} + \omega_I^{cs}(t)]$, we can apply Taylor expansion to the square root factors:

$$\sqrt{\{\frac{[2\pi J + 2\omega_{IS}^D(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1} = 1 + \frac{1}{2}\{\frac{[2\pi J + 2\omega_{IS}^D(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2$$

$$\sqrt{\{\frac{[2\pi J + 2\omega_{IS}^D(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 + 1} = 1 + \frac{1}{2}\{\frac{[2\pi J + 2\omega_{IS}^D(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2$$

Hence:

$$\omega^{3,4}(t) = [\omega_S^{iso} + \omega_S^{cs}(t)] \pm$$

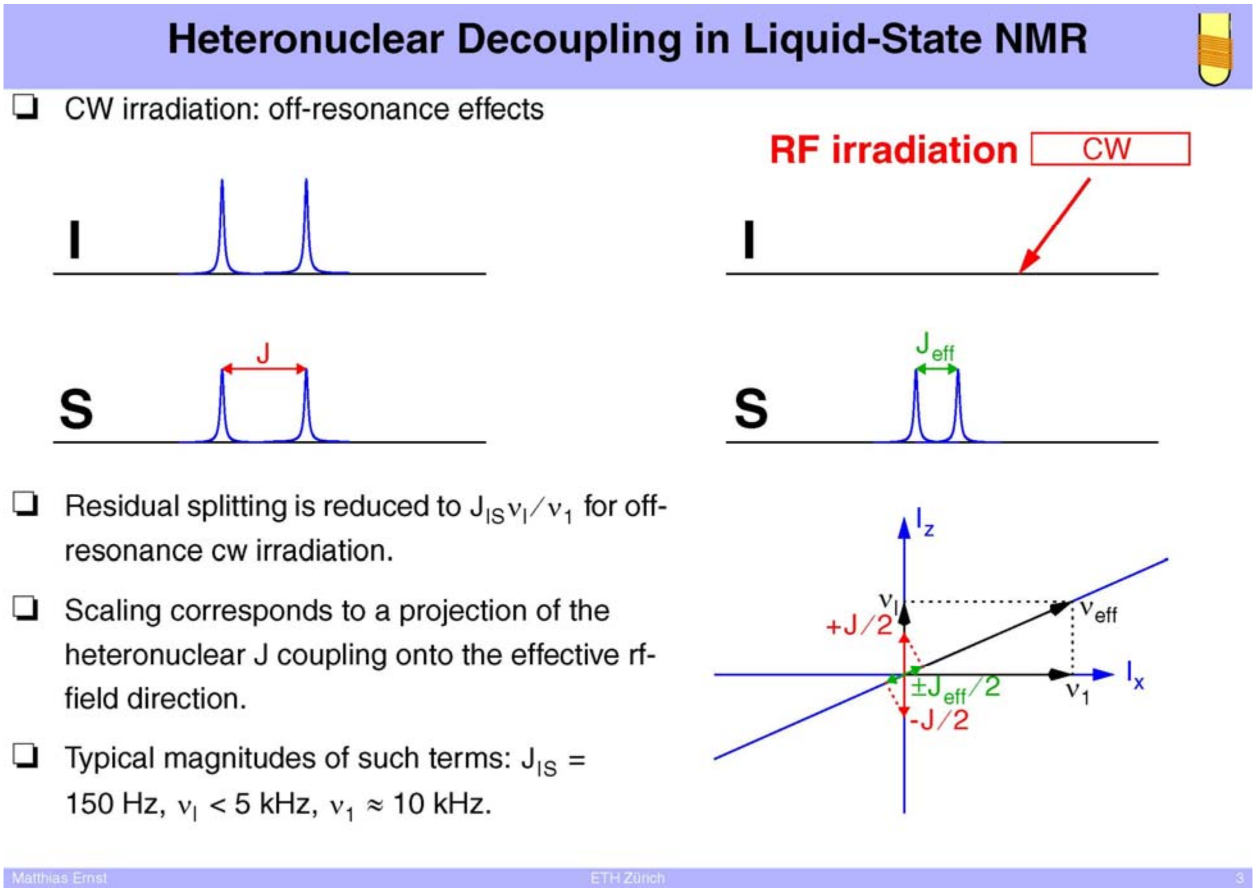
$$\frac{\omega_1}{2}\left[\frac{1}{2}\{\frac{[2\pi J + 2\omega_{IS}^D(t)] + [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2 - \frac{1}{2}\left\{\frac{[2\pi J + 2\omega_{IS}^D(t)] - [\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1}\}^2\right]\right.$$

$$\omega^{3,4}(t) = [\omega_S^{iso} + \omega_S^{cs}(t)] \pm \frac{[2\pi J + 2\omega_{IS}^D(t)][\omega_I^{iso} + \omega_I^{cs}(t)]}{\omega_1} \tag{7.57}$$

Similarly, you can show that:

$$\omega^{1,2}(t) = [\omega_S^{iso} + \omega_S^{cs}(t)] \pm [\omega_1 + \frac{[2\pi J + 2\omega_{IS}^D(t)]^2 + [\omega_I^{iso} + \omega_I^{cs}(t)]^2}{\omega_1}] \tag{7.58}$$

You can apply the same Taylor expansion to the intensity of each transition.



Heteronuclear Decoupling in Liquid-State NMR

☐ CW irradiation: off-resonance effects

☐ Residual splitting is reduced to $J_{IS}\nu_I/\nu_1$ for off-resonance cw irradiation.

☐ Scaling corresponds to a projection of the heteronuclear J coupling onto the effective rf-field direction.

☐ Typical magnitudes of such terms: J_{IS} = 150 Hz, ν_I < 5 kHz, $\nu_1 \approx$ 10 kHz.

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Figure 7.2. Decoupling by continuous wave RF irradiation scales down J coupling split. Adapted from M. Ernst's lecturenote at 2008 ENC, Heteronuclear spin decoupling in Magic Angle Spinning Solid State NMR.

Hence, we can see that $\omega^{1,2}(t)$ are just frequencies corresponding to the side-bands generated by strong decoupling field, at $\sim\omega_1$ away from the original noninteracting chemical shift position $[\omega_S^{iso} + \omega_S^{cs}(t)]$, with diminishing intensity as ω_1 increases.

$\omega^{3,4}(t)$ correspond to the new strong isotropic central transition, with a splitting frequency scaled by ω_1. Particularly, in solution NMR, we just have J coupling. Without RF irradiation, the spin S resonance will exhibit a J splitting due to the J coupling to spin I. This is shown in Fig. 7.2. However, when a continuous wave RF decoupling is applied, the J splitting will become smaller. The above derivation shows the underlying mechanism. The shrinking J splitting is due to the scaling factor:

$$J_{RF} = \frac{[2\pi J + 2\omega_{IS}^{D}(t)]\left[\omega_I^{iso} + \omega_I^{cs}(t)\right]}{\omega_1} \tag{7.59}$$

You can think this scaling as due to the combined effect of resonance offset $\omega_I^{iso} + \omega_I^{cs}(t)$ over ω_1, which is the direction of the effective field in the rotating frame. So essentially it is equivalent to a projection of the heteronuclear interaction onto the effective field direction.

Therefore, under nonzero chemical shift offset and anisotropy, to achieve better decoupling effect, we need larger ω_1, which is limited by our sample condition and hardware capacity. If the sample is hydrated and salty, too strong a RF decoupling will induce significant dielectric heating, $Q = \omega_1 \varepsilon' \varepsilon_0 E^2$, which may burn our precious protein samples. Of course, specially designed low E probe such as those by S. Opella or Peter Gork'ov may alleviate this concern to a certain degree. On the other hand, higher decoupling power also puts more stress on amplifier and probe, so normally we don't go much higher than 100 kHz on proton decoupling.

Meanwhile we can also see the effect of proton anisotropy and chemical shift offset is playing against a better decoupling effect according to the scaling factor. If there were no chemical shift offset(on resonance), J splitting would collapse under continuous RF irradiation, with no requirement on the amplitude of the RF power. However, with continuous wave RF irradiation, we can't satisfy $\omega_I^{iso} = 0$ for all different protons. So continuous wave decoupling does not play very well. That is why phase cycling and frequency shift are adopted in composite pulse decoupling sequences, such as WALTZ, GARP or WURST. They give much better performance by compensating the nonzero chemical shift offset and csa.

7.5 Analysis of RF irradiation on linewidth in the presence of MAS by Average Hamiltonian Theory.

Things are different in our solid state protein samples, since we now have MAS. As we derived in Eq. 5.62 and 5.64, $\omega_{IS}^{D}(t)$ and $\omega_I^{cs}(t)$ are both second rank tensors, while J and ω_I^{iso} remain a scalar. In addition, there are strong proton homonuclear dipolar interactions to be accounted for. To do that, at least we need a system of three coupled spin, two spins I and one spin S, so at least a $2^3 \times 2^3$ matrix is needed to describe such a system, even if we assume all interactions are scalars. You can see quickly the manual analysis will go out of hand if we still attempt the matrix method above.

Intuitively, RF irradiation will decrease the corresponding interaction constant by a factor of 4 in decoupling. How does this come by?

We can still adopt the same approach as our analysis of recoupling, by computing the Hamiltonians in the interaction frame of RF irradiation first, then use the Magnus expansion to derive higher order approximations. But before we do that, let's take a quick estimate of what we get:

$$\begin{aligned}\widetilde{H}^{\Lambda} &= e^{i\hat{H}_1\tau} R(\omega_r\tau, 0,0) \left[T_{\lambda 0}^{\Lambda} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda} \exp(-im\omega_r t) \right] R^{-1}(\omega_r\tau, 0,0) e^{-i\hat{H}_1\tau} \\ &= \sum_{\mu=-\lambda}^{\lambda} T_{\lambda\mu}^{\Lambda}\, e^{-i\mu\alpha(\tau)} d_{\mu 0}^{\lambda}[-\beta(\tau)] \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\Lambda}\, e^{-im\omega_r\tau}\end{aligned}$$

In the lowest order, we just keep $T_{\lambda 0}^{\Lambda}$, due to the dipolar truncation effect. So the time-dependent terms of the spin part of Hamiltonians due to continuous RF irradiation, is accounted for by $d_{00}^{\lambda}[-\beta(t)] = \frac{1}{2}[3\cos^2(\omega_{rf}t) - 1]$, together with the spatial part of $e^{-im\omega_r t}$:

$$\widetilde{H}^{\Lambda}(t) = \int_0^{t=\omega_{sequence}} dt \frac{1}{2}[3\cos^2(\omega_{rf}t) - 1] e^{-im\omega_r t} \tag{7.60}$$

We have two frequencies in the integration. If ω_{rf} is much stronger than ω_r, we can neglect the time dependence by MAS, and integrate just $\frac{1}{2}[3\cos^2(\omega_{rf}t) - 1]$ over the period of ω_{rf}. It will give us $\frac{1}{4}$, which means the interaction is scaled down by a factor of 4 with RF irradiation.

To see the effect of RF irradiation, let's compute all the Hamiltonians in the interaction frame of the RF irradiation. Assume that the RF irradiation is applied along the x axis in the rotating frame. Because the transformation to the interaction frame of RF irradiation only affects the irradiated spin, we can treat isotropic chemical shift and chemical shielding as the same category, heteronuclear dipolar and J coupling as the same category, and homonuclear dipolar and J coupling as the same category. Their representative forms in the interaction frame of RF irradiation are as follow:

$$\widetilde{H}_{cs} = \sum_{m=-2}^{2} \omega_{2m}^{\mathrm{cs}}\, e^{im\omega_r t} e^{i\omega_1 I_x t} I_z e^{-i\omega_1 I_x t} \tag{7.61}$$

$$= \sum_{m=-2}^{2} \omega_{2m}^{\mathrm{cs}}\, e^{im\omega_r t}\left(I_z \cos\omega_1 t + I_y \sin\omega_1 t\right)$$

$$= \sum_{m=-2}^{2} \frac{\omega_{2m}^{\mathrm{cs}}}{2} e^{im\omega_r t}\left[I_z\left(e^{i\omega_1 t} + e^{-i\omega_1 t}\right) - iI_y\left(e^{i\omega_1 t} - e^{-i\omega_1 t}\right)\right]$$

$$= \sum_{m=-2}^{2} \frac{\omega_{2m}^{\mathrm{cs}}}{2} [e^{im\omega_r t} e^{i\omega_1 t}\left(I_z - iI_y\right) + e^{im\omega_r t} e^{-i\omega_1 t}\left(I_z + iI_y\right)]$$

Here we absorb isotropic and anisotropic chemical shift into one expression.

For heteronuclear dipolar coupling:

$$\widetilde{H}_{D_{IS}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{IS}}\, e^{im\omega_r t} S_z e^{i\omega_1 I_x t} I_z e^{-i\omega_1 I_x t} \tag{7.62}$$

$$= \sum_{m=-2}^{2} \omega_{2m}^{D_{IS}}\, e^{im\omega_r t} S_z\left(I_z \cos\omega_1 t + I_y \sin\omega_1 t\right)$$

$$= \sum_{m=-2}^{2} \frac{\omega_{2m}^{D_{IS}}}{2} e^{im\omega_r t}\left[I_z\left(e^{i\omega_1 t} + e^{-i\omega_1 t}\right) - iI_y\left(e^{i\omega_1 t} - e^{-i\omega_1 t}\right)\right]$$

$$= \sum_{m=-2}^{2} \frac{\omega_{2m}^{D_{IS}}}{2} [e^{im\omega_r t} e^{i\omega_1 t}\left(I_z - iI_y\right) + e^{im\omega_r t} e^{-i\omega_1 t}\left(I_z + iI_y\right)]$$

For heteronuclear J coupling, $2\pi J_{IS} I_z S_z$, so there is no summation over different $\omega_{2m}^{\mathrm{IS}}$ or $e^{im\omega_r t}$.

$$\widetilde{H}_{J_{IS}} = 2\pi J_{IS} S_z e^{i\omega_1 I_x t} I_z e^{-i\omega_1 I_x t} \tag{7.63}$$

$$= 2\pi J_{IS} S_z [e^{i\omega_1 t}\left(I_z - iI_y\right) + e^{-i\omega_1 t}\left(I_z + iI_y\right)]$$

For homonuclear J coupling, we have:

$$\widetilde{H}_{J_{II}} = 2\pi J_{II} e^{i\omega_1 I_x t} I_i \cdot I_j e^{-i\omega_1 I_x t} \tag{7.64}$$

$$= 2\pi J_{II}\left(I_{xi}I_{xj} + e^{i\omega_1 I_x t} I_{yi}I_{yj} e^{-i\omega_1 I_x t} + e^{i\omega_1 I_x t} I_{zi}I_{zj} e^{-i\omega_1 I_x t}\right)$$

$$= 2\pi J_{II}\big[I_{xi}I_{xj} + \left(I_{yi}\cos\omega_1 t - I_{zi}\sin\omega_1 t\right)\left(I_{yj}\cos\omega_1 t - I_{zj}\sin\omega_1 t\right) + \left(I_{zi}\cos\omega_1 t + I_{yi}\sin\omega_1 t\right)\left(I_{zj}\cos\omega_1 t + I_{yj}\sin\omega_1 t\right)\big]$$

$$= 2\pi J_{II}\left[I_{xi}I_{xj} + I_{yi}I_{yj}(\cos^2\omega_1 t + \sin^2\omega_1 t) + I_{zi}I_{zj}(\cos^2\omega_1 t + \sin^2\omega_1 t)\right]$$

$$= 2\pi J_{II} I_i \cdot I_j$$

This is as expected that $I_i \cdot I_j$ is a scalar under the simultaneous rotation of two spins.

For homonuclear dipolar coupling:

$$\widetilde{H}_{D_{II}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{II}} e^{im\omega_r t} e^{i\omega_1 I_x t}(3I_{zi}I_{zj} - I_i \cdot I_j) e^{-i\omega_1 I_x t} \tag{7.65}$$

As we showed, $I_i \cdot I_j$ is a scalar under the simultaneous rotation of two spins, we just have to compute the transformation of $I_{zi}I_{zj}$:

$$e^{i\omega_1 I_x t} I_{zi}I_{zj} e^{-i\omega_1 I_x t} = (e^{i\omega_1 I_x t} I_{zi} e^{-i\omega_1 I_x t})(e^{i\omega_1 I_x t} I_{zj} e^{-i\omega_1 I_x t})$$

$$= \left(I_{zi}\cos\omega_1 t + I_{yi}\sin\omega_1 t\right)\left(I_{zj}\cos\omega_1 t + I_{yj}\sin\omega_1 t\right)$$

$$= I_{zi}I_{zj}\cos^2\omega_1 t + I_{yi}I_{yj}\sin^2\omega_1 t + \sin\omega_1 t\cos\omega_1 t\left(I_{zi}I_{yj} + I_{yi}I_{zj}\right)$$

$$= \frac{1}{2}\left(I_{zi}I_{zj} + I_{yi}I_{yj}\right) + \frac{1}{2}\cos 2\omega_1 t\left(I_{zi}I_{zj} - I_{yi}I_{yj}\right) + \frac{1}{2}\sin 2\omega_1 t\left(I_{zi}I_{yj} + I_{yi}I_{zj}\right)$$

$$= \frac{1}{2}\left(I_{zi}I_{zj} + I_{yi}I_{yj}\right) + \frac{1}{4}\left(e^{i2\omega_1 t} + e^{-i2\omega_1 t}\right)\left(I_{zi}I_{zj} - I_{yi}I_{yj}\right) + \frac{1}{4i}\left(e^{i2\omega_1 t} - e^{-i2\omega_1 t}\right)\left(I_{zi}I_{yj} + I_{yi}I_{zj}\right)$$

$$= \frac{1}{2}\left(I_{zi}I_{zj} + I_{yi}I_{yj}\right) + \frac{1}{4}e^{i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} - iI_{zi}I_{yj} - iI_{yi}I_{zj}\right)$$

$$+ \frac{1}{4}e^{-i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} + iI_{zi}I_{yj} + iI_{yi}I_{zj}\right)$$

So we have:

$$\widetilde{H}_{D_{II}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{II}} e^{im\omega_r t}[\frac{3}{2}\left(I_{zi}I_{zj} + I_{yi}I_{yj}\right) - I_i \cdot I_j + \frac{3}{4}e^{i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} - iI_{zi}I_{yj} - iI_{yi}I_{zj}\right)$$

$$+ \frac{3}{4i}e^{-i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} + iI_{zi}I_{yj} + iI_{yi}I_{zj}\right)]$$

$$\widetilde{H}_{D_{II}} = \tag{7.66}$$

$$\sum_{m=-2}^{2} \omega_{2m}^{D_I} e^{im\omega_r t}[\frac{1}{2}\left(I_{zi}I_{zj} + I_{yi}I_{yj} - 2I_{xi}I_{xj}\right) + \frac{3}{4}e^{i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} - iI_{zi}I_{yj} - iI_{yi}I_{zj}\right)$$

$$+\frac{3}{4}e^{-i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} + iI_{zi}I_{yj} + iI_{yi}I_{zj}\right)]$$

Note that the pattern of transformed spin parts of Hamiltonians would look much simpler, if we transform our frame of observation around the y axis by a negative $\frac{\pi}{2}$ (which is to rotate the spin operators a positive $\frac{\pi}{2}$). By that, the original z axis for I spin turns into the x axis, and the original –x axis become the new z axis.

This transformation of reference frame doesn't change any physics, but makes operations on spin operators more convenient. After this swapping of axes, we can exploit the commutation relationships in terms of the fictitious spin 0 operators. In fact, it makes sense to do so, as in the rotating frame, the irradiation of RF acts like spin locking, in the same role as the quantization of spin direction as the external magnetic field.

Under this axis transformation, we essentially apply a $e^{-i\frac{\pi}{2}I_y}$ to transform the perspective of observation. It rotates the z axis to the x axis, and the new x axis is the old –z axis, with the y axis overlapping with the old. This transformation is the same as to apply a reverse transformation $e^{i\frac{\pi}{2}I_y}$ to Hamiltonians. It is the same operation as our transformation to tilted reference frame demonstrated in Sect. 3.2 and 4.12.

Following this transformation, the above computed Hamiltonians become:

$$\widetilde{H}_{csa} = \sum_{\substack{m=-2\\ m\neq 0}}^{2} \frac{\omega_{2m}^{\mathrm{csa}}}{2}\left[e^{im\omega_r t}e^{i\omega_1 t}\left(I_z - iI_y\right) + e^{im\omega_r t}e^{-i\omega_1 t}\left(I_z + iI_y\right)\right]$$

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} \frac{\omega_{2m}^{\mathrm{csa}}}{2}\left[e^{im\omega_r t}e^{i\omega_1 t}\left(-I_x - iI_y\right) + e^{im\omega_r t}e^{-i\omega_1 t}\left(-I_x + iI_y\right)\right]$$

$$= \sum_{\substack{m=-2\\ m\neq 0}}^{2} \frac{\omega_{2m}^{\mathrm{csa}}}{2}\left[-e^{im\omega_r t}e^{i\omega_1 t}\left(I_x + iI_y\right) - e^{im\omega_r t}e^{-i\omega_1 t}\left(I_x - iI_y\right)\right]$$

$$\widetilde{H}_{csa} = \sum_{\substack{m=-2\\ m\neq 0}}^{2} \frac{\omega_{2m}^{\mathrm{cs}}}{2} e^{im\omega_r t}\left[-I^{+}e^{i\omega_1 t} - I^{-}e^{-i\omega_1 t}\right] \tag{7.67}$$

While

$$\widetilde{H}_{cs} = \frac{\omega_{iso}}{2}\left[-I^{+}e^{i\omega_1 t_2} - I^{-}e^{-i\omega_1 t_2}\right] \tag{7.68}$$

And for heteronuclear dipolar interaction:

$$\widetilde{H}_{D_{IS}} = \sum_{m=-2}^{2} \frac{\omega_{2m}^{D_{IS}}}{2}\left[e^{im\omega_r t}e^{i\omega_1 t}\left(I_z - iI_y\right) + e^{im\omega_r t}e^{-i\omega_1 t}\left(I_z + iI_y\right)\right]$$

$$\tilde{H}_{D_{IS}} = \sum_{m=-2}^{2} \frac{\omega_{2m}^{D_{IS}}}{2} S_z e^{im\omega_r t}\left[-I^{+}e^{i\omega_1 t} - I^{-}e^{-i\omega_1 t}\right] \tag{7.69}$$

Similarly we have

$$\tilde{H}_{J_{IS}} = \pi J_{IS} S_z\left[e^{i\omega_1 t}\left(I_z - iI_y\right) + e^{-i\omega_1 t}\left(I_z + iI_y\right)\right]$$

$$\tilde{H}_{J_{IS}} = \pi J_{IS} S_z\left[-I^{+}e^{i\omega_1 t} - I^{-}e^{-i\omega_1 t}\right] \tag{7.70}$$

For the convenience of discussion, in experiments when there are simultaneous irradiations on I and S spin, we will have the heteronuclear dipolar and J coupling as:

$$\tilde{H}_{D_{IS}} = \sum_{m=-2}^{2} \frac{\omega_{2m}^{D_{IS}}}{4} e^{im\omega_r t}\left[-I^{+}e^{i\omega_{1I} t} - I^{-}e^{-i\omega_{1I} t}\right]\left[-S^{+}e^{i\omega_{1S} t} - S^{-}e^{-i\omega_{1S} t}\right] \tag{7.71}$$

$$\tilde{H}_{J_{IS}} = \frac{\pi}{2} J_{IS}\left[-I^{+}e^{i\omega_{1I} t} - I^{-}e^{-i\omega_{1I} t}\right]\left[-S^{+}e^{i\omega_{1S} t} - S^{-}e^{-i\omega_{1S} t}\right] \tag{7.72}$$

We note here the scaling of the interaction constant goes from ½ to ¼, when irradiated spins go from one to two at the same time. This is consistent with our rough estimation earlier estimation in Eq. 7.60.

For the homonuclear dipolar interaction,

$$\tilde{H}_{D_{II}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{II}}\, e^{im\omega_r t} e^{i\frac{\pi}{2}I_y} e^{i\omega_1 I_x t}\left(3I_{zi}I_{zj} - I_i \cdot I_j\right) e^{-i\omega_1 I_x t} e^{-i\frac{\pi}{2}I_y}$$

$$\tilde{H}_{D_{II}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{II}}\, e^{im\omega_r t} e^{i\frac{\pi}{2}I_y}[\frac{1}{2}\left(I_{zi}I_{zj} + I_{yi}I_{yj} - 2I_{xi}I_{xj}\right) + \frac{3}{4}e^{i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} - iI_{zi}I_{yj} - iI_{yi}I_{zj}\right)$$

$$+\frac{3}{4}e^{-i2\omega_1 t}\left(I_{zi}I_{zj} - I_{yi}I_{yj} + iI_{zi}I_{yj} + iI_{yi}I_{zj}\right) - I_i \cdot I_j]\, e^{-i\frac{\pi}{2}I_y}$$

$$= \sum_{m=-2}^{2} \omega_{2m}^{D_{II}}\, e^{im\omega_r t}[\frac{1}{2}\left(I_{xi}I_{xj} + I_{yi}I_{yj} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t}\left(I_{xi}I_{xj} - I_{yi}I_{yj} + iI_{xi}I_{yj} + iI_{yi}I_{xj}\right)$$

$$+\frac{3}{4}e^{-i2\omega_1 t}\left(I_{xi}I_{xj} - I_{yi}I_{yj} - iI_{xi}I_{yj} - iI_{yi}I_{xj}\right) - I_i \cdot I_j]$$

$$= \sum_{m=-2}^{2} \omega_{2m}^{D_{II}}\, e^{im\omega_r t}[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t}\left(I_2^{xij} + iI_2^{yij}\right) + \frac{3}{4}e^{-i2\omega_1 t}\left(I_2^{xij} - iI_2^{yij}\right) - I_i \cdot I_j]$$

Recall $I_2^x = \frac{1}{2}(I^+S^+ + I^-S^-)$, $I_2^y = \frac{1}{2i}(I^+S^+ - I^-S^-)$, we can rearrange the above as:

$$\tilde{H}_{D_{II}} = \tag{7.73}$$

$$\sum_{m=-2}^{2} \omega_{2m}^{D_{II}} e^{im\omega_r t}[\frac{1}{2}(I_0^{xij} - 2I_{zi}I_{zj}) + \frac{3}{4}e^{i2\omega_1 t}I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t}I_i^- I_j^- - I_i \cdot I_j]$$

We see now the advantage of transforming the frame of reference by $e^{i\frac{\pi}{2}I_y}$. All Hamiltonians exhibit a much simpler form. They consist of fictitious spin 0 (zero quantum) and spin 1 (double quantum) operators, which will make our computation of commutator more convenient.

To calculate the evolution of a system using density matrix method, the time-dependent Hamiltonian can be approximated by the Magnus expansion shown in Eq. 5.45:

$$H(t) = H^0 + H^1 + H^2 + \cdots$$

$$H^0 = \frac{\omega}{2\pi}\int_0^{t=\frac{2\pi}{\omega}} H(t)dt$$

$$H^1 = -\frac{i}{2t\hbar}\int_0^{t=\frac{2\pi}{\omega}} dt_2 \int_0^{t_2} dt_1 [H(t_2), H(t_1)]$$

$$H^2 = \frac{1}{6t\hbar^2}\int_0^{t=\frac{2\pi}{\omega}} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \{[H(t_3), [H(t_2), H(t_1)]] + [H(t_1), [H(t_2), H(t_3)]]\}$$

All the interactions will be averaged to zero at the zeroth order approximation if the interaction Hamiltonian carries either $e^{im\omega_r t}$ or $e^{i\omega_1 t}$. The integral is zero over period of either physical rotation, or RF irradiation. Normally the average is performed over the shorter period first. Naturally, if only I spin is irradiated,

$$H^0 = \bar{\bar{\tilde{H}}}_{cs(s)} + \bar{\bar{\tilde{H}}}_{J_{II}}$$

However, interactions that carry both $e^{im\omega_r t}$ and $e^{i\omega_1 t}$ can have potential interference effect with each other. When $k = 1{,}2$, even in the zeroth order term, we will have nonzero contribution from various interactions due to such “rotary resonance” conditions.

This corresponds to the recoupling of such interactions at rotary resonance conditions, and it is possible for $\tilde{H}_{csa}$, $\tilde{H}_{D_{IS}}$, and $\tilde{H}_{D_{II}}$. For $\tilde{H}_{csa}$ and $\tilde{H}_{D_{IS}}$, they share a common term:

$$-e^{im\omega_r t}e^{i\omega_1 t}(I_x + iI_y) - e^{im\omega_r t}e^{-i\omega_1 t}(I_x - iI_y) \tag{7.74}$$

So

$$H^0 = \frac{1}{t}\int_0^{t=\frac{2\pi}{\omega}} H(t)dt$$

With $\omega_1 = k\omega_r, k = 1{,}2$, we will have:

$$\frac{1}{t}\int_0^{t=\frac{2\pi}{\omega}} dt\,[-e^{im\omega_r t}e^{i\omega_1 t}(I_x + iI_y) - e^{im\omega_r t}e^{-i\omega_1 t}(I_x - iI_y)]$$

$$= \frac{1}{t}\int_0^{t=\frac{2\pi}{\omega}} dt \left[-e^{i(k+m)\omega_r t}\left(I_x + iI_y\right) - e^{i(m-k)\omega_r t}\left(I_x - iI_y\right)\right]$$

$$= -\frac{1}{t}\left[\frac{1}{i(k+m)\omega_r}\left(e^{i(k+m)\omega_r t} - 1\right)\left(I_x + iI_y\right) + \frac{1}{i(k-m)\omega_r}\left(e^{-i(k-m)\omega_r t} - 1\right)\left(I_x - iI_y\right)\right]$$

Again, by applying L'Hopital Rule at $k = \pm m$, this common term becomes:

$$= -\left(I_x + iI_y\right) \, or \left(I_x - iI_y\right) \tag{7.75}$$

For simultaneous irradiation on both spin I and S, the heteronuclear dipolar interaction becomes:

$$\frac{1}{t}\int_0^{t=\frac{2\pi}{\omega}} dt \left[e^{im\omega_r t}\left[-I^+ e^{i\omega_{1I}t} - I^- e^{-i\omega_{1I}t}\right]\left[-S^+ e^{i\omega_{1S}t} - S^- e^{-i\omega_{1S}t}\right]\right] \tag{7.76}$$

$$= \frac{1}{t}\int_0^{t=\frac{2\pi}{\omega}} dt \left[e^{im\omega_r t}\left(I^+ S^+ e^{i(\omega_{1I}+\omega_{1S})t} + I^- S^- e^{-i(\omega_{1I}+\omega_{1S})t} + I^+ S^- e^{i(\omega_{1I}-\omega_{1S})t} + I^- S^+ e^{-i(\omega_{1I}-\omega_{1S})t}\right]\right.$$

Hence, we will have the rotary resonance conditions at $\pm(\omega_{1I} + \omega_{1S}) = m\omega_r$ and $\pm(\omega_{1I} - \omega_{1S}) = m\omega_r$. These corresponds to the zero double and zero quantum recoupling condition we discussed for CP in Sect.4.12.

At each resonance condition, the spin part of the commutator will survive corresponding integral terms and be responsible for the recoupling of csa and heteronuclear dipolar interaction:

$$\overline{\overline{\widetilde{H}}}{}^0_{csa} = -\sum_{\substack{m=-2 \\ m\neq 0}}^{2} \frac{\omega_{2m}^{cs}}{2}\left(I^+ \, or \, I^-\right) = -\frac{1}{2}\overline{\omega_{2m}^{cs}}\left(I^+ \, or \, I^-\right) \tag{7.77}$$

$$\overline{\overline{\widetilde{H}}}{}^0_{D_{IS}} = -\sum_{m=-2}^{2} \frac{\omega_{2m}^{D_{IS}}}{2} S_z\left(I^+ \, or \, I^-\right) = -\frac{1}{2}\overline{\omega_{2m}^{D_{IS}}} S_z\left(I^+ \, or \, I^-\right) \tag{7.78}$$

Here I use the $\overline{\omega_{2m}^{cs}}$ and $\overline{\omega_{2m}^{D_{IS}}}$ to represent their summation.

Similarly, we will have residual terms in the zeroth order Magnus expansion from $\widetilde{H}_{D_{II}}$ at rotary resonant condition $\omega_1 = \pm\frac{m}{2}\omega_r$ (HORROR condition) due to resonant conditions between:

$$\overline{\overline{\widetilde{H}}}{}^0_{D_{II}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{II}}\left[\frac{3}{4} e^{\pm i2\omega_1 t} I_i^{\pm} I_j^{\pm}\right] e^{im\omega_r t} \longrightarrow \frac{3}{4}\overline{\omega_{2m}^{D_{II}}} I_i^{\pm} I_j^{\pm} \tag{7.79}$$

I will leave this as a homework for you to show the derivation process.

We need to remind ourselves that the spin operators are now in the interaction frame of the RF irradiation: the $I_x, I_y, and\ I_z$ correspond to in the rotating frame $-I_z, I_{y,}\ and\ I_x$.

This explains why we need to avoid such resonance conditions during decoupling, or utilize such rotary resonance conditions when needed. It will lead to recoupling of csa, homonuclear and heteronuclear dipolar interaction involving I spins, which in return will broaden the S spin linewidth. This is nothing new, as we have shown in Chap 6 the derivation of various rotary resonance conditions.

Table 7.1 Rotary resonance at zeroth order approximation for RF irradiation along x axis in the rotating frame in the presence of MAS.

Interactions	Hamiltonian in the interaction frame of RF	Hamiltonian in in the rotating frame	Resonance conditions
$\overline{\overline{\tilde{H}}}{}^0_{csa}$	$-\frac{1}{2}\overline{\omega_{2m}^{cs}}(I^+ \; or \; I^-)$	$-\frac{1}{2}\overline{\omega_{2m}^{cs}}(I_z \pm iI_y)$	$\pm(\omega_{1I}+\omega_{1S}) = m\omega_r$; $\pm(\omega_{1I}-\omega_{1S}) = m\omega_r$
$\overline{\overline{\tilde{H}}}{}^0_{D_{IS}}$	$-\frac{1}{2}\overline{\omega_{2m}^{D_{IS}}}S_z(I^+ \; or \; I^-)$	$-\frac{1}{2}\overline{\omega_{2m}^{D_{IS}}}S_z(I_z \pm iI_y)$	$\pm(\omega_{1I}+\omega_{1S}) = m\omega_r$; $\pm(\omega_{1I}-\omega_{1S}) = m\omega_r$
$\overline{\overline{\tilde{H}}}{}^0_{D_{II}}$	$\frac{3}{4}\overline{\omega_{2m}^{D_{II}}}I_i^{\pm}I_j^{\pm}$	$\frac{3}{4}\overline{\omega_{2m}^{D_{II}}}(I_{zi} \pm iI_{yi})(I_{zj} \pm iI_{yj})$	$\omega_1 = \pm\frac{m}{2}\omega_r$

Here we assume RF irradiation is applied to both I and S spins.

Under more general situations, we need to perform two levels of average over both RF irradiation and MAS rotation. This can be difficult to do analytically. Only when ω_1/ω_r or ω_r/ω_1 is integer, a simple analytical expression can be obtained. Such conditions will be $\omega_1 = p\omega_r$ for high power decoupling and $\omega_r = p\omega_1$ for low power decoupling at high MAS. In experiments, normal setup will have $p > 2$ to avoid the rotary resonance conditions. With only I spin irradiated, you can easily show that all interactions involving I spin operator zero are averaged to zero at zeroth order.

For the first order approximation, we need to compute the cross terms between different interactions, which include the commutators of their spin parts. The magnitude of the spatial parts will be important to see which cross terms dominate the first order approximation. But first, let's focus on the spin parts of the commutators, together with the time-dependent exponents:

1. We have nonzero commutator of isotropic chemical shift, due to the irradiation of RF:

$$[\tilde{H}_{cs}(t_2), \tilde{H}_{cs}(t_1)] = \left[\frac{\omega_{iso}}{2}\left[-I^+e^{i\omega_1 t_2} - I^-e^{-i\omega_1 t_2}\right], \frac{\omega_{iso}}{2}\left[-I^+e^{i\omega_1 t_1} - I^-e^{-i\omega_1 t_1}\right]\right]$$

$$= \frac{1}{4}\omega_{iso}^2[(I^+e^{i\omega_1 t_2} + I^-e^{-i\omega_1 t_2}), (I^+e^{i\omega_1 t_1} + I^-e^{-i\omega_1 t_1})]$$

Recall $[I^+, I^-] = 2\hbar I_z$

$$= \frac{1}{4}\omega_{iso}^2 2I_z(e^{i\omega_1(t_2-t_1)} - e^{-i\omega_1(t_2-t_1)})$$

Hence we have:

$$[\tilde{H}_{cs}(t_2), \tilde{H}_{cs}(t_1)] = i\omega_{iso}^2 I_z \sin\omega_1(t_2 - t_1) \qquad (7.80)$$

2. We will also have the nonzero commutator of the csa with csa itself, under RF irradiation:

$$[\tilde{H}_{csa}(t_2), \tilde{H}_{csa}(t_1)]$$

$$= \left[\sum_{\substack{n=-2\\ n\neq 0}}^{2} \frac{\omega_{2n}^{\text{csa}}}{2}\left[-I^+ e^{in\omega_r t_2} e^{i\omega_1 t_2} - I^- e^{in\omega_r t_2} e^{-i\omega_1 t_2}\right], \sum_{\substack{m=-2\\ m\neq 0}}^{2} \frac{\omega_{2m}^{\text{csa}}}{2}\left[-I^+ e^{im\omega_r t_1} e^{i\omega_1 t_1} - I^- e^{im\omega_r t_1} e^{-i\omega_1 t_1}\right]\right]$$

$$= \frac{1}{4} \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2n}^{\text{csa}} \omega_{2m}^{\text{csa}}\, 2I_z e^{in\omega_r t_2} e^{im\omega_r t_1} \left(e^{i\omega_1 (t_2-t_1)} - e^{-i\omega_1 (t_2-t_1)}\right)$$

Hence, utilizing our shor-handed notation for the coefficients of summation, it can be written as:

$$\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{csa}(t_1)\right] = \frac{1}{2}\overline{\omega_{2n}^{\text{csa}} \omega_{2m}^{\text{csa}}} I_z e^{in\omega_r t_2} e^{im\omega_r t_1} \left(e^{i\omega_1 (t_2-t_1)} - e^{-i\omega_1 (t_2-t_1)}\right) \tag{7.81}$$

3. Similarly, we will also have nonzero commutator of $\widetilde{H}_{D_{IS}}(t_2)$ with itself. Let's look at the situation when the sample is under continuous RF irradiation of both spin I and S:

$$\left[\widetilde{H}_{D_{IS}}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right] = \frac{1}{4} \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2n}^{D_{IS}} \omega_{2m}^{D_{IS}}\, 2I_z 2S_z \, e^{in\omega_r t_2} e^{im\omega_r t_1} \left(e^{i\omega_{1I} (t_2-t_1)} - e^{-i\omega_{1I} (t_2-t_1)}\right)\left(e^{i\omega_{1S} (t_2-t_1)} - e^{-i\omega_{1S} (t_2-t_1)}\right)$$

Hence, it can be written as:

$$\left[\widetilde{H}_{D_{IS}}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right] = \overline{\omega_{2n}^{D_{IS}} \omega_{2m}^{D_{IS}}} I_z S_z e^{in\omega_r t_2} e^{im\omega_r t_1} \left(e^{i\omega_{1I} (t_2-t_1)} - e^{-i\omega_{1I} (t_2-t_1)}\right)\left(e^{i\omega_{1S} (t_2-t_1)} - e^{-i\omega_{1S} (t_2-t_1)}\right) \tag{7.82}$$

4. Likewise, $\widetilde{H}_{D_{II}}^{ij}$ doesn't commute with itself either:

$$\left[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ij}\right] \tag{7.83}$$

$$= [\sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij)\, e^{im\omega_r t_2} \left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4} e^{i2\omega_1 t_2} I_i^+ I_j^+ + \frac{3}{4} e^{-i2\omega_1 t_2} I_i^- I_j^-\right],$$

$$\sum_{\substack{n=-2\\ n\neq 0}}^{2} \omega_{2n}^{D_{II}}(ij)\, e^{in\omega_r t_1} \left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4} e^{i2\omega_1 t_1} I_i^+ I_j^+ + \frac{3}{4} e^{-i2\omega_1 t_1} I_i^- I_j^-\right]]$$

$$= \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij) \omega_{2n}^{D_{II}}(ij)\, e^{im\omega_r t_2} e^{in\omega_r t_1}$$

$$[\left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t_2}I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_2}I_i^- I_j^-\right], [\frac{1}{2}\left(I_0^{xik} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t_1}I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_1}I_i^- I_j^-]]$$

The computation is a bit long. But it is not that complicated, as we can decompose the commutator into the following basic commutators:

$$\frac{1}{4}\left[\left(I_0^{xij} - 2I_{zi}I_{zj}\right), \left(I_0^{xij} - 2I_{zi}I_{zj}\right)\right] + \frac{3}{8}e^{i2\omega_1 t_1}\left[\left(I_0^{xij} - 2I_{zi}I_{zj}\right), I_i^+ I_j^+\right]$$
$$+\frac{3}{8}e^{-i2\omega_1 t_1}\left[\left(I_0^{xij} - 2I_{zi}I_{zj}\right), I_i^- I_j^-\right] + \frac{3}{8}e^{i2\omega_1 t_2}\left[I_i^+ I_j^+, \left(I_0^{xij} - 2I_{zi}I_{zj}\right)\right] + \frac{9}{16}e^{i2\omega_1(t_2+t_1)}\left[I_i^+ I_j^+, I_i^+ I_j^+\right]$$
$$+\frac{9}{16}e^{i2\omega_1(t_2-t_1)}\left[I_i^+ I_j^+, I_i^- I_j^-\right] + \frac{3}{8}e^{-i2\omega_1 t_2}\left[I_i^- I_j^-, \left(I_0^{xik} - 2I_{zi}I_{zj}\right)\right] + \frac{9}{16}e^{-i2\omega_1(t_2-t_1)}\left[I_i^- I_j^-, I_i^+ I_j^+\right]$$
$$+\frac{9}{16}e^{-i2\omega_1(t_2+t_1)}[I_i^- I_j^-, I_i^- I_j^-]$$

Here a few commutation relationship of fictitious spin 0 operators (similar to Eq. 7.12) can come handy:

$$\left[I_0^{xij}, I_i^+\right] = -I_{zi}I_j^+;\ \left[I_0^{xij}, I_i^-\right] = I_{zi}I_j^-;\ \left[I_{zi}, I_0^{xij}\right] = iI_0^{yij}; \left[I_0^{xij}, I_{zi}I_{zj}\right] = 0 \tag{7.84}$$

We can show that:

$$\left[I_0^{xij}, I_i^+ I_j^+\right] = \frac{1}{2}\left[I_i^+ I_j^- + I_i^- I_j^+, I_i^+ I_j^+\right] = 0; \left[I_0^{xij}, I_i^- I_j^-\right] = 0 \tag{7.85}$$

This is easy to prove, as $I_i^+ I_j^+$ and $I_i^- I_j^-$ belong to the double quantum space, and won't interact with any zero quantum operators formed by the same pair of spins.

We can show that:

$$\left[I_i^+ I_j^+, I_i^- I_j^-\right] = \left(\frac{1}{2} - iI_{zi}\right)\left(\frac{1}{2} - iI_{zj}\right) - \left(\frac{1}{2} + iI_{zi}\right)\left(\frac{1}{2} + iI_{zj}\right) = -i(I_{zi} + I_{zj}) \tag{7.86}$$

Meanwhile, recall:

$$\left[I_{zi}I_{zj}, I_i^+\right] = I_i^+ I_{zj};\ \left[I_{zi}I_{zj}, I_i^-\right] = -I_i^- I_{zj};\ [I^+, I^-] = 2\hbar I_z \tag{7.87}$$

you can show that:

$$\left[I_{zi}I_{zj}, I_i^+ I_j^+\right] = 0;\ \left[I_{zi}I_{zj}, I_i^- I_j^-\right] = 0 \tag{7.88}$$

So we can plug these commutators in to Eq. 7.83 and work out the commutation now:

$$[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ij}] \tag{7.89}$$

$$= \frac{9}{16} \sum_{\substack{m,n=-2 \\ m,n\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij)\omega_{2n}^{D_{II}}(ij)\, e^{im\omega_r t_2} e^{in\omega_r t_1} i\left(I_{zi} + I_{zj}\right)\left(e^{-i2\omega_1(t_2-t_1)} - e^{i2\omega_1(t_2-t_1)}\right)$$

Hence we have:

$$\left[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ij}\right] = \frac{9}{16} \overline{\omega_{2m}^{D_{II}}(ij)\omega_{2n}^{D_{II}}(ij)} e^{im\omega_r t_2} e^{in\omega_r t_1} i\left(I_{zi} + I_{zj}\right)\left(e^{-i2\omega_1(t_2-t_1)} - e^{i2\omega_1(t_2-t_1)}\right) \tag{7.90}$$

This makes sense. The mutual spin flip-flop of the same pair of spins conserves the total polarization $\left(I_{zi} + I_{zj}\right)$, with out polarization spread to a third spin.

We note all the above self-commutators of these interactions end up with I_{zi}/S_{zi} in their spin part of operators. But recall that the spin operators are now in the interaction frame of the RF irradiation, the $I_x, I_y, and\ I_z$ correspond to in the rotating frame $-I_z, I_{y,}\ and\ I_x$. So the spin part of these self-commutators are in fact I_x operators in the lab frame, which essentially means the RF irradiation spin locks the spins along the irradiated x axis direction. The spin locked I_x will induce spin diffusion by flip-flop style interactions between different eigenstates of Zeeman interactions and broaden NMR transitions, with a relaxation time similar to the $T_{1\rho}$ in the rotating frame, different from (but longer than) the standard spin lattice relaxation time.

Thus we can sum up the zeroth order and first approximation of various interactions due to the self-average or self-commutation, as shown in Table 7.1 and 7.2.

Table 7.2 Rotary resonance due to non-zero self-commutation at 1st order approximation for RF irradiation along the x axis in the rotating frame in the presence of MAS. Here H^1 is computed by integration:

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega}} dt_2 \int_0^{t_2} dt_1 [H(t_2), H(t_1)]$$

Interactions	Hamiltonian in the interaction frame of RF	Resonance conditions
$\left[\widetilde{H}_{cs}(t_2), \widetilde{H}_{cs}(t_1)\right]$	$i\omega_{iso}^2 I_z \sin\omega_1(t_2 - t_1)$	
H^1	$\frac{1}{4\omega_1}\omega_{iso}^2 I_z$	
$\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{csa}(t_1)\right]$	$\frac{1}{2}\overline{\omega_{2n}^{\mathrm{csa}}\omega_{2m}^{\mathrm{csa}}} I_z e^{in\omega_r t_2} e^{im\omega_r t_1}\left(e^{i\omega_1(t_2-t_1)} - e^{-i\omega_1(t_2-t_1)}\right)$	$\pm\omega_{1I} = m/n\omega_r$;
$\left[\widetilde{H}_{D_{IS}}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]$	$\overline{\omega_{2n}^{D_{IS}}\omega_{2m}^{D_{IS}}} I_z S_z e^{in\omega_r t_2} e^{im\omega_r t_1}\left(e^{i\omega_{1I}(t_2-t_1)} - e^{-i\omega_{1I}(t_2-t_1)}\right)\left(e^{i\omega_{1S}(t_2-t_1)} - e^{-i\omega_{1S}(t_2-t_1)}\right)$	$\pm(\omega_{1I} + \omega_{1S}) = m/n\omega_r$; $\pm(\omega_{1I} - \omega_{1S}) = m\omega_r$
$\left[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ij}\right]$	$\frac{9}{16}\overline{\omega_{2m}^{D_{II}}(ij)\omega_{2n}^{D_{II}}(ij)} e^{im\omega_r t_2} e^{in\omega_r t_1} i\left(I_{zi} + I_{zj}\right)\left(e^{-i2\omega_1(t_2-t_1)} - e^{i2\omega_1(t_2-t_1)}\right)$	$\omega_1 = \pm\frac{m}{2}/\frac{n}{2}\omega_r$

Next we will have cross commutators between different interactions.

5. Isotropic chemical shift with csa: without RF irradiation, their spin parts of Hamiltonian commute, and won't give us any cross term. But now, their spin part won't commute anymore:

$$\left[\widetilde{H}_{cs}(t_2), \widetilde{H}_{csa}(t_1)\right]$$

$$= \left[\frac{\omega_{iso}}{2}\left[-I^+ e^{i\omega_1 t_2} - I^- e^{-i\omega_1 t_2}\right], \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \frac{\omega_{2m}^{\text{csa}}}{2}\left[-I^+ e^{im\omega_r t_1} e^{i\omega_1 t_1} - I^- e^{im\omega_r t_1} e^{-i\omega_1 t_1}\right]\right]$$

$$= \frac{1}{4}\omega_{iso} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\text{csa}}\left[I^+ e^{i\omega_1 t_2} + I^- e^{-i\omega_1 t_2}, I^+ e^{im\omega_r t_1} e^{i\omega_1 t_1} + I^- e^{im\omega_r t_1} e^{-i\omega_1 t_1}\right]$$

Recall $[I^+, I^-] = 2\hbar I_z$

$$= \frac{1}{4}\omega_{iso} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\text{csa}} \times 2I_z e^{im\omega_r t_1}\left(e^{i\omega_1(t_2-t_1)} - e^{-i\omega_1(t_2-t_1)}\right)$$

$$= \frac{1}{2}\omega_{iso} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{\text{csa}} I_z e^{im\omega_r t_1}\left(e^{i\omega_1(t_2-t_1)} - e^{-i\omega_1(t_2-t_1)}\right)$$

$$\left[\widetilde{H}_{cs}(t_2), \widetilde{H}_{csa}(t_1)\right] = \frac{1}{2}\omega_{iso}\overline{\omega_{2m}^{\text{csa}}} e^{im\omega_r t_1} I_z\left(e^{i\omega_1(t_2-t_1)} - e^{-i\omega_1(t_2-t_1)}\right) \tag{7.91}$$

6. For the first order approximation of heteronuclear dipolar interactions with simultaneous irradiation of both spin I and S, we can use the similarity to Eq. 7.91 and show

$$\left[\widetilde{H}_{cs}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]$$

$$= \frac{1}{4}\omega_{iso} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{D_{IS}} I_z e^{im\omega_r t_1}\left(e^{i\omega_{1I}(t_2-t_1)} - e^{-i\omega_{1I}(t_2-t_1)}\right)\left(-S^+ e^{i\omega_{1S} t_1} - S^- e^{-i\omega_{1S} t_1}\right)$$

$$\frac{1}{4}\omega_{iso} \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{D_{IS}} I_z(-S^+ e^{i(m\omega_r - \omega_{1I} + \omega_{1s})t_1} e^{i\omega_{1I} t_2} + S^+ e^{i(m\omega_r + \omega_{1I} + \omega_{1s})t_1} e^{-i\omega_{1I} t_2}$$

$$-S^- e^{i(m\omega_r - \omega_{1I} - \omega_{1s})t_1} e^{i\omega_{1I} t_2} + S^- e^{i(m\omega_r + \omega_{1I} - \omega_{1s})t_1} e^{-i\omega_{1I} t_2})$$

$$\left[\widetilde{H}_{cs}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right] = \frac{1}{4}\omega_{iso}\overline{\omega_{2m}^{D_{IS}}} I_z(-S^+ e^{i(m\omega_r - \omega_{1I} + \omega_{1s})t_1} e^{i\omega_{1I} t_2} + S^+ e^{i(m\omega_r + \omega_{1I} + \omega_{1s})t_1} e^{-i\omega_{1I} t_2} \tag{7.92}$$

$$-S^{-}e^{i(m\omega_r-\omega_{1I}-\omega_{1s})t_1}e^{i\omega_{1I}t_2}+S^{-}e^{i(m\omega_r+\omega_{1I}-\omega_{1s})t_1}e^{-i\omega_{1I}t_2})$$

If only I spin is irradiated, then:

$$[\widetilde{H}_{cs}(t_2),\widetilde{H}_{D_{IS}}(t_1)] \tag{7.93}$$
$$=\frac{1}{2}\omega_{iso}\overline{\omega_{2m}^{D_{IS}}}I_zS_ze^{im\omega_rt_1}\left(e^{i\omega_1(t_2-t_1)}-e^{-i\omega_1(t_2-t_1)}\right)$$

7. Similarly, we can use Eq. 7.92 and 7.93 to derive the commutator between csa and heteronuclear dipolar interaction is computed:

$$[\widetilde{H}_{csa}(t_2),\widetilde{H}_{D_{IS}}(t_1)]$$

$$=\frac{1}{4}\sum_{\substack{m,n=-2\\m,n\neq0}}^{2}\omega_{2m}^{D_{IS}}\omega_{2n}^{\text{csa}}\,I_ze^{im\omega_rt_1}e^{in\omega_rt_2}\left(e^{i\omega_{1I}(t_2-t_1)}-e^{-i\omega_{1I}(t_2-t_1)}\right)\left(-S^{+}e^{i\omega_{1S}t_1}-S^{-}e^{-i\omega_{1S}t_1}\right)$$

$$=\frac{1}{4}\sum_{\substack{m=-2\\m\neq0}}^{2}\omega_{2m}^{D_{IS}}\omega_{2n}^{\text{csa}}\,I_z(-S^{+}e^{i(m\omega_r-\omega_{1I}+\omega_{1s})t_1}e^{i(n\omega_r+\omega_{1I})t_2}+S^{+}e^{i(m\omega_r+\omega_{1I}+\omega_{1s})t_1}e^{i(n\omega_r-\omega_{1I})t_2}$$

$$-S^{-}e^{i(m\omega_r-\omega_{1I}-\omega_{1s})t_1}e^{i(n\omega_r+\omega_{1I})t_2}+S^{-}e^{i(m\omega_r+\omega_{1I}-\omega_{1s})t_1}e^{i(n\omega_r-\omega_{1I})t_2})$$

$$[\widetilde{H}_{csa}(t_2),\widetilde{H}_{D_{IS}}(t_1)] \tag{7.94}$$
$$=\frac{1}{4}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{2n}^{\text{csa}}}I_z(-S^{+}e^{i(m\omega_r-\omega_{1I}+\omega_{1s})t_1}e^{i(n\omega_r+\omega_{1I})t_2}+S^{+}e^{i(m\omega_r+\omega_{1I}+\omega_{1s})t_1}e^{i(n\omega_r-\omega_{1I})t_2}$$

$$-S^{-}e^{i(m\omega_r-\omega_{1I}-\omega_{1s})t_1}e^{i(n\omega_r+\omega_{1I})t_2}+S^{-}e^{i(m\omega_r+\omega_{1I}-\omega_{1s})t_1}e^{i(n\omega_r-\omega_{1I})t_2})$$

If only I spin is irradiated, then:

$$[\widetilde{H}_{csa}(t_2),\widetilde{H}_{D_{IS}}(t_1)] \tag{7.95}$$
$$=\frac{1}{2}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{2n}^{\text{csa}}}I_zS_ze^{in\omega_rt_2}e^{im\omega_rt_1}\left(e^{i\omega_{1I}(t_2-t_1)}-e^{-i\omega_{1I}(t_2-t_1)}\right)$$

8. Next, the homonuclear dipolar interactions can have similar resonant terms with its commutator with isotropic chemical shift, or heteronuclear J coupling:

$$[\widetilde{H}_{D_{II}}(t_2),\widetilde{H}_{cs}(t_1)]$$

$$=[\sum_{\substack{m=-2\\m\neq0}}^{2}\omega_{2m}^{D_{II}}e^{im\omega_rt_2}\left[\frac{1}{2}\left(I_0^{xij}-2I_{zi}I_{zj}\right)+\frac{3}{4}e^{i2\omega_1t_2}I_i^{+}I_j^{+}+\frac{3}{4}e^{-i2\omega_1t_2}I_i^{-}I_j^{-}\right],$$

$$\frac{\omega_{iso}}{2}\left[-I^{+}e^{i\omega_1t_1}-I^{-}e^{-i\omega_1t_1}\right]]$$

$$= \frac{\omega_{iso}}{2} \sum_{m=-2}^{2} \omega_{2m}^{D_{II}} e^{im\omega_r t_2}$$

$$\left[\left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t_2} I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_2} I_i^- I_j^-\right], \left[I_i^+ e^{i\omega_1 t_1} + I_i^- e^{-i\omega_1 t_1}\right]\right]$$

Let's assume the spin in $\widetilde{H}_{cs}$ is spin I_i, and let's focus on the commutator for now. We can work out the commutator term by term. Recall the relations we derived in Eq. 7.84 to 7.88:

$$\left[I_0^{xij}, I_i^+\right] = -I_{zi}I_j^+; \;\; \left[I_0^{xij}, I_i^-\right] = I_{zi}I_j^-$$

Meanwhile, with $[I^{\pm}, I_z] = \mp\hbar I^{\pm}$, you can show:

$$\left[I_{zi}I_{zj}, I_i^+\right] = I_i^+ I_{zj}; \;\; \left[I_{zi}I_{zj}, I_i^-\right] = -I_i^- I_{zj}$$

The second and third term in dipolar interaction part consists of commutators I_i^+ and I_i^- , so just recall:

$$[I^+, I^-] = 2\hbar I_z$$

Therefore, the total commutator is:

$$\left[\left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t_2} I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_2} I_i^- I_j^-\right], \left[I_i^+ e^{i\omega_1 t_1} + I_i^- e^{-i\omega_1 t_1}\right]\right] \quad (7.96)$$

$$= \frac{1}{2} I_{zi}\left(-I_j^+ e^{i\omega_1 t_1} + I_j^- e^{-i\omega_1 t_1}\right) - I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)$$

$$+ \frac{3}{2} I_{zi}\left(I_j^+ e^{i2\omega_1 t_2} e^{-i\omega_1 t_1} - I_j^- e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right)$$

$$= I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right) + I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right)$$

$$-\frac{1}{2} I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)$$

So combined with the spatial part we have:

$$\left[\widetilde{H}_{D_{II}}, \widetilde{H}_{cs}\right] \quad (7.97)$$

$$= \frac{\omega_{iso}}{2} \overline{\omega_{2m}^{D_{II}}} e^{im\omega_r t_2} \left[I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right) + I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right)\right.$$

$$\left. -\frac{1}{2} I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)\right]$$

9. Similar to Eq. 7.97, the homonuclear dipolar interactions can have similar resonant terms with its commutator with csa:

$$\left[\widetilde{H}_{D_{II}}(t_2), \widetilde{H}_{csa}(t_1)\right]$$

$$= [\sum_{\substack{m=-2\\ m\neq 0}}^{2} \omega_{2m}^{D_{II}} e^{im\omega_r t_2} \left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4}e^{i2\omega_1 t_2} I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_2} I_i^- I_j^-\right],$$

$$\sum_{\substack{n=-2\\ n\neq 0}}^{2} \omega_{2m}^{csa} e^{in\omega_r t_1}\left[-I^+ e^{i\omega_1 t_1} - I^- e^{-i\omega_1 t_1}\right]]$$

$$= \frac{1}{2}\sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2m}^{csa}\omega_{2m}^{D_{II}} e^{im\omega_r t_2} e^{in\omega_r t_1}[I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right)$$

$$+ I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right) - \frac{1}{2}I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)]$$

$$\left[\widetilde{H}_{D_{II}}(t_2), \widetilde{H}_{csa}(t_1)\right] \tag{7.98}$$

$$= \frac{1}{2}\overline{\omega_{2m}^{csa}}\,\overline{\omega_{2m}^{D_{II}}} e^{im\omega_r t_2} e^{in\omega_r t_1}[I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right)$$

$$+ I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right) - \frac{1}{2}I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)]$$

10. For cross terms $\left[\widetilde{H}_{D_{II}}, \widetilde{H}_{D_{IS}}\right]$ with simultaneous irradiation on spin I and S:

$$\left[\widetilde{H}_{D_{II}}, \widetilde{H}_{D_{IS}}\right] = \frac{1}{4}\sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2m}^{D_{II}}\,\omega_{2n}^{D_{IS}} e^{im\omega_r t_2} e^{in\omega_r t_1}[I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right)$$

$$+ I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right) - \frac{1}{2}I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)] \times$$

$$\left(-S^+ e^{i\omega_{1S} t_1} - S^- e^{-i\omega_{1S} t_1}\right)$$

$$\left[\widetilde{H}_{D_{II}}, \widetilde{H}_{D_{IS}}\right] \tag{7.99}$$

$$= \frac{1}{4}\overline{\omega_{2m}^{D_{II}}\omega_{2n}^{D_{IS}}} e^{im\omega_r t_2} e^{in\omega_r t_1}[I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right)$$

$$+ I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right) - \frac{1}{2}I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)] \times$$

$$\left(-S^+ e^{i\omega_{1S} t_1} - S^- e^{-i\omega_{1S} t_1}\right)$$

If only I spin is irradiated, then:

$$\left[\widetilde{H}_{D_{II}}, \widetilde{H}_{D_{IS}}\right] \tag{7.100}$$

$$= \frac{1}{2}\overline{\omega_{2m}^{D_{II}}\omega_{2n}^{D_{IS}}} e^{im\omega_r t_2} e^{in\omega_r t_1} S_z[I_{zi}I_j^+ \left(-\frac{1}{2}e^{i\omega_1 t_1} + \frac{3}{2}e^{i2\omega_1 t_2} e^{-i\omega_1 t_1}\right)$$

$$+ I_{zi}I_j^- \left(\frac{1}{2}e^{-i\omega_1 t_1} - \frac{3}{2}e^{-i2\omega_1 t_2} e^{i\omega_1 t_1}\right) - \frac{1}{2}I_{zj}\left(I_i^+ e^{i\omega_1 t_1} - I_i^- e^{-i\omega_1 t_1}\right)]$$

11. At last, let's see the grand evil of all evils, the cross terms due to $\widetilde{H}_D$ itself of different spin pairs that share one common spin:

$$[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ik}] = [\sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij)\, e^{im\omega_r t_2} \Big[\frac{1}{2}\big(I_0^{xij} - 2I_{zi}I_{zj}\big) + \frac{3}{4}e^{i2\omega_1 t_2} I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_2} I_i^- I_j^-\Big],$$

$$\sum_{\substack{n=-2 \\ n\neq 0}}^{2} \omega_{2n}^{D_{II}}(ik)\, e^{in\omega_r t_1} \Big[\frac{1}{2}\big(I_0^{xik} - 2I_{zi}I_{zk}\big) + \frac{3}{4}e^{i2\omega_1 t_1} I_i^+ I_k^+ + \frac{3}{4}e^{-i2\omega_1 t_1} I_i^- I_k^-\Big]]$$

$$= \sum_{\substack{m,n=-2 \\ m,n\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij)\, \omega_{2n}^{D_{II}}(ik) e^{im\omega_r t_2} e^{in\omega_r t_1} \times$$

$$[\Big[\frac{1}{2}\big(I_0^{xij} - 2I_{zi}I_{zj}\big) + \frac{3}{4}e^{i2\omega_1 t_2} I_i^+ I_j^+ + \frac{3}{4}e^{-i2\omega_1 t_2} I_i^- I_j^-\Big],$$

$$[\frac{1}{2}\big(I_0^{xik} - 2I_{zi}I_{zk}\big) + \frac{3}{4}e^{i2\omega_1 t_1} I_i^+ I_k^+ + \frac{3}{4}e^{-i2\omega_1 t_1} I_i^- I_k^-]]$$

This essentially can be decomposed into the following basic commutators:

$$\begin{aligned} &\frac{1}{4}\big[\big(I_0^{xij} - 2I_{zi}I_{zj}\big), \big(I_0^{xik} - 2I_{zi}I_{zk}\big)\big] + \frac{3}{8}e^{i2\omega_1 t_1}\big[\big(I_0^{xij} - 2I_{zi}I_{zj}\big), I_i^+ I_k^+\big] \\ &+ \frac{3}{8}e^{-i2\omega_1 t_1}\big[\big(I_0^{xij} - 2I_{zi}I_{zj}\big), I_i^- I_k^-\big] + \frac{3}{8}e^{i2\omega_1 t_2}\big[I_i^+ I_j^+, \big(I_0^{xik} - 2I_{zi}I_{zk}\big)\big] + \frac{9}{16}e^{i2\omega_1 (t_2+t_1)}\big[I_i^+ I_j^+, I_i^+ I_k^+\big] \\ &+ \frac{9}{16}e^{i2\omega_1 (t_2-t_1)}\big[I_i^+ I_j^+, I_i^- I_k^-\big] + \frac{3}{8}e^{-i2\omega_1 t_2}\big[I_i^- I_j^-, \big(I_0^{xik} - 2I_{zi}I_{zk}\big)\big] + \frac{9}{16}e^{-i2\omega_1 (t_2-t_1)}\big[I_i^- I_j^-, I_i^+ I_k^+\big] \\ &+ \frac{9}{16}e^{-i2\omega_1 (t_2+t_1)}[I_i^- I_j^-, I_i^- I_k^-] \end{aligned} \tag{7.101}$$

Again, recall Eq. 7.84 to Eq. 7.88:

$$\big[I_0^{xij}, I_i^+\big] = -I_{zi}I_j^+; \;\; \big[I_0^{xij}, I_i^-\big] = I_{zi}I_j^-; \;\; \big[I_{zi}, I_0^{xij}\big] = iI_0^{yij}$$

So we can show:

$$\begin{aligned} &\big[I_0^{xij}, I_0^{xik}\big] \\ &= \big[I_{xi}I_{xj}, I_0^{xik}\big] + \big[I_{yi}I_{yj}, I_0^{xik}\big] = iI_{zi}I_{xj}I_{yk} - iI_{zi}I_{xk}I_{yj} = iI_{zi}I_0^{yjk} \end{aligned} \tag{7.102}$$

Meanwhile, recall:

$$\big[I_{zi}I_{zj}, I_i^+\big] = I_i^+ I_{zj}; \;\; \big[I_{zi}I_{zj}, I_i^-\big] = -I_i^- I_{zj}; \;\; [I^+, I^-] = 2\hbar I_z$$

So we can work out the commutation now:

$$\frac{1}{4}iI_{zi}I_0^{yjk} + \frac{1}{2}iI_{zk}I_0^{yij} - \frac{1}{2}I_{zj}I_0^{yij} - \frac{3}{8}e^{i2\omega_1 t_1}\big[I_{zi}I_j^+ I_k^+ + 2I_{zj}I_i^+ I_k^+\big] + \frac{3}{8}e^{-i2\omega_1 t_1}\big[I_{zi}I_j^- I_k^- + 2I_{zj}I_i^- I_k^-\big]$$

$$+\frac{3}{8}e^{i2\omega_1 t_2}\left[I_{zi}I_j^+I_k^+ + 2I_{zk}I_i^+I_j^+\right] + \frac{9}{8}e^{i2\omega_1(t_2-t_1)}I_{zi}I_j^+I_k^- - \frac{3}{8}e^{-i2\omega_1 t_2}\left[I_{zi}I_j^-I_k^- + 2I_{zk}I_i^-I_j^-\right]$$

$$-\frac{9}{8}e^{-i2\omega_1(t_2-t_1)}I_{zi}I_j^-I_k^+$$

$$[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ik}] = \sum_{\substack{m,n=-2\\ m,n\neq 0}}^{2} \omega_{2m}^{D_{II}}(ij)\,\omega_{2n}^{D_{II}}(ik)e^{im\omega_r t_2}e^{in\omega_r t_1}[\frac{1}{4}iI_{zi}I_0^{yjk} + \frac{1}{2}iI_{zk}I_0^{yij} - \frac{1}{2}I_{zj}I_0^{yij}$$

$$-\frac{3}{8}e^{i2\omega_1 t_1}(I_{zi}I_j^+I_k^+ + 2I_{zj}I_i^+I_k^+) + \frac{3}{8}e^{-i2\omega_1 t_1}(I_{zi}I_j^-I_k^- + 2I_{zj}I_i^-I_k^-)$$

$$+\frac{3}{8}e^{i2\omega_1 t_2}(I_{zi}I_j^+I_k^+ + 2I_{zk}I_i^+I_j^+) + \frac{9}{8}e^{i2\omega_1(t_2-t_1)}I_{zi}I_j^+I_k^- - \frac{3}{8}e^{-i2\omega_1 t_2}(I_{zi}I_j^-I_k^- + 2I_{zk}I_i^-I_j^-)$$

$$-\frac{9}{8}e^{-i2\omega_1(t_2-t_1)}I_{zi}I_j^-I_k^+]$$

$$[\widetilde{H}_{D_{II}}^{ij}, \widetilde{H}_{D_{II}}^{ik}] \tag{7.103}$$

$$= \overline{\omega_{2m}^{D_{II}}(ij)\omega_{2n}^{D_{II}}(ik)}e^{im\omega_r t_2}e^{in\omega_r t_1}[\frac{1}{4}iI_{zi}I_0^{yjk} + \frac{1}{2}iI_{zk}I_0^{yij} - \frac{1}{2}I_{zj}I_0^{yij} - \frac{3}{8}e^{i2\omega_1 t_1}(I_{zi}I_j^+I_k^+ + 2I_{zj}I_i^+I_k^+)$$

$$+\frac{3}{8}e^{-i2\omega_1 t_1}\left(I_{zi}I_j^-I_k^- + 2I_{zj}I_i^-I_k^-\right) + \frac{3}{8}e^{i2\omega_1 t_2}\left(I_{zi}I_j^+I_k^+ + 2I_{zk}I_i^+I_j^+\right) + \frac{9}{8}e^{i2\omega_1(t_2-t_1)}I_{zi}I_j^+I_k^-$$

$$-\frac{3}{8}e^{-i2\omega_1 t_2}(I_{zi}I_j^-I_k^- + 2I_{zk}I_i^-I_j^-) - \frac{9}{8}e^{-i2\omega_1(t_2-t_1)}I_{zi}I_j^-I_k^+]$$

Note that we have terms exhibiting no frequency dependent terms, and terms depending on $e^{\pm i2\omega_1 t_2}$, $e^{\pm i2\omega_1 t_1}$, $e^{\pm i2\omega_1(t_1+t_2)}$, $e^{\pm i2\omega_1(t_1-t_2)}$.

Now we have to complete the two layers of integration over t_1 first and then over t_2, as shown in the first order Magnus expansion in Eq. 5.45.

But here we have two periods: ω_r and ω_1. Which one should we take as the final integration limit?

When $\omega_r \gg \omega_1$(ultra fast MAS spinning with low decoupling), the MAS period is shorter than the spin rotation period. We have to average over the MAS rotation period first before average over RF frequency. The two layers of integration of $e^{im\omega_r t_2}e^{in\omega_r t_1}$ will be similar to our derivation in Eq. 7.30, which will result in:$\frac{1}{2m\omega_r}$.

The remaining integration over longer period of RF irradiation will be a bit tricky. If convergence is not an issue over this period, cross terms carrying just $e^{\pm i2\omega_1 t_2}$ and $e^{\pm i2\omega_1(t_1+t_2)}$ will vanish after the two layers of integral. Cross terms carrying $e^{\pm i2\omega_1 t_1}$ and $e^{\pm i2\omega_1(t_1-t_2)}$ will contribute a nonzero $\frac{1}{\pm i2\omega_1}$ term after integration. In addition, the terms without dependence on ω_1 will survive the average and carry a factor $\frac{1}{\omega_1}$: $\frac{1}{4}iI_{zi}I_0^{yjk} + \frac{1}{2}iI_{zk}I_0^{yij} - \frac{1}{2}I_{zj}I_0^{yij}$.

In addition, we will have higher order rotary resonance conditions due to the interplay between ω_1 and ω_r, since we have $e^{im\omega_r t_2}e^{in\omega_r t_1}$ in the commutator:

$2\omega_1 = \pm(m+n)\omega_r$; where $(m+n) = \pm 4, \pm 3, \pm 2, \pm 1, 0$. Note this implies $\omega_1 = \frac{3}{2}\omega_r$ would recouple dipolar interactions due to the cross terms.

Before detailed computation of the integration, let's think about what is the physics picture underneath the commutation terms.

This is manifested by the raising and lowering operators. In original interactions that carry only one spin I operators, they represent the polarization on spin I_i, since they have just I_{zi} involved. The commutation with homonulcear dipolar interactions gives rise to the $I_j^{\pm}$ operators coupled with I_{zi}. This can be thought as the spin diffusion process transferring of the polarization from spin I_i to spin I_j, or we say the relaxation process. When $\widetilde{H}_{J_{IS}}$ and $\widetilde{H}_{D_{IS}}$ are involved in the commutator, it means the spin diffusion from spin I_{zi} and S to I_j, across different nuclei. Essentially, these are the decoherence process activating the spin diffusion. Note there is a transformation of observation of reference frame in our analysis shown in Eq. 7.67 to 7.73. So these raising and lower operators are acting to accelerate the spin relation in the transformed frame, or we say, speed up the $T_{1\rho}$.

In summary, we have shown the complicated rotary resonance conditions for the first order terms between various interactions. The new rotary resonance conditions we didn't see in previous zeroth order analysis or recoupling conditions in chapter 6, are the higher order matching conditions up to $4\omega_r$, between sum or difference of irradiation field on spin I and S, or $2\omega_{1I}$. This not only gives us the familiar HORROR dipolar recoupling in Sect. 6.2, or the CP matching condition in Sect. 4.12, but also new matching conditions such as $\omega_1 = \frac{3}{2}\omega_r$ and $\omega_1 = k\omega_r$ with $k = 3 \; and \; 4$.

The presence of $I^{\pm}$ operators in the cross terms shows their effect is to activate spin diffusion and relaxation, as well as broaden transition lines. Their combinations give rise to zero and double quantum operators, which alerts us such terms can further interact with chemical shift offset or sum of chemical shifts, just like what we analyzed the different mechanisms of CP in Sect. 4.12. These interactions can further recouple heteronuclear interactions between proton and carbon, and broaden the NMR transitions.

Here we didn't include the commutation with J coupling for simplicity of discussion. The heteronuclear J coupling will have the same format of commutator as the isotropic chemical shift, with no dependence on MAS modulation term. Even without consideration of J coupling, we already have 3 nonzero zeroth order contribution and 11 nonzero commutators from first order approximation.

Now let's try a bit more detailed derivation for the two layered integration.

Since we are considering the decoupling effect, we would focus on terms that impact on the resolution of ^{13}C dimension, which is the most common detection channel in ssNMR, although ^{1}H detection is gaining traction with the ultra fast MAS. Let's take $\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]$ for example:

$$\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]$$

$$= \frac{1}{4}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{2n}^{\text{csa}}} I_z S_z e^{in\omega_r t_2} e^{im\omega_r t_1}\left(e^{i\omega_{1I}(t_2-t_1)} - e^{-i\omega_{1I}(t_2-t_1)}\right)$$

We need to perform integration to complete the evaluation:

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega}} dt_2 \int_0^{t_2} dt_1 [H(t_2), H(t_1)]$$

Again, an analytical solution can be obtained only when the ratio of ω_r and ω_{1I} is an integer. We need to differentiate over the different regimes: $\omega_r = p\omega_{1I}$ for fast MAS with low RF irradiation, and $\omega_{1I} = p\omega_r$ for high power decoupling.

Let's try $\omega_{1I} = p\omega_r$. Assume the convergence is not an issue, we will take a simplified approach to set the integration limit to $t = \frac{2\pi}{\omega_r}$. A more rigorous approach should take the integration over shorter period of RF irradiation, then integrate over the MAS period.

We will only deal with time-dependent part to complete the integration, and temporarily leave aside all the rest terms:

$$H^1 = -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \int_0^{t_2} dt_1 e^{in\omega_r t_2} e^{im\omega_r t_1}\left(e^{i\omega_{1I}(t_2-t_1)} - e^{-i\omega_{1I}(t_2-t_1)}\right) \tag{7.104}$$

$$= -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \int_0^{t_2} dt_1 e^{in\omega_r t_2} e^{im\omega_r t_1}\left(e^{ip\omega_r(t_2-t_1)} - e^{-ip\omega_r(t_2-t_1)}\right)$$

$$= -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega_r}} dt_2 \int_0^{t_2} dt_1 \left[e^{i(n+p)\omega_r t_2} e^{i(m-p)\omega_r t_1} - e^{i(n-p)\omega_r t_2} e^{i(m+p)\omega_r t_1}\right]$$

$$= -\frac{i}{2t}\int_0^{t=\frac{2\pi}{\omega_r}} dt_2$$

$$\left[e^{i(n+p)\omega_r t_2}\frac{1}{i(m-p)\omega_r}\left(e^{i(m-p)\omega_r t_2} - 1\right) - e^{i(n-p)\omega_r t_2}\frac{1}{i(m+p)\omega_r}\left(e^{i(m+p)\omega_r t_2} - 1\right)\right]$$

$$= -\frac{i}{2t}\{\frac{1}{i(m-p)\omega_r}\left[\frac{1}{i(n+m)\omega_r}\left(e^{i(n+m)\omega_r t} - 1\right) - \frac{1}{i(n+p)\omega_r}\left(e^{i(n+p)\omega_r t} - 1\right)\right]\}$$

$$+\frac{i}{2t}\left\{\frac{1}{i(m+p)\omega_r}\left[\frac{1}{i(n+m)\omega_r}\left(e^{i(n+m)\omega_r t} - 1\right) - \frac{1}{i(n-p)\omega_r}\left(e^{i(n-p)\omega_r t} - 1\right)\right]\right\}$$

$$= -\frac{i}{2t}\frac{1}{i(n+m)\omega_r}\left(e^{i(n+m)\omega_r t} - 1\right)\left[\frac{1}{i(m-p)\omega_r} - \frac{1}{i(m+p)\omega_r}\right]$$

$$+\frac{i}{2t}\left[\frac{1}{i(n+p)\omega_r}\frac{1}{i(m-p)\omega_r}\left(e^{i(n+p)\omega_r t} - 1\right) - \frac{1}{i(n-p)\omega_r}\frac{1}{i(m+p)\omega_r}\left(e^{i(n-p)\omega_r t} - 1\right)\right]$$

$$= -\frac{i}{2t}\frac{1}{i(n+m)\omega_r}\left(e^{i(n+m)\omega_r t} - 1\right)\frac{2p}{i(m-p)(m+p)\omega_r}$$

$$+\frac{i}{2t}\left[\frac{1}{i(n+p)\omega_r}\frac{1}{i(m-p)\omega_r}\left(e^{i(n+p)\omega_r t} - 1\right) - \frac{1}{i(n-p)\omega_r}\frac{1}{i(m+p)\omega_r}\left(e^{i(n-p)\omega_r t} - 1\right)\right]$$

Here we note $t = \frac{2\pi}{\omega_r}$, so when $n = -m$, $p = \pm m$, we will have nonzero contribution from various terms.

For the first parenthesis, we should have $n = -m$, apply l'Hopital's rule:

$$= -\frac{i}{2t}\frac{i\omega_r t}{i\omega_r}\frac{2p}{i(m-p)(m+p)\omega_r} = -\frac{p}{(m-p)(m+p)\omega_r} \tag{7.105}$$

Now remember to put back the time-independent terms $\frac{1}{4}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{2n}^{\text{csa}}}I_z S_z$:

$$= -\frac{1}{4}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{2,-m}^{\text{csa}}}I_z S_z \frac{p}{(m-p)(m+p)\omega_r} \tag{7.106}$$

For the second parenthesis, we have to deal it one by one with l'Hopital's rule: the first term will have nozero contribution at $p = -n = -m$, and $p = n = m$ for the second term, where $n, m = \pm 1, \pm 2$. However, this will be just the rotary resonance conditions. Recall we want to have high power decoupling, so $p > 2$ will not satisfy this $p = -n = -m$ condition, hence all terms in the second parenthesis will be zero due to $e^{i(n\pm p)\omega_r t} = 1$.

Hence the final surviving term will be just

$$H^1\left(\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]\right) = -\frac{1}{4}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{-2m}^{\text{csa}}}I_z S_z \frac{p}{(m-p)(m+p)\omega_r} \tag{7.107}$$

$$= -\frac{p}{4\omega_r}I_z S_z\left[\frac{\omega_{21}^{D_{IS}}\omega_{2-1}^{\text{csa}}}{(1-p)(1+p)} + \frac{\omega_{2-1}^{D_{IS}}\omega_{21}^{\text{csa}}}{(-1-p)(-1+p)} + \frac{\omega_{22}^{D_{IS}}\omega_{2-2}^{\text{csa}}}{(2-p)(2+p)} + \frac{\omega_{2-2}^{D_{IS}}\omega_{22}^{\text{csa}}}{(-2-p)(-2+p)}\right]$$

$$= -\frac{p}{4\omega_r}I_z S_z[\frac{\omega_{21}^{D_{IS}}\omega_{2-1}^{\text{csa}} + \omega_{2-1}^{D_{IS}}\omega_{21}^{\text{csa}}}{(1-p)(1+p)} + \frac{\omega_{22}^{D_{IS}}\omega_{2-2}^{\text{csa}} + \omega_{2-2}^{D_{IS}}\omega_{22}^{\text{csa}}}{(2-p)(2+p)}]$$

When p is very large, we can see that:

$$H^1\left(\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]\right) \sim \frac{1}{4\omega_r p}I_z S_z \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{D_{IS}}\omega_{2-m}^{\text{csa}} \tag{7.108}$$

Let's take a moment to think about the implication. This shows that the linewidth would further decrease inversely proportional to the decoupling power level p, compared to the MAS alone factor $\frac{1}{\omega_r}$. You should find similar results for the other commutators involving spin S operators.

We should also be aware that the I_z operator is in the tilted reference frame. In lab frame, it is actually $I_x \sim I^{\pm}$, hence this commutator works as relaxation by flip-flopping the *I* spins in its rotating frame and initiate the broadening to *S* spin by coupling to S_z. You can think this RF irradiation converts the original T_2 relaxation in the lab frame (which is short) to a longer $T_{1\rho}$ process, thus decrease the linewidth of the coupled *S* spin.

Reversely, we can compute the contribution of the first order Magnus expansion term for the same $\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]$ if $\omega_r = p\omega_{1I}$ at ultra high MAS with low decoupling setup. You will see a similar factor. I will leave that as a homework for you to prove it. Please be aware the upper limit of integral for that case should be $t = \frac{2\pi}{\omega_1} = \frac{2\pi p}{\omega_r}$.

With such expression, you can put in respective parameters and estimate which commutator term would dominant the first order contribution, which will be trivial for you to figure out.

In summary, at different regime of MAS vs. ω_1, we need to change the decoupling setup for optimal performance: if you can spin faster than 2 folds of $\widetilde{H}_{D_{II}}$, which is more than 100 kHz, please use low power decoupling. In either case, you will find the first order term from commutator between proton chemical shielding tensor and ^{1}H-^{13}C heteronuclear coupling dominates the carbon linewidth, with $\frac{1}{4\omega_r p} I_z S_z \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \omega_{2m}^{D_{IS}} \omega_{2-m}^{\text{csa}}$.

Well, the above is an approximated derivation, but we do get some very interesting insights.

It is obvious that the contributions can be further suppressed if we alternate the RF irradiation axis, from positive x to negative x axis, then if we reverse the I_z to $-I_z$ (remember this I_z is in the tilted reference frame, corresponding to the x axis of RF irradiation in the rotating frame), the contribution from two pulses of equal length (and tip angle) with opposite polarity should cancel their respective first order contribution. This is a qualitative argument behind the TPPM and XiX decoupling pulse sequence. In reality, since there is a strong proton coupling network, each with their own isotropic chemical shift and anisotropy. This would mean for each proton its x axis in the rotating frame is different. Therefore, a perfect cancellation is not possible even if you alternate the RF irradiation from x to –x.

In addition, we have to acknowledge the stochastic process involved, which also forfeits perfect cancellation. This is in analogy to the Hahn Echo: the π pulse can only focus decoherence due to static inhomogeneity, while the stochastic process is beyond the π pulse.

Moreover, the strong ^{1}H-^{1}H dipolar coupling network also affect the spin diffusion and contribute the ^{13}C resonance broadening via the nonzero commutator with the ^{1}H-^{13}C heteronuclear dipolar Hamiltonian. All these complications make it difficult to explain the mechanism of multiple pulse decoupling sequences by AHT, as we demonstrated above for continuous wave decoupling. But we do get some insights into their mechanism after the above derivation, at the least.

The commutation relationships we derived from Eq. 7.80 to 7.103 will come handy in actual computation of various terms in the Van-Vleck approximation of Floquet theory.

7.6 Floquet theory for analysis of combined effect of RF irradiation and MAS

This part of introduction to Floque theory refers heavily to a series of paper: Matthias Ernst, Ago Samoson and Beat H. Meier, JCP 123, 064102 (2005); Ingo Scholz, Jacco D. van Beek, and Matthias Ernst, ssNMR 37, 39-59 (2010); Ingo Scholz, Beat H. Meier, and Matthias Ernst JCP 127, 024504 (2007); and Michal Leskes, P.K. Madhu, and Shimon Vega, Progess in NMR spectroscopy 57, 345-380 (2010).

Special thanks to Matthias Ernst's help to derive the formalism of Van-Vleck perturbation treatment in the Floquet space.

Instead of showing how to apply Floquet theory, I will focus on why and how Floquet theory framework is developed. This is because the actual application of Floquet theory is based on the same density matrix theory framework, and it is essentially a plug and play style process. The challenge is to understand how the theory is formulated, which requires a deeper understanding and can also help the actual application.

This reasoning of mechanism of Floquet theory stems from my own logical understanding and is based on my own knowledge background, and may not be the actual historical fact. However, as there are many who may share my knowledge background, this narrative may help you embrace the new technique.

The motivation to introduce Floquet theory to ssNMR is very clear. We have just witnessed the limitation of AHT: there are often multiple incommensurate time-dependent frequencies in the decoupling situations. For example, the frequency/period of MAS and decoupling pulses. It is difficult to understand their interplay, and derive an analytical expression. In fact, in order to avoid recoupling conditions, we normally avoid intentionally the commensurate conditions between MAS and decoupling RF irradiation. A different theory framework is needed to elucidate the physics inside such situations, for example, $\frac{\omega_r}{\omega_{1I}} \neq p$ and $\frac{\omega_{1I}}{\omega_r} \neq p$, where p is some natural number.

Meanwhile, the analysis by AHT already becomes hard to keep track of even for the simple decoupling of continuous RF irradiation. With the first order approximation by the Magnus expansion, there are already over 6 nonzero commutators of various interactions. We have not even started to account for alternation of phase or pulse length.

Let's review what we have and what we are facing at the moment, so we can better understand why and how Floquet framework is designed?

We already have a very mature platform, the density matrix method, to compute physical observables. We can review a bit what we did in Chapter 4. By defining the density matrix for systems in a pure state:

$$\rho = \sum_{i,j=1}^{n} c_i c_j^* \, |u_i\rangle\langle u_j| \tag{7.109}$$

Or more generally and practical for our NMR experiments, systems in a mixed state:

$$\rho = \sum_{i} P_i \, |\psi_i\rangle\langle\psi_i| \tag{7.110}$$

Both obey the rate equation (or so called LvN equation):

$$\frac{d\rho}{dt} = \frac{H}{i\hbar}|\psi\rangle\langle\psi| + |\psi\rangle\frac{\langle\psi|H}{-i\hbar} = i\hbar(-H\rho + \rho H) = i\hbar[\rho, H] \tag{7.111}$$

Which allows us to derive the time evolution of the density matrix, if the system Hamiltonian is known:

$$\rho(t) = U\rho(0)U^{-1} \tag{7.112}$$

Where U is the unitary time evolution operator:

$$U =$$

$$= \exp[-\frac{i}{\hbar}\int_{t_{n-1}}^{t_n} d\tau H_n(\tau)]\exp[-\frac{i}{\hbar}\int_{t_{n-2}}^{t_{n-1}} d\tau H_{n-1}(\tau)] \dots \exp[-\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau H_2(\tau)]\exp[-\frac{i}{\hbar}\int_{0}^{t_1} d\tau H_1(\tau)]$$

$$= \vec{T}\exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)]$$

$$\rho(t) = U\rho(0)U^{-1} = \exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)] \;\; \rho(0)\exp[\frac{i}{\hbar}\int_0^t d\tau H(\tau)] \tag{7.113}$$

More importantly, we can use this knowledge to compute the expectation value of physical observables that correspond to actual experimental measurements by:

$$\langle A\rangle = \overline{\langle\psi|A\psi\rangle} = \sum_{m=1}^{n}\langle m|\,\rho A|m\rangle = trace\{\rho A\} \tag{7.114}$$

Here the piece-wise Hamiltonian in each time interval in Eq. 7.113 should be time-independent, so we can compute the integration without diagonalization.

If the Hamiltonian is time-dependent, as the case with recoupling and decoupling sequence in the presence of MAS, Magnus expansion can be applied. This converts the time-dependent Hamiltonian within each small time interval to time-independent ones, provided the magnitude(the norm of the Hamiltonian times the time interval) is sufficiently small (smaller than π). Subsequently, we can use these time-independent Hamiltonian in each time interval to compute the density matrix, and derive the time evolution of any physical observables.

Now with the presence of time dependence $e^{i\omega_{1I}t}$ due to RF irradiation, in addition to the MAS $e^{im\omega_r t}$, we can't easily find a common period to do the integral after Magnus expansion and remove the time dependence in Hamiltonian. This obstructs the application of the density matrix to derive the time evolution of the system.

Our goal is to remove these annoying $e^{i\omega_{1I}t}$ and $e^{im\omega_r t}$ without jeopardizing the integrity of our existing density matrix platform, so that we can still enjoy the convenience of this platform to easily compute the time evolution of any physical observables with the knowledge of time-independent Hamiltonian.

How can we do that?

These $e^{i\omega_{1I}t}$ and $e^{im\omega_r t}$ factors remind us of Fourier transformation. If we can introduce some special operator to create these terms in Hamiltonian, and then transform to the "interaction frame of reference" associated with the operator, it would remove these terms, just like what we did in the transformation to rotating frame or interaction frame of the RF irradiation.

Then our Hamiltonian in this new interaction frame would be time-independent, and we can apply again density matrix method to compute the evolution of any physical observables. We just need to guarantee that the introduction of such new operators preserves the LvN rate equation for the density matrix. Then we can transform back the computed physical observables to our standard reference frame (rotating frame, or interaction frame of the RF irradiation), so we can obtain direct insights into the spin physics of the system, and compare with experimental results.

Ok, the general strategy is clear now. Let's first conceive what properties these new operators should have to achieve this goal.

These special operators should interact only with their counter parts, and do not interact with any of our spin operators to mess up the spin physics, which is already a self-consistent system. However, we can draw inspiration from the spin operators. There are operators in our spin physics can produce similar time-dependent phase factors to $e^{in\omega_{1I}t}$ and $e^{im\omega_r t}$:

$$\exp(-i\phi I_z)\, I^{\pm} \exp(i\phi I_z) = \exp(\mp i\phi) I^{\pm} \tag{7.115}$$

The difference is that now we also have numerical factor n in $e^{in\omega_{1I}t}$ corresponding to the coherence factor due to RF irradiation and m in $e^{im\omega_r t}$ arising from the transformation of second rank tensors due to MAS. So the new operators have to produce some integer numerical factors.

Now we have the blueprint. All we need to do now is to create a set of the operators that obey the similar commutation relationships, and then they should naturally bring in the desired exponential $e^{in\omega_{1I}t}$ and $e^{im\omega_r t}$ factors:

$$I^{\pm} = I_x \pm iI_y;\ \ [I^{\pm}, I_z] = \mp\hbar I_{\pm};\ \ [I^{+}, I^{-}] = 2\hbar I_z;\ \ [I^{-}, I^{+}] = -2\hbar I_z$$

The price we have to pay is, we need to create additional "physical space" in addition to current Hilbert space (spin up and down states as the eigenstates of Zeeman interaction spanned in the Hilbert space) for these new operators to "live in", as they will operate on the wave functions of the system and manifest their effect accordingly. They are just like the spin I and S operators present in our Hamiltonian: when you introduce an additional spin operator into the Hamiltonian of the original single spin system, your wave function of the new system requires expansion from the original α_S or β_S to $\alpha_S\alpha_I$ and $\beta_S\beta_I$.

As these new operators don't interact with existing spin operators, it means that the new wave functions of our system are direct product between the eigenstates of these new operators and the original spin up and down eigenstates of Zeeman interactions. The new wave functions formed by the joint product are called "dressed states", as if our old spin physics wave functions put on an additional layer of dress.

With the situation and goal all clear, we can define our new Floquet operators now: F_n, the ladder operator, and N, the number operator.

The ladder operator F_n works just like the spin ladder operators $I^{\pm}$, while the number operator N plays a similar role as I_z. Let's register the corresponding Fourier eigenstates of N to as $|\nu\rangle$:

$$\langle \nu | N | \nu' \rangle = \nu \delta_{\nu\nu'} \boldsymbol{I} \tag{7.116}$$

where $\boldsymbol{I}$ is the unitary operator with the dimension of each unit(or so called block) matching the Hilbert space of the spin system, and the entire matrix of $\boldsymbol{I}$ has infinite units labeled by ν, as shown in Fig. 7.3. If we deal with a two spin system, each block in this new system will have 2×2=4 states since each spin has its own spin up and down states. In general, if we have a N spin systems, the dimension of the wave function in Hilbert space is $N_h = (2I+1)^N$, where I is the spin quantum number.

Here ν adopts discrete integer numbers, so it can account for any integer terms in the $e^{in\omega_{1I}t}$ or $e^{im\omega_r t}$ factors, with values going from $-\infty$ to ∞, just like the upper and lower limit in standard Fourier transformation.

The Floquet ladder operator F_n would shift the system from one Fourier eigenstate to another that is separated by their difference of eigenvalues:

$$\langle \nu + n | F_n | \nu \rangle = \boldsymbol{I} \tag{7.117}$$

This will lead operations between multiple ladder operators corresponding to the same kind of Fourier states to have an accumulative effect of level shifting:

$$F_n F_m = \langle \nu + m + n | F_n | \nu + m \rangle \langle \nu + m | F_m | \nu \rangle = \langle \nu + m + n | F_n F_m | \nu \rangle = F_{n+m} \qquad (7.118)$$

Accompanied with these definition is their commutation relation:

$$[N, F_n] = nF_n \qquad (7.119)$$

Which we notice the commutation produces an extra factor of n. This is very critical, as this will naturally lead to:

$$e^{i\omega Nt} F_n e^{-i\omega Nt} = F_n e^{i\omega nt} \qquad (7.120)$$

This can be approved by the following method, as what C. P. Slichter showed to derive the commutation relation of single spin operator in Eq. 5.3. Define a function $f(t)$:

$$f(t) = e^{i\omega Nt} F_n e^{-i\omega Nt}$$

$$\frac{d}{dt} f(t) = i\omega N e^{i\omega Nt} F_n e^{-i\omega Nt} + e^{i\omega Nt} F_n (-i\omega N) e^{-i\omega Nt}$$

We note here N is an operator but ω is just a numerical factor. N and $e^{i\omega Nt}$ commute with each other, hence:

$$\frac{d}{dt} f(t) = i\omega e^{i\omega Nt} N F_n e^{-i\omega Nt} - i\omega e^{i\omega Nt} F_n N e^{-i\omega Nt} = i\omega e^{i\omega Nt} [N, F_n] e^{-i\omega Nt} = in\omega e^{i\omega Nt} F_n e^{-i\omega Nt}$$

Hence it means:

$$\frac{d}{dt} f(t) = in\omega f(t)$$

Follow the same approach, you can show

$$\frac{d^2}{dt^2} f(t) = (in\omega)^2 e^{i\omega Nt} F_n e^{-i\omega Nt} = (in\omega)^2 f(t)$$

Hence according to the standard solution for differential equations, we know that:

$$f(t) = A \cos n\omega t + B \sin n\omega t$$

By setting $t = 0$,

$$f(0) = A = F_n$$

$$\frac{d}{dt} f(0) = n\omega B = in\omega F_n$$

Therefore, we proved Eq. 7.120 is true:

$$f(t) = e^{i\omega Nt} F_n e^{-i\omega Nt} = F_n e^{i\omega nt}$$

This relation enables us to enact transformations reminiscent of that into the interaction frame of RF pulses, which eliminates the dependence of the exponential factor caused by RF irradiation, or, transformation into the rotating frame, which eliminates the exponential factor due to Larmor precessing. However, the difference for our nearly established Floquet transformation is highly selective, with their respective Fourier index integer. This enables us to separate Hamiltonian with $e^{in\omega_1 I t}$ and $e^{im\omega_r t}$ of different n and m values into different block unit in the Floquet space, as shown in Fig. 7.4.

For this purpose, we can introduce multiple distinct sets of ladder and number operators, so we can use respective set of Floquet operators to eliminate distinct frequency factors. This is so called multiple modes of Floquet theory. For example, F_n^1 and N^1 for $e^{in\omega_1 I t}$, and F_n^2 and N^2 for $e^{im\omega_r t}$. F_n^i and N^i will only interact with their respective Floquet operator F_n^i and N^i. It works just like spin operators associated with different nuclei: I_i will only interact with I_i, and will not affect I_j or S_i.

Now, we have the operators and the rules of transformation to eliminate the frequency dependence in Hamiltonians. Next is to construct associated wave functions of the newly expanded Hamiltonians and correlate with our original system Hamiltonian.

Let's review the Hamiltonian that we derived in Sect. 7.4. They assume a generic form of:

$$H(t) = \sum_{m,n} H_{m,n} e^{im\omega_r t} e^{in\omega_1 I t} \tag{7.121}$$

For example, we derived Eq. 7.67:

$$\widetilde{H}_{csa} = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \frac{\omega_{2m}^{cs}}{2} e^{im\omega_r t}\left[-I^+ e^{i\omega_1 t} - I^- e^{-i\omega_1 t}\right]$$

so

$$\widetilde{H}_{csa} = \sum_{\substack{m=-2 \\ m\neq 0}}^{2} \sum_{\substack{n=-1 \\ n\neq 0}}^{1} H_{m,n}^{csa} e^{im\omega_r t} e^{in\omega_1 I t}$$

Where $H_{m,1}^{csa} = -\frac{\omega_{2m}^{cs}}{2} I^+$, and $H_{m,-1}^{csa} = -\frac{\omega_{2m}^{cs}}{2} I^-$, where $m = \pm 1,2$

You can show $\widetilde{H}_{D_{IS}}$ in Eq. 7.71 can be decompose into similar terms when RF irradiation applies only to spin I.

For another example, Eq. 7.68:

$$\widetilde{H}_{cs} = \frac{\omega_{iso}}{2}\left[-I^+ e^{i\omega_1 t_2} - I^- e^{-i\omega_1 t_2}\right] = \sum_{\substack{n=-1 \\ n\neq 0}}^{1} H_n^{cs} e^{in\omega_1 I t}$$

Where $H_{0,1}^{cs} = -\frac{\omega_{iso}}{2} I^+$, and $H_{0,-1}^{cs} = -\frac{\omega_{iso}}{2} I^-$

For homonuclear dipolar interactions shown in Eq. 7.73:

$$\widetilde{H}_{D_{II}} = \sum_{m=-2}^{2} \omega_{2m}^{D_{II}} e^{im\omega_r t}\left[\frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) + \frac{3}{4} e^{i2\omega_1 t} I_i^+ I_j^+ + \frac{3}{4} e^{-i2\omega_1 t} I_i^- I_j^-\right]$$

You can show

$$\widetilde{H}_{D_{II}} = \sum_{\substack{m=-2\\ m\neq 0}}^{2} \sum_{\substack{n=-1\\ n\neq 0}}^{1} H_{m,n}^{D_{II}} e^{im\omega_r t} e^{in\omega_{1I} t}$$

Where $H_{m,0}^{D_{II}} = \frac{1}{2}\left(I_0^{xij} - 2I_{zi}I_{zj}\right) = \frac{1}{2}I_0^{xij} + I_0^{zij} - I_2^{zij}$. Here I_0^{zij} *and* I_2^{zij} are z component of the fictitious zero and double quantum operators formed by spin I_i and I_j.

And $H_{m,\pm 2}^{D_{II}} = \frac{3}{4} I_i^{\pm} I_j^{\pm}$, where $m = \pm 1,2$.

Similarly, for the first order expansion terms arising from commutators between different interactions, there are similar terms in Floquet theory, and we can specify their decompositions.

For example, the commutator between csa and heteronuclear dipolar coupling with RF irradiation applied only to spin I, derived from Eq. 7.94:

$$\left[\widetilde{H}_{csa}(t_2), \widetilde{H}_{D_{IS}}(t_1)\right]$$

$$= \frac{1}{4}\overline{\omega_{2m}^{D_{IS}}}\,\overline{\omega_{2n}^{\mathrm{csa}}} I_z S_z e^{in\omega_r t_2} e^{im\omega_r t_1}\left(e^{i\omega_{1I}(t_2-t_1)} - e^{-i\omega_{1I}(t_2-t_1)}\right)$$

Here we need to combine the factors $e^{in\omega_r t_2} e^{im\omega_r t_1} = e^{i(n+m)\omega_r t} = e^{ik\omega_r t}$, where $k = \pm 1,2,3,4$ *and* 0. since they both arise from the same cause, MAS, with the same frequency.

Note that we drop the subscript t_i here, as the time subscript is associated with the rule of Magnus expansion, In Floquet theory, we will incorporate similar commutators as different orders of approximation. However, we don't differentiate time that is incurred by integration over different time intervals. Instead, we ascribe the differences to summation over different frequencies.

Note as we progress to higher order of commutators, the index of summation integer of the frequency goes up: $k = 0, \pm 1,2,3,4$. We can see that at infinite accuracy (which need infinite layers of commutators), the summation of frequency index would also approach infinitely large integers. This is the tradeoff we have to make by replacing layers of time integrals with layers of frequency summation. This reminds us of Fourier transform, right?

What we accomplished above at this point is the transformation of Hilbert space Hamiltonian into Floquet space. By doing this, we convert the time-dependent exponential terms into respective time-independent Fourier components in Floquet space, and space them away from the diagonal direction to be the off-diagonal blocks, shown in Fig. 7.4.

To sum up what we do as the first step in the application of Floquet theory: we need to transform the Hamiltonian of the system into its interaction frame of RF irradiation, together with MAS caused exponent factors. The Hamiltonian then in this interaction frame should be written in the form of Eq. 7.121, which helps us obtain respective Fourier components as we demonstrated above. These Fourier components are actually the off-diagonal blocks of the Hamiltonian in the Floquet space that register the same frequency component, shown in Fig 7.4.. These off-diagonal blocks will be removed later in Van-Vleck approximation to diagonalize the Hamiltonian and derive the time evolution of density matrix.

Hence the decomposed Hamiltonians of respective $H_{m,n}^{\Lambda}$terms with the same subscript that signifying the same Fourier factors would live in the same Fourier subspace in the Floquet space, as shown in Fig. 7.4 for a system with only one Fourier factor. We also note that only the time-independent terms of the Hamiltonian in Eq. 7.121 lives along the diagonal blocks of the Floquet matrix, while any terms dependent on time are now distributed at their respective off-diagonal Floquet blocks.

Next, we will show how to implement density matrix to Hamiltonians in this Floquet space. To simply the demonstration of principles, let's assume that we just have one frequency component.

Let's step back to the original Hilbert space. With our above demonstrations, it is clear now that the generic Hamiltonian in the Hilbert space assumes the form:

$$H(t) = \sum_n H_n e^{in\omega t} \tag{7.122}$$

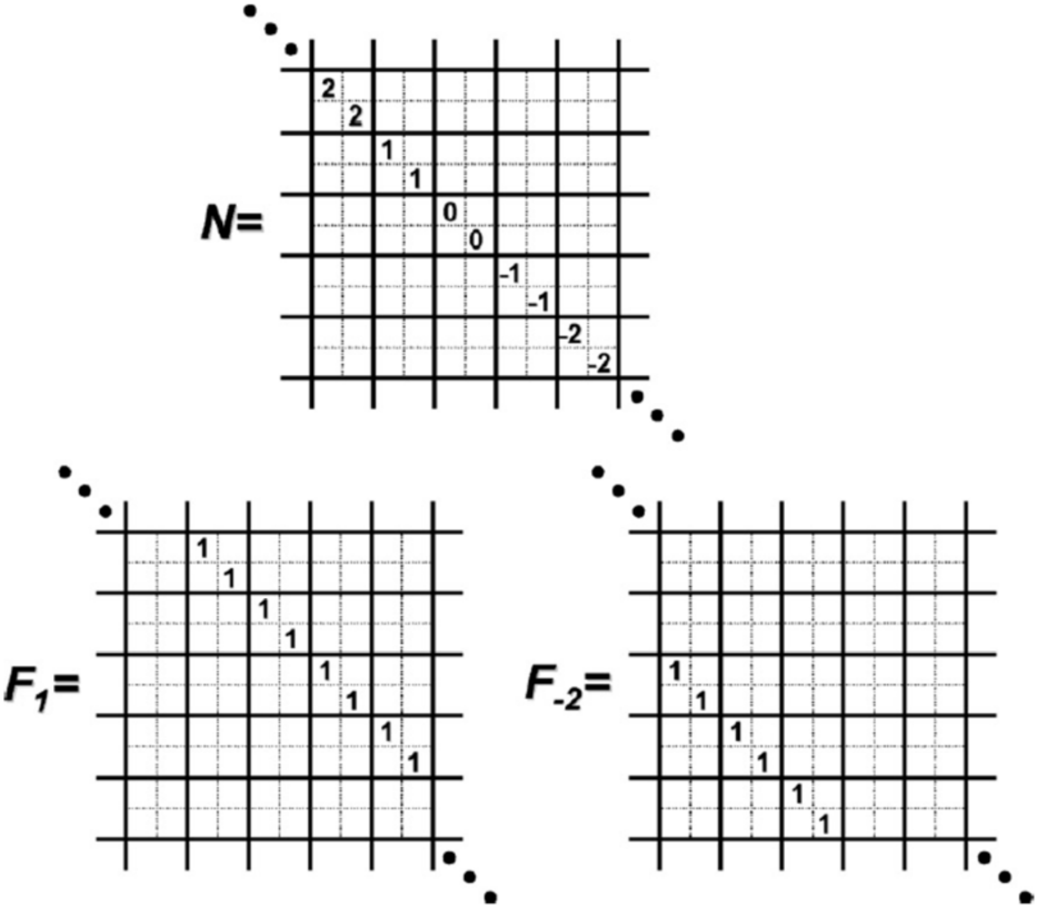


Figure 7.3. Schematic representation of Floquet operator, in the basis of direct product of Hilbert space and Floquet operator. Each block comprises sub-Hilbert space of identical dimension that matches the spin system $N_h = (2I + 1)^N$. The presented system shows four sub-entries indicated by dashed lines, which means it is a single spin system. Adapted from Progess in NMR spectroscopy 57, 345-380 (2010).

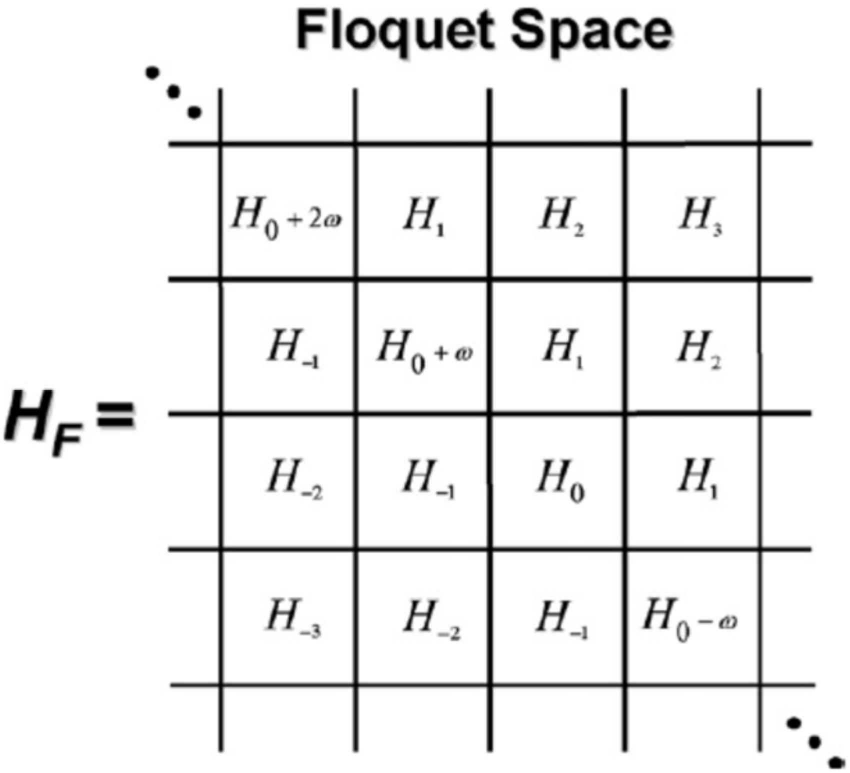


Figure 7.4 Schematic representation of Hamltonian in the Floquet space as an matrix of infinite dimensions. Each H_n is a block of sub-matrix with dimensions matching that of the spin system in Hilbert space, and therefore, consists of multiple entries. Adapted from Progess in NMR spectroscopy 57, 345-380 (2010).

Just like a normal quantum mechanical problems, imagine if we solve the Schodinger equation with the Hamiltonian shown in Eq. 7.122 and obtain its eigensates $\{|\psi\rangle\}$, then we can construct corresponding density matrix $\rho = |\psi\rangle\langle\psi|$, which obviously obeys the LvN rate equation:

$$\frac{d\rho}{dt} = \frac{H}{i\hbar}|\psi\rangle\langle\psi| + |\psi\rangle\frac{\langle\psi|H}{-i\hbar} = i\hbar(-H\rho + \rho H) = i\hbar[\rho, H]$$

$$\rho(t) = U\rho(0)U^{-1}$$

Where U is the unitary time evolution operator:

$$U = \vec{T}\exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)]$$

Hence:

$$\frac{d}{dt}U(t) = -i\, H(t)\vec{T}\exp[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)] \ = -iH(t)U(t)$$

In fact, the general solution to such an equation with $H(t) = \sum_n H_n e^{in\omega_1 t}$ was shown by Floquet and Shirley in G. Floquet, Ann. Sci. Ecole Norm. Sup. 47, 12 (1883) and J. H. Shirley, PRB 138, 979 (1965):

$$U(t) = u(t)e^{-i\Lambda t}u^{-1}(0) \tag{7.123}$$

$$u(t) = \sum_n u_n e^{in\omega t}$$

We will show in our derivation how this form comes by. But for now, let’s accept that this is true.

Hence we have:

$$\rho(t) \tag{7.124}$$

$$\left[\sum_n u_n e^{in\omega t} e^{-i\Lambda t} u^{-1}(0)\right] \rho(0) \left[u(0) e^{-i\Lambda t} \sum_m u_m^{-1} e^{im\omega t}\right] = \sum_{m,n} u_n \tilde{\rho}(t)\, u_m^{-1} e^{i(n+m)\omega t}$$

$$= \sum_k \big(\sum_l u_{k-l} \tilde{\rho}(t) u_l^{-1}\big)\, e^{ik\omega t} = \sum_k \rho_k(t)\, e^{ik\omega t}$$

Where we have the Fourier coefficient of the density operator as:

$$\rho_k(t) = \sum_l u_{k-l} e^{-i\Lambda t} u^{-1}(0) \rho(0) u(0) e^{-i\Lambda t} u_l^{-1} \tag{7.125}$$

We don’t know what $e^{-i\Lambda t}, u(0)$ and u_n are at the moment, but they will be revealed as we progress, so please bear with us for a moment. Here our motivation is to show that the density matrix shares a similar dependence on the Fourier component as our system Hamiltonian. $\rho(t) = \sum_k \rho_k(t)\, e^{ik\omega t}$

Since

$$\frac{d\rho}{dt} = i\hbar[\rho, H] = i[\rho, H]$$

Here we again omit $\hbar$, as all our computations are in unit of $\hbar$. Plug the Hamiltonian in Eq. 7.122 and derived density matrix f into this rate equation:

$$\frac{d\left(\sum_k \rho_k(t)\, e^{ik\omega t}\right)}{dt} = \frac{d \sum_k \rho_k(t)}{dt} e^{ik\omega t} + ik\omega \sum_k \rho_k(t)\, e^{ik\omega t} \tag{7.126}$$

$$= i \sum_k \rho_k(t)\, e^{ik\omega t} \sum_n H_n e^{in\omega t} - i \sum_n H_n e^{in\omega t} \sum_k \rho_k(t)\, e^{ik\omega t}$$

Recall we showed earlier in Eq. 7.120:

$$e^{i\omega Nt} F_n e^{-i\omega Nt} = F_n e^{i\omega nt}$$

So we can remove the $e^{ik\omega t}$ terms by performing the transformation into Floquet space, by the above relationship:

$$\frac{d(\sum_k \rho_k(t) F_n)}{dt} = \frac{d \sum_k \rho_k(t)}{dt} F_k + ik\omega \sum_k \rho_k(t)\, F_k \tag{7.127}$$

$$= i\left[\sum_k \rho_k(t) F_k \sum_n H_n F_n - i \sum_n H_n F_n \sum_k \rho_k(t) F_k\right]$$

Also recall the other commutation relation in Eq. 7.119:

$$[N, F_n] = nF_n$$

We can apply this to transform:

$$ik\omega \sum_k \rho_k(t)\, F_k = i\omega \sum_k \rho_k(t)\, [N, F_k]$$

Hence Eq. 7.127 becomes:

$$\frac{d \sum_k \rho_k(t)}{dt} F_k + i \sum_k \rho_k(t)\, [N\omega, F_k]$$

$$= i\left[\sum_k \rho_k(t) F_k \sum_n H_n F_n - i \sum_n H_n F_n \sum_k \rho_k(t) F_k\right] = i[\sum_k \rho_k(t) F_k\, , \sum_n H_n F_n]$$

Which can be rearranged if we move the second term to the right side:

$$\frac{d \sum_k \rho_k(t)}{dt} F_k = i[\sum_k \rho_k(t) F_k\, , (\sum_n H_n F_n + N\omega)] \tag{7.128}$$

This shows if we formally define the transformation conducted above as the procedure to transform operators from the Hilbert space system to Floquet space, we can replace respective time-dependent Fourier coefficient factors with symbolic F_n and turn the operators into time-independent :

$$H(t) = \sum_n H_n e^{in\omega t} F_n = e^{i\omega Nt}[\sum_n H_n F_n] e^{-i\omega Nt} \tag{7.129}$$

$$\rho(t) = \sum_n \rho_n(t)\, e^{in\omega t} F_n = e^{i\omega Nt}[\sum_n \rho_n(t) F_n] e^{-i\omega Nt} \tag{7.130}$$

So Eq. 7.129 describes the process we went through earlier to decompose Hamiltonians of various interactions into their respective frequency components, which correspond to the Floquet space Hamilonians in their respective diagonal(if it carries no frequency component) or off-diagonal blocks.

Note that it requires the Hamiltonian in Floquet space to acquire an additional ωN factor, so that the density matrix will obey the same format of LvN rate equation in the Floquet space:

$$H_F = \sum_n H_n F_n + \omega N \tag{7.131}$$

$$\rho_F(t) = \sum_n \rho_n(t) F_n \tag{7.132}$$

The benefit of such a transformation is more than mere formality. Once we proved the density matrix obeys the same LvN equations, all the standard practice of the normal density matrix computation can be directly replicated. So it is convenience to compute all physical observables in Floquet space. But first let’s take a closer look at the density operator:

$$U_F(t) = \exp(-iH_F t) \tag{7.133}$$

With the initial point $t = 0$ density operator:

$$\rho_F(0) = \rho(0)F_0 \tag{7.134}$$

Here it implies that $\rho(0)$ at $t = 0$ in Hilbert space should carry no frequency component, corresponding to the time-independent terms in the Hilbert space Hamiltonian.

With this setup, the Hamiltonian H_F becomes time-independent, and avoid the multiple layers of integration challenge encountered in AHT. All we need to do is to diagonalize H_F. Then the time evolution of the system in the Floquet space is simply:

$$\rho_F(t) = \exp(-iH_F t)\rho(0)F_0 \exp(iH_F t) \tag{7.135}$$

Where $\exp(-iH_F t)$ becomes some simple numerical exponential factor after diagnolization of H_F. Following this, it allows us to use the same formalism to compute any physical observables A_F in Floquet space:

$$\langle A_F \rangle = Tr\{\sum_n \rho_n(t)F_n A\} \tag{7.136}$$

Now to obtain the corresponding expectation value of the same observable in the Hilbert space, we just have to transform the above expression back to the Hilbert space and sum over the trace of the Fourier states:

$$\langle A \rangle = \sum_{n,\phi_i} \langle n, \phi_i | \rho_n(t) F_n A | n, \phi_i \rangle\, e^{in\omega t} \tag{7.137}$$

Here the summation is over the trace of all eigenstates ϕ_i of spins, and Fourier states n.

As we commented earlier, to achieve infinite accuracy, the Magnus expansion to higher order will lead the summation of Fourier components to infinite. So this summation over n for Floquet states will be over the range of infinitely, if you want infinitely high accuracy. However, this is not possible for realistic computation (unless it is some known converging series in Maths). Assume this is not a problem, all we need to do is to find the effective diagonalized Hamiltonian in Floquet space, and the rest is to plug into the above formula Eq. 7.136 and 7.137 for some routine computation.

So now the question becomes how to find this diagnolization matrix D_F for our Floquet Hamiltonian H_F:

$$\Lambda_F = D_F^{-1} H_F D_F = \Lambda_0 F_0 + \omega N \tag{7.138}$$

Which means:

$$H_F = D_F \Lambda_F D_F^{-1} \tag{7.139}$$

Hence the time evolution operator becomes:

$$U_F(t) = \exp(-iH_F t) = \exp(-iD_F \Lambda_F D_F^{-1} t) = D_F \exp(-i\Lambda_F t) D_F^{-1} \tag{7.140}$$

Here we use the relationship:

$$Ae^{B}A^{-1} = e^{ABA^{-1}}$$

Like any operators, its conversion to Hilbert space is Eq. 7.137, where we just need to just sum over the Fourier states n in the direct product Floquet dressing states:

$$U(t) = \sum_{n} \langle n|U_F(t)|n\rangle\, e^{in\omega t} = \sum_{n} \langle n\left|D_F \exp(-i\Lambda_F t)\, D_F^{-1}\right|n\rangle\, e^{in\omega t}$$
$$= \sum_{n,m,k} \langle n\left|D_F\right|m\rangle\langle m|\exp(-i\Lambda_F t)|k\rangle\langle k|D_F^{-1}|n\rangle\, e^{in\omega t} \tag{7.142}$$

As the diagnolized Hamiltonian:

$$\Lambda_F = D_F^{-1}H_F D_F = \Lambda_0 F_0 + \omega N$$

The F_0 operator restricts the summation $\langle m|\exp(-i\Lambda_F t)|k\rangle$ to $m = k = 0$. Hence Eq. 7.142 becomes:

$$U(t) = \sum_{n} \langle n\left|D_F\right|0\rangle\langle 0|\exp(-i\Lambda_0 t)\,|0\rangle\langle 0|D_F^{-1}\left|n\right\rangle\, e^{in\omega t}$$
$$= \sum_{n} \langle n\left|D_F\right|0\rangle e^{in\omega t} \exp(-i\Lambda_0 t)\langle 0|D_F^{-1}\left|n\right\rangle$$
$$= \sum_{n} D_n\, e^{in\omega t} \exp(-i\Lambda_0 t)\, D_n^{-1} \tag{7.143}$$

Where $D_n = \langle n|D_F|0\rangle$, and $D_n^{-1} = \langle 0|D_F^{-1}|n\rangle$.

This means:

$$u(t) = \sum_{n} D_n\, e^{in\omega t} \tag{7.144}$$

$$u^{-1}(0) = \sum_{n} D_n^{-1} \tag{7.145}$$

So now all the left is to find the diagonalization matrix D_F in the Floquet space, since the Hamiltonian H_F is not diagnolized in the Floquet space.

This is where the Van-Vleck approximation comes in. Instead of finding a matrix that completely diagonalize H_F, which is an infinite dimension matrix in the Floquet space, it provides an approximation to block diagonalize H_F. As we have shown in Fig. 7.4, H_F in Floquet space consists of many sub-blocks of matrices. By block diagonalizing, it means there is a method to eliminate all the off-diagonal blocks of the Floquet Hamiltonian, and convert them somehow to the diagonal direction. This can be achieved by another expansion theorem in linear algebra, called the Baker-Cambell-Haussdorf (BCH) expansion.

According to the BCH expansion, for symmetric matrix, you can find a Hermitian operator:

$$D_F = e^{iS_F} \tag{7.146}$$

This D_F can remove the off-diagonal matrices to achieve so called block-diagonalization, in a fashion very similar to Magnus expansion (M. M. Marciq showed the AHT and Floquet theory are in fact equivalent, in PRB 25, 6622 (1982)):

$$\begin{gathered} D_F^{-1}H_FD_F \\ = H_F + i[H_F,S_F] - \frac{1}{2}\big[[H_F,S_F],S_F\big] + \cdots + \frac{1}{n!}\overbrace{\Big[-iS_F,\Big[-iS_F,\big[-iS_F,\dots\big[-iS_F,H_F\big]\big]\Big]\Big]}^{n\ -iS_F\ layers} \end{gathered} \tag{7.147}$$

If you are interested, you can show the proof of this expansion by first defining an operator-valued function of the c-number x:

$$F(x) = e^{xA}Be^{-xA} = \sum_{n=0}^{\infty}\frac{1}{n!}F(n)x^n \tag{7.148}$$

There are many online proofs in more detail, so readers can dig into this if they feel interested. I will not expand further.

So once the S_F is identified, we can use this recursive relationship to block diagnolize H_F to the degree that we are content with. In his paper Phys. Rev. 33 467 (1929), Van-Vleck showed how to obtain S_F to different orders of approximation, with the first order:

$$S_F^{(1)} = \sum_{n\neq 0}\frac{iH_n}{n\omega}F_n \tag{7.149}$$

M. Ernst gave his proof for various orders of S_F in JCP 123, 064102 (2005). He gave an equivalent solution of S_F, without the prefactor of i.

With this choice, and commutation relation in Eq. 7.119:

$$[N,F_n] = nF_n$$

You can see that

$$i\left[\omega N, S_F^{(1)}\right] = -\sum_{n\neq 0}H_n\,F_n \tag{7.150}$$

Thus after insertion 7.150 into the BCH expansion in Eq. 7.147, it will cancel the old off-diagonal sub-matrices in original H_F. We can show this by inserting the expression into the expansion. Let's try the first two commutators:

$$D_F^{-1}H_FD_F = H_F + i[H_F,S_F] - \frac{1}{2}\big[[H_F,S_F],S_F\big] \tag{7.151}$$

We will compute the two commutators step by step. First:

$$\begin{gathered} i[H_F,S_F] \\ = -\left[\sum_n H_nF_n + \omega N\,,\sum_{n'\neq 0}\frac{H_{n'}}{n'\omega}F_{n'}\right] = -\left[\sum_n H_nF_n\,,\sum_{n'\neq 0}\frac{H_{n'}}{n'\omega}F_{n'}\right] - \left[\omega N,\sum_{n'\neq 0}\frac{H_{n'}}{n'\omega}F_{n'}\right] \end{gathered} \tag{7.152}$$

$$= -\sum_{n,n'\neq 0} \frac{1}{n'\omega}[H_n, H_{n'}]\, F_{n+n'} - \sum_{n'\neq 0} \frac{1}{n'\omega}[H_0, H_{n'}]\, F_{n'+0} - \sum_{n'\neq 0} H_{n'}\, F_{n'}$$

$$= -\sum_{n,n'\neq 0} \frac{1}{n'\omega}[H_n, H_{n'}]\, F_{n+n'} - \sum_{n'\neq 0} \frac{1}{n'\omega}[H_0, H_{n'}]\, F_{n'} - \sum_{n'\neq 0} H_{n'}\, F_{n'}$$

Here we separate $n \neq 0$ and $n = 0$ in the $\sum_n H_n F_n$, and use the relationship $[F_n, F_{n'}] = 0$, and $F_n F_{n'} = F_{n+n'}$.

We can see now that the last term in Eq. 7.152 will cancel with positive $\sum_{n'\neq 0} H_{n'}\, F_{n'}$ in the first term H_F of expansion in $D_F^{-1} H_F D_F$ in Eq. 7.151.

We can take a closer look at what this means. This can be shown in the matrix representation of H_F in Fig. 7.4. We can see that for $n \neq 0$, all $\sum_{n'\neq 0} H_{n'}\, F_{n'}$ are located in the off diagonal blocks in the matrix. So essentially with the definition of $S_F^{(1)}$, we are able to eliminate the off-diagonal terms of H_F (which correspond to those terms exhibit frequency dependence in Hilbert space).

However, the price we paid is, it also introduced at the same time off diagonal terms $-\sum_{n,n'\neq 0} \frac{1}{n'\omega}[H_n, H_{n'}]\, F_{n+n'} - \sum_{n'\neq 0} \frac{1}{n'\omega}[H_0, H_{n'}]\, F_{n'}$. If you recall our estimation in Sect. 7.4, these are reminiscent of the first order Magnus expansion. As we estimated in the linewidth computation, their sizes are smaller than the original $H_{n'}$, due to the $\frac{1}{n'\omega}$. So this is a good bargain, that we eliminate something big, by admitting something a bit smaller. It will get better, if we continue to compute the second commutator:

$$\frac{1}{2}\big[[H_F, S_F], S_F\big] \tag{7.153}$$

$$= \frac{1}{2}\Big[i \sum_{n,n'\neq 0} \frac{1}{n'\omega}[H_n, H_{n'}]\, F_{n+n'} + i \sum_{n'\neq 0} \frac{1}{n'\omega}[H_0, H_{n'}]\, F_{n'} + i \sum_{n'\neq 0} H_{n'}\, F_{n'}$$

$$, \sum_{m\neq 0} \frac{iH_m}{m\omega} F_m\Big] = -\frac{1}{2}\left[\sum_{n,n'\neq 0} \frac{1}{n'\omega}[H_n, H_{n'}]\, F_{n+n'} \sum_{m\neq 0} \frac{H_m}{m\omega} F_m\right] - \frac{1}{2}\left[\sum_{n'\neq 0} \frac{1}{n'\omega}[H_0, H_{n'}]\, F_{n'}, \sum_{m\neq 0} \frac{H_m}{m\omega} F_m\right]$$

$$-\frac{1}{2}\left[\sum_{n\neq 0} H_n\, F_n, \sum_{m\neq 0} \frac{H_m}{m\omega} F_m\right]$$

$$= -\frac{1}{2} \sum_{n,n',m\neq 0} \frac{1}{mn'\omega^2}\big[[H_n, H_{n'}], H_m\big] F_{n+n'+m} - \frac{1}{2} \sum_{m,n'\neq 0} \frac{1}{mn'\omega^2}\big[\big[[H_0, H_{n'}], H_m\big] F_{n'+m}$$

$$-\frac{1}{2} \sum_{m,n'\neq 0} \frac{1}{m\omega}[H_{n'}, H_m]\, F_{m+n'}$$

Hence, counting in the negative sign in front of $\frac{1}{2}\big[[H_F, S_F], S_F\big]$ in the expansion, we see the last term in Eq. 7.153, will partially cancel the first term in the first commutator in Eq. 7.152. At the same time, it pays a bit of price by admitting two more terms with $\frac{1}{mn'\omega^2}$ prefactors, which should be smaller than the cancelled terms.

If we stop here and collect only terms proportional to $\frac{1}{n'\omega}[H_n, H_{n'}]$, we have the first order approximation of the effective Hamiltonian in Floquet space:

$$\Lambda_F^{(1)} = D_F^{-1} H_F D_F \tag{7.154}$$
$$= H_0 + \omega N - \frac{1}{2}\sum_{n,n'\neq 0} \frac{1}{n'\omega}[H_n, H_{n'}]\, F_{n+n'} - \frac{1}{2}\sum_{n'\neq 0}\frac{1}{n'\omega}[H_0, H_{n'}]\, F_{n'}$$

Here we can neglect smaller (higher order $\sim\frac{1}{\omega^2}$) off-diagonal terms. This is normally justified for the Hamiltonian in NMR, as the off-diagonal terms are smaller. You can inspect the spin part of Hamiltonian and you will see the off-diagonal terms always involving $I^{\pm}$, which is smaller than the diagonal terms in Hamiltonian carrying only I_z operators.

Also note when summing up ωN, the numerical number in the matrix is symmetric going from integer positive to negative, so ωN will perfectly cancel out. The reason for the symmetric distribution arises from the original Hamiltonian in Hilbert space is Hermitian, which requires whenever there is a specific H_n in the Fourier decomposition, there must be a H_{-n}^*, which automatically balances the specific $n\omega$ with a $-n\omega$ in the Floquet space.

Hence we can collect the diagonal terms as the effective diagonalized Hamiltonian to the first order approximation in Floquet space as:

$$\widetilde{H}_{eff} \cong \widetilde{H}_{eff}^{(0)} + \widetilde{H}_{eff}^{(1)} = H_0 - \frac{1}{2}\sum_{n\neq 0}\frac{1}{n\omega}[H_n, H_{-n}]\, F_0 \tag{7.155}$$

Again, we emphasize the premise of this operation is based on the fact that $\frac{H_n}{n\omega} < 1$. You can see immediately that this $\frac{1}{n\omega}[H_n, H_{-n}]$ format of the first order effective Hamiltonian matches our prior first order approximation from the Magnus expansion, after integration. This shows that they are in fact equivalent.

Following this strategy, you can push the expansion to higher order and show:

$$\widetilde{H}_{eff}^{(2)} \tag{7.156}$$
$$= -\frac{1}{3}\sum_{\substack{n'\neq 0\\ n\neq 0\\ n\neq n'}} \frac{1}{nn'\omega^2}[[H_{n-n'}, H_{n'}], H_{-n}]F_0 - \frac{1}{2}\sum_{n\neq 0}\frac{1}{n^2\omega^2}\big[[H_0, H_n], H_{-n}\big]\, F_0$$

With second order rotation generator:

$$S_F^{(2)} = \sum_{\substack{n\neq 0\\ n'\neq 0}} \frac{i[H_{n'}, H_{n-n'}]}{2n'n\omega^2}(1 + 2\delta_{nn'})F_n \tag{7.157}$$

Similarly, we can process systems with Hamiltonians exhibiting multiple frequency dependent by multimode Floquet theory. I will skip the derivation, as it will be repetitive to what was demonstrated above, and just copy the summarized result from Leskes' review article, shown in Fig. 7.5.

We can now see the advantage of Floquet Theory over AHT very clearly now. By introducing the level shifting and number operators, the Fourier coefficient style time-dependent factors are removed from system Hamiltonian. They are converted into corresponding off-diagonal blocks H_n in Floquet space. The new Hamiltonian and its Floquet space eigenstates still satisfy the premise of the density matrix method. With Van-Vleck approximation, we can convert the block-wise Floquet Hamiltonian into desired ordered approximation diagonal Hamiltonian. In this process, the cumbersome multilayer integration over time in AHT is replaced by summation over different frequencies by the Van-Vleck expansion.

This tradeoff is especially worthwhile to probe into systems with dependence over incommensurate multiple frequencies, which is not able to achieve an analytic solution by integration, but now we can easily obtain analytical format of system Hamiltonian to any specific order of approximation with Floquet summation. All we need to do is to plug in the corresponding commutators we computed earlier in Eq. 7.80 to 7.103 into Eq. 7.155.

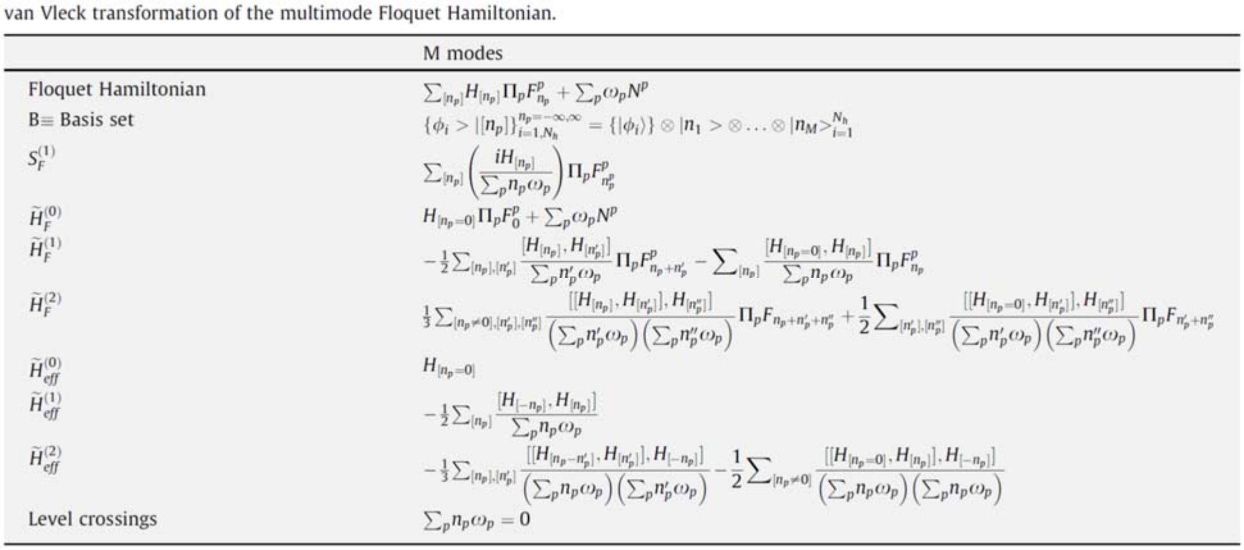
Subsequently, we can use this approximated and diagonalized effective Hamiltonian to compute the time evolution of density operator in Eq. 7.135. The computation of any other physical observables follows the standard density matrix method in Eq. 7.137.

Basically all the spin dynamics of the system can be solved by such a plug-and-play style approach. To recap the process, all we need to do is to decompose first our system Hamiltonians into different Fourier components H_n . They are then plugged into Van-Vleck expansion, to compute corresponding commutations between H_n.

I would say you can't beat this in simplicity. This also makes simulation programming easy with the strict formality and modularity. You can basically code the simulation program with a main and subroutines for the system Hamiltonians, or import the system Hamiltonian to the main program as an external input file that you can modify according to a specific system of interest. All the following computation of the system Hamiltonian to different orders of approximation is handled the same way by the main program.

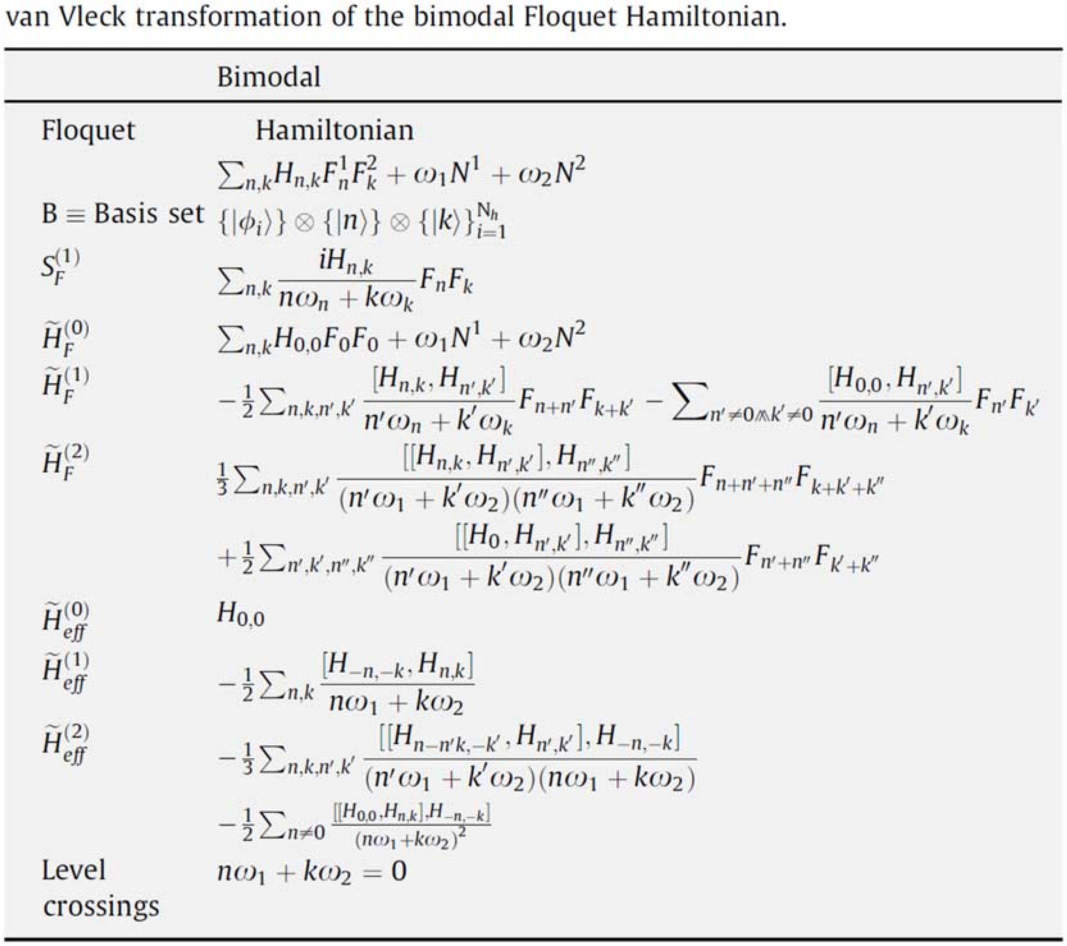
In addition to compute incommensurate multimode frequencies, when we have commensurate systems, the rotary resonance conditions or so called "level crossing" effect as shown in Fig. 7.5 is trivial to identify. They are the conditions where the denominators in various ordered expansion become zero.

Both the review paper by Leskes et al. and those by Matthias Ernst provide specific application examples of Floquet theory. I will not replicate those here. All you need is a bit of patience, the rest is the plug-and-play. The review paper by Leskes et al. are filled with sufficient details with very nice pictorial plot showing the layout of Hamiltonian matrix for specific examples, which greatly helps you to visualize the physical picture of the process. I would highly recommend you to read it carefully.



van Vleck transformation of the multimode Floquet Hamiltonian.

	M modes
Floquet Hamiltonian	$\sum_{[n_p]} H_{[n_p]} \Pi_p F^p_{n_p} + \sum_p \omega_p N^p$
B≡ Basis set	$\{\phi_i > \vert[n_p]\}^{n_p=-\infty,\infty}_{i=1,N_h} = \{\vert\phi_i\rangle\} \otimes \vert n_1 > \otimes \ldots \otimes \vert n_M >^{N_h}_{i=1}$
$S^{(1)}_F$	$\sum_{[n_p]} \left(\frac{iH_{[n_p]}}{\sum_p n_p \omega_p} \right) \Pi_p F^p_{n^p_p}$
$\widetilde{H}^{(0)}_F$	$H_{[n_p=0]} \Pi_p F^p_0 + \sum_p \omega_p N^p$
$\widetilde{H}^{(1)}_F$	$-\frac{1}{2} \sum_{[n_p],[n'_p]} \frac{[H_{[n_p]}, H_{[n'_p]}]}{\sum_p n'_p \omega_p} \Pi_p F^p_{n_p+n'_p} - \sum_{[n_p]} \frac{[H_{[n_p=0]}, H_{[n_p]}]}{\sum_p n_p \omega_p} \Pi_p F^p_{n_p}$
$\widetilde{H}^{(2)}_F$	$\frac{1}{3} \sum_{[n_p\neq 0],[n'_p],[n''_p]} \frac{[[H_{[n_p]}, H_{[n'_p]}], H_{[n''_p]}]}{\left(\sum_p n'_p \omega_p\right)\left(\sum_p n''_p \omega_p\right)} \Pi_p F_{n_p+n'_p+n''_p} + \frac{1}{2} \sum_{[n'_p],[n''_p]} \frac{[[H_{[n_p=0]}, H_{[n'_p]}], H_{[n''_p]}]}{\left(\sum_p n'_p \omega_p\right)\left(\sum_p n''_p \omega_p\right)} \Pi_p F_{n'_p+n''_p}$
$\widetilde{H}^{(0)}_{eff}$	$H_{[n_p=0]}$
$\widetilde{H}^{(1)}_{eff}$	$-\frac{1}{2} \sum_{[n_p]} \frac{[H_{[-n_p]}, H_{[n_p]}]}{\sum_p n_p \omega_p}$
$\widetilde{H}^{(2)}_{eff}$	$-\frac{1}{3} \sum_{[n_p],[n'_p]} \frac{[[H_{[n_p-n'_p]}, H_{[n'_p]}], H_{[-n_p]}]}{\left(\sum_p n_p \omega_p\right)\left(\sum_p n'_p \omega_p\right)} - \frac{1}{2} \sum_{[n_p\neq 0]} \frac{[[H_{[n_p=0]}, H_{[n_p]}], H_{[-n_p]}]}{\left(\sum_p n_p \omega_p\right)\left(\sum_p n_p \omega_p\right)}$
Level crossings	$\sum_p n_p \omega_p = 0$



van Vleck transformation of the bimodal Floquet Hamiltonian.

	Bimodal
Floquet	Hamiltonian
	$\sum_{n,k} H_{n,k} F^1_n F^2_k + \omega_1 N^1 + \omega_2 N^2$
B ≡ Basis set	$\{\vert\phi_i\rangle\} \otimes \{\vert n\rangle\} \otimes \{\vert k\rangle\}^{N_h}_{i=1}$
$S^{(1)}_F$	$\sum_{n,k} \frac{iH_{n,k}}{n\omega_n + k\omega_k} F_n F_k$
$\widetilde{H}^{(0)}_F$	$\sum_{n,k} H_{0,0} F_0 F_0 + \omega_1 N^1 + \omega_2 N^2$
$\widetilde{H}^{(1)}_F$	$-\frac{1}{2} \sum_{n,k,n',k'} \frac{[H_{n,k}, H_{n',k'}]}{n'\omega_n + k'\omega_k} F_{n+n'} F_{k+k'} - \sum_{n'\neq 0 \wedge k'\neq 0} \frac{[H_{0,0}, H_{n',k'}]}{n'\omega_n + k'\omega_k} F_{n'} F_{k'}$
$\widetilde{H}^{(2)}_F$	$\frac{1}{3} \sum_{n,k,n',k'} \frac{[[H_{n,k}, H_{n',k'}], H_{n'',k''}]}{(n'\omega_1 + k'\omega_2)(n''\omega_1 + k''\omega_2)} F_{n+n'+n''} F_{k+k'+k''}$ $+\frac{1}{2} \sum_{n',k',n'',k''} \frac{[[H_0, H_{n',k'}], H_{n'',k''}]}{(n'\omega_1 + k'\omega_2)(n''\omega_1 + k''\omega_2)} F_{n'+n''} F_{k'+k''}$
$\widetilde{H}^{(0)}_{eff}$	$H_{0,0}$
$\widetilde{H}^{(1)}_{eff}$	$-\frac{1}{2} \sum_{n,k} \frac{[H_{-n,-k}, H_{n,k}]}{n\omega_1 + k\omega_2}$
$\widetilde{H}^{(2)}_{eff}$	$-\frac{1}{3} \sum_{n,k,n',k'} \frac{[[H_{n-n'k,-k'}, H_{n',k'}], H_{-n,-k}]}{(n'\omega_1 + k'\omega_2)(n\omega_1 + k\omega_2)}$ $-\frac{1}{2} \sum_{n\neq 0} \frac{[[H_{0,0}, H_{n,k}], H_{-n,-k}]}{(n\omega_1 + k\omega_2)^2}$
Level crossings	$n\omega_1 + k\omega_2 = 0$

Figure 7.5. Van Vleck transformation of multimode and bimodal Floquet Hamiltonian summary. Adapted from Progess in NMR spectroscopy 57, 345-380 (2010).