NMR Spectroscopy: Principles and Applications

Nagarajan Murali

Advanced Tools

Lecture 4

Advanced Tools – Quantum Approach

We know by now that NMR is a branch of Spectroscopy and the MNR spectrum is an outcome of nuclear spin interaction with external magnetic field and electromagnetic radiation. This is a subject best tackled by quantum mechanics.

We also know that NMR is a bulk effect and it is indeed very hard to describe NMR of a real sample by quantum theory as it becomes a complex many body problem. But, surprisingly, we can focus on a single spin or few coupled spins and then predict the course of NMR experiment to represent our real systems. The statistical ensemble of nuclear spins behave exactly like the isolated model spin system.

Interaction of Spin with External Magnetic Field

We learnt in Lecture 1, the interaction of nuclear magnetic moment $\boldsymbol{\mu}$ *with external magnetic field* $\boldsymbol{B_0}$ *is known as* ***Zeeman interaction*** *and the interaction energy known as* ***Zeeman energy*** *is given as:*

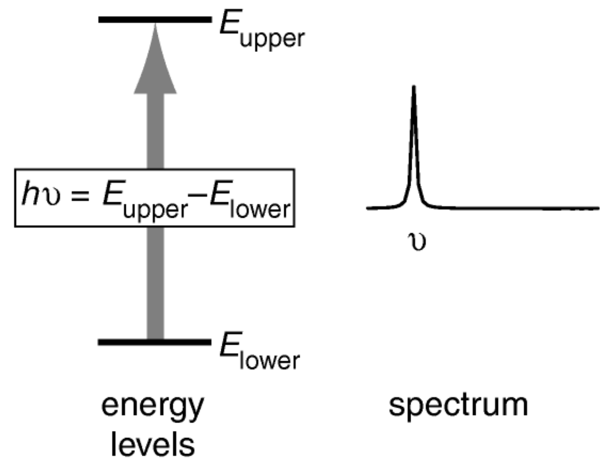
$$E = -\boldsymbol{\mu} \bullet \boldsymbol{B_0} = -\gamma\hbar \mathbf{I} \bullet \boldsymbol{B_0} = -\gamma\hbar \hat{\mathbf{I}}_z B_0$$

$$E = -\gamma\hbar B_0 m_I = \hbar\omega_0 m_I$$

where

$$\omega_0 = -\gamma B_0 = 2\pi\upsilon_0$$

$$m_I \rightarrow -I, -I+1, \ldots, +I$$

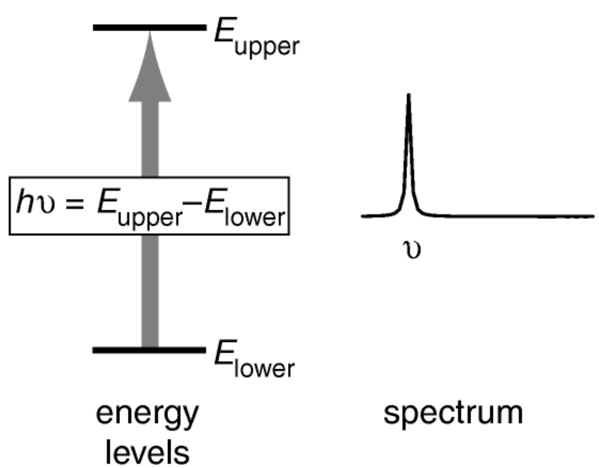


NMR is a branch of spectroscopy and so it describes the nature of the energy levels of the material system and transitions induced between them through absorption or emission of electromagnetic radiation.

Resonance

Resonance Method implies that the frequency of irradiation is same as that of the separation of energy levels in frequency unit.

Detection of Resonance is reduced to the measurement of frequency at which there is detectable change in the rate of transition of spin state.



Hamiltonian

In quantum mechanics the energy of a system is an important quantity and is described by an ***operator*** *with a special name* ***Hamiltonian****. Operators are important in that that we observe their magnitude when a suitable experiment is performed to measure them. Such measurable quantities are called observables and the operator corresponding to such quantities are called observable operators. For a single spin the Hamiltonian is given as*

$$\widehat{\boldsymbol{H}} = -\widehat{\boldsymbol{\mu}} \bullet \boldsymbol{B_0} = -\gamma\hbar\widehat{\mathbf{I}} \bullet \boldsymbol{B_0}$$

The terms that are operators have a "hat" over them. We knew this interaction is called Zeeman energy and this term is called Zeeman term.

Hamiltonian

The static field is applied along the z-axis of the laboratory frame. Then the Hamiltonian is reduced to

$$\widehat{\boldsymbol{H}} = -\gamma\hbar\widehat{\mathbf{I}} \bullet \boldsymbol{B_0} = -\gamma\hbar\widehat{\mathbf{I}}_z B_0$$

Only the operator I_z is relevant as the scalar product is non-vanishing for this term. The possible eigen values m_I of the I_z operator is –I,-I+1,…,I (i.e. 2I+1 values).

Zeeman Energy

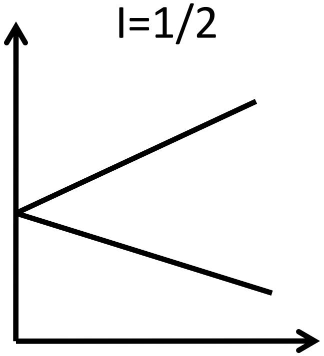
Thus the interaction energy of a single spin in a static field applied along the z-axis of the laboratory frame is

$$E = -\gamma \hbar B_0 m_I$$

m_I takes (2I+1) values from –I to +I in steps of 1.

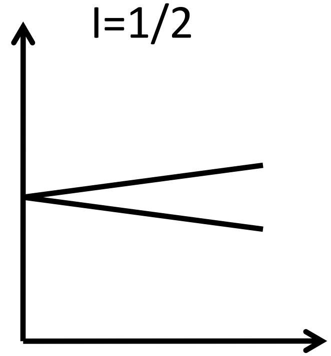
^{1}H
I=1/2

Energy



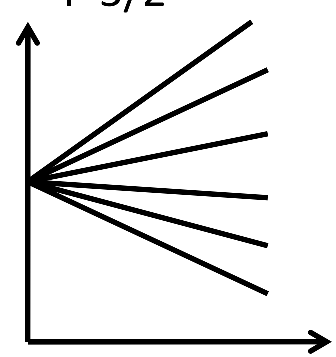
Magnetic Field

^{15}N
I=1/2



Magnetic Field

^{27}Al
I=5/2



Magnetic Field

Resonance of a single spin I=1/2

For I=1/2, m_I can be +1/2 or -1/2. Usually the 1/2 state is referred as α and the -1/2 state as β.

$$E = -\gamma\hbar B_0 m_I$$

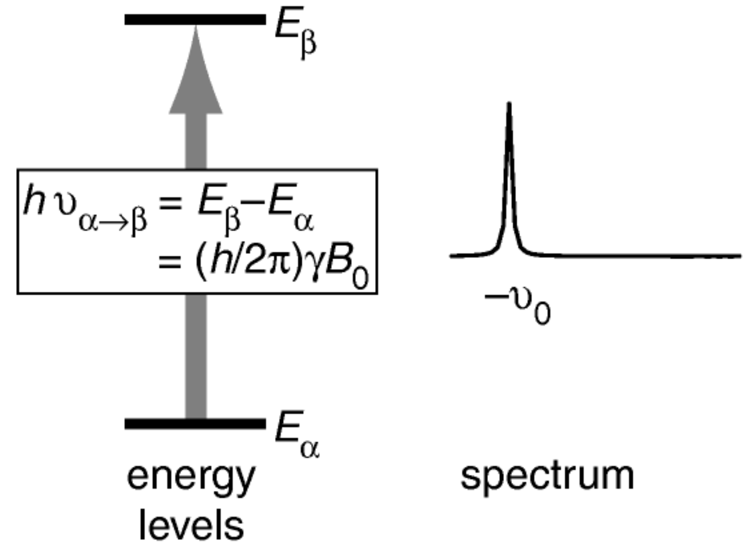
$$E_\alpha = -\frac{1}{2}\gamma\hbar B_0$$

$$E_\beta = +\frac{1}{2}\gamma\hbar B_0$$

$$\Delta E_{\alpha\to\beta} = E_\beta - E_\alpha = \frac{1}{2}\gamma\hbar B_0 - \left(-\frac{1}{2}\gamma\hbar B_0\right)$$

$$\Delta E_{\alpha\to\beta} = \gamma\hbar B_0 = -\hbar\omega_0 = -h\upsilon_0$$

$$\Delta m_{\alpha\to\beta} = -\frac{1}{2} - \left(+\frac{1}{2}\right) = -1$$

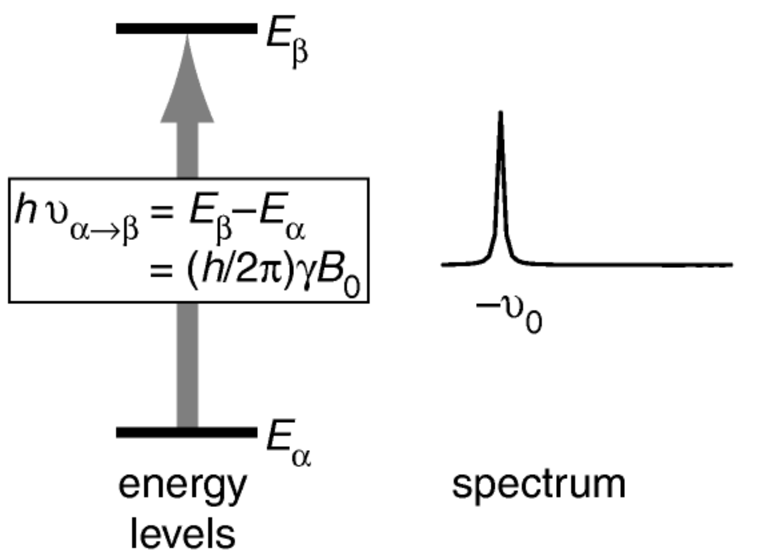


Resonance of a single spin I=1/2

Quantum mechanics says that a transition is allowed if the change of quantum number m is +1 or -1. So the transition between α to β state is allowed and is called a one quantum or single quantum transition.

$$\Delta E_{\alpha\rightarrow\beta} = \gamma\hbar B_0 = -\hbar\omega_0 = -h\upsilon_0$$

$$\Delta m_{\alpha\rightarrow\beta} = -\frac{1}{2} - \left(+\frac{1}{2}\right) = -1$$

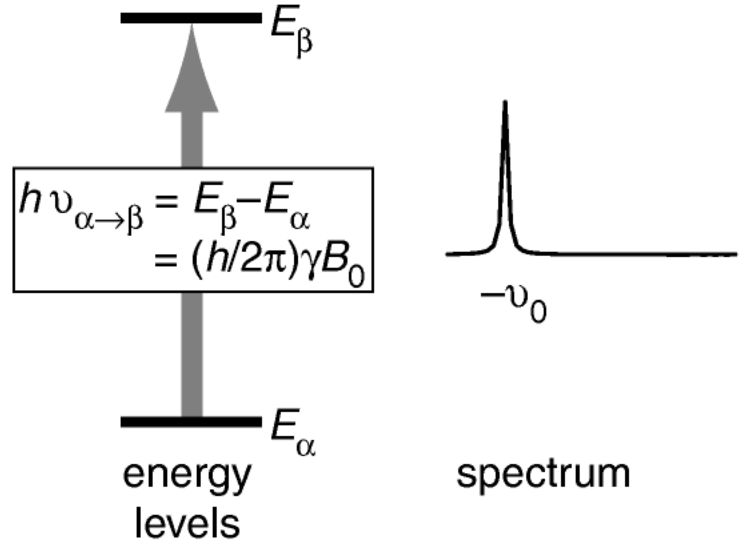


Hamiltonian in Frequency Units

Since energy can be expressed in terms of frequency unit, we can also write the Hamiltonian in frequency unit. Since,

$$\Delta E_{\alpha\rightarrow\beta} = \gamma\hbar B_0 = -\hbar\omega_0 = -h\upsilon_0$$

$$\Delta m_{\alpha\rightarrow\beta} = -\frac{1}{2} - \left(+\frac{1}{2}\right) = -1$$



We can write the Hamiltonian as,

$$\widehat{\boldsymbol{H}} = \omega_0 \widehat{\boldsymbol{I}}_{\boldsymbol{z}} \ \text{ in rad s}^{-1}$$

or

$$\widehat{\boldsymbol{H}} = \upsilon_0 \widehat{\boldsymbol{I}}_{\boldsymbol{z}} \ \text{ in Hz}$$

Spin I=1/2 Hamiltonian Summary

m	state	energy units	Frequency rad / s	Frequency Hz
+1/2	α	$-(1/2)\hbar\gamma B_0$	$(1/2)\omega_0$	$(1/2)\upsilon_0$
-1/2	β	$(1/2)\hbar\gamma B_0$	$-(1/2)\omega_0$	$-(1/2)\upsilon_0$

Two Spins I=1/2 Hamiltonian

Let us extend this idea of writing Hamiltonian to two spins each with spin I=1/2

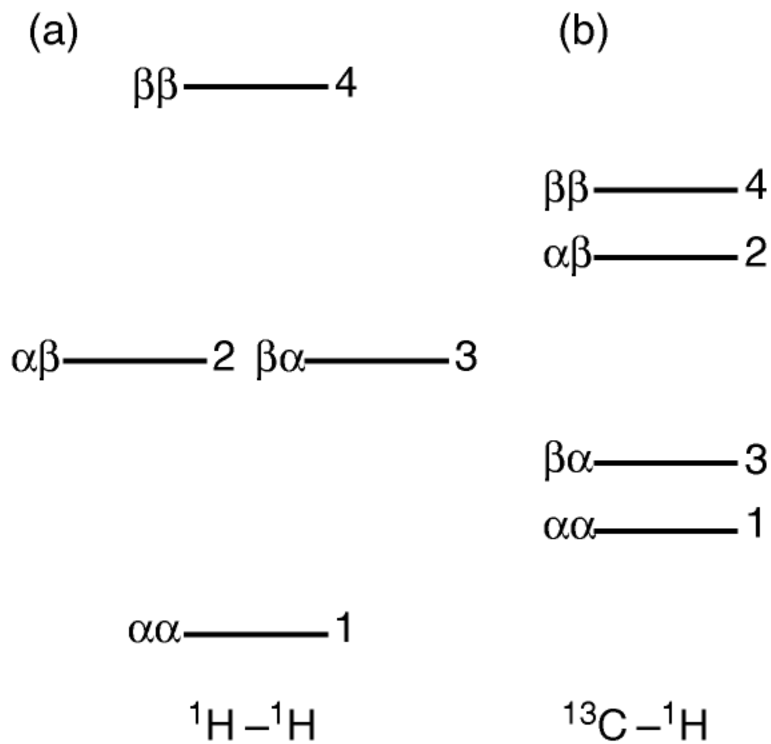
$$\widehat{\boldsymbol{H}} = \upsilon_{01}\widehat{\boldsymbol{I}}_{1z} + \upsilon_{02}\widehat{\boldsymbol{I}}_{2z} \quad \text{in Hz}$$

m_1	m_2	state	Frequency Hz
+1/2	+1/2	αα	$(1/2)\upsilon_{01}+(1/2)\upsilon_{02}$
+1/2	-1/2	αβ	$(1/2)\upsilon_{01}-(1/2)\upsilon_{02}$
-1/2	+1/2	βα	$-(1/2)\upsilon_{01}+(1/2)\upsilon_{02}$
-1/2	-1/2	ββ	$-(1/2)\upsilon_{01}-(1/2)\upsilon_{02}$

Two Spins I=1/2 Energy Levels

The energy level diagram could be presented as below (a) Two proton spins and (b) ^{13}C-^{1}H pair.

$$E_{m_1,m_2} = \upsilon_{01} m_1 + \upsilon_{02} m_2 \quad \text{in Hz}$$



Hamiltonian
Two Spins I=1/2 and J Coupling

Let us extend this idea of writing Hamiltonian to two spins each with spin I=1/2 and J Coupling between them.

$$\widehat{\boldsymbol{H}} = \upsilon_{01}\widehat{\boldsymbol{I}}_{1\mathbf{z}} + \upsilon_{02}\widehat{\boldsymbol{I}}_{2\mathbf{z}} + J_{12}\widehat{\boldsymbol{I}}_{1} \bullet \widehat{\boldsymbol{I}}_{2} \quad \text{in Hz}$$

$$\widehat{\boldsymbol{H}} = \upsilon_{01}\widehat{\boldsymbol{I}}_{1\mathbf{z}} + \upsilon_{02}\widehat{\boldsymbol{I}}_{2\mathbf{z}} + J_{12}\left(\widehat{\boldsymbol{I}}_{1x}\widehat{\boldsymbol{I}}_{2x} + \widehat{\boldsymbol{I}}_{1y}\widehat{\boldsymbol{I}}_{2y} + \widehat{\boldsymbol{I}}_{1\mathbf{z}}\widehat{\boldsymbol{I}}_{2\mathbf{z}}\right) \quad \text{in Hz}$$

$$\widehat{\boldsymbol{H}} = \upsilon_{01}\widehat{\boldsymbol{I}}_{1\mathbf{z}} + \upsilon_{02}\widehat{\boldsymbol{I}}_{2\mathbf{z}} + J_{12}\widehat{\boldsymbol{I}}_{1\mathbf{z}}\widehat{\boldsymbol{I}}_{2\mathbf{z}} \quad \text{in Hz for the case } \left|\upsilon_{01} - \upsilon_{02}\right| >> J_{12}$$

The J coupling is also known as scalar coupling as the operators involved are expressed as a scalar product. Note that there is no applied field dependent term in this interaction – means the coupling value is independent of field strength. The nuclear magnetic moments sense the presence of other spins trough the chemical bond between them.

Energy Levels
Two Spins I=1/2 and J Coupling

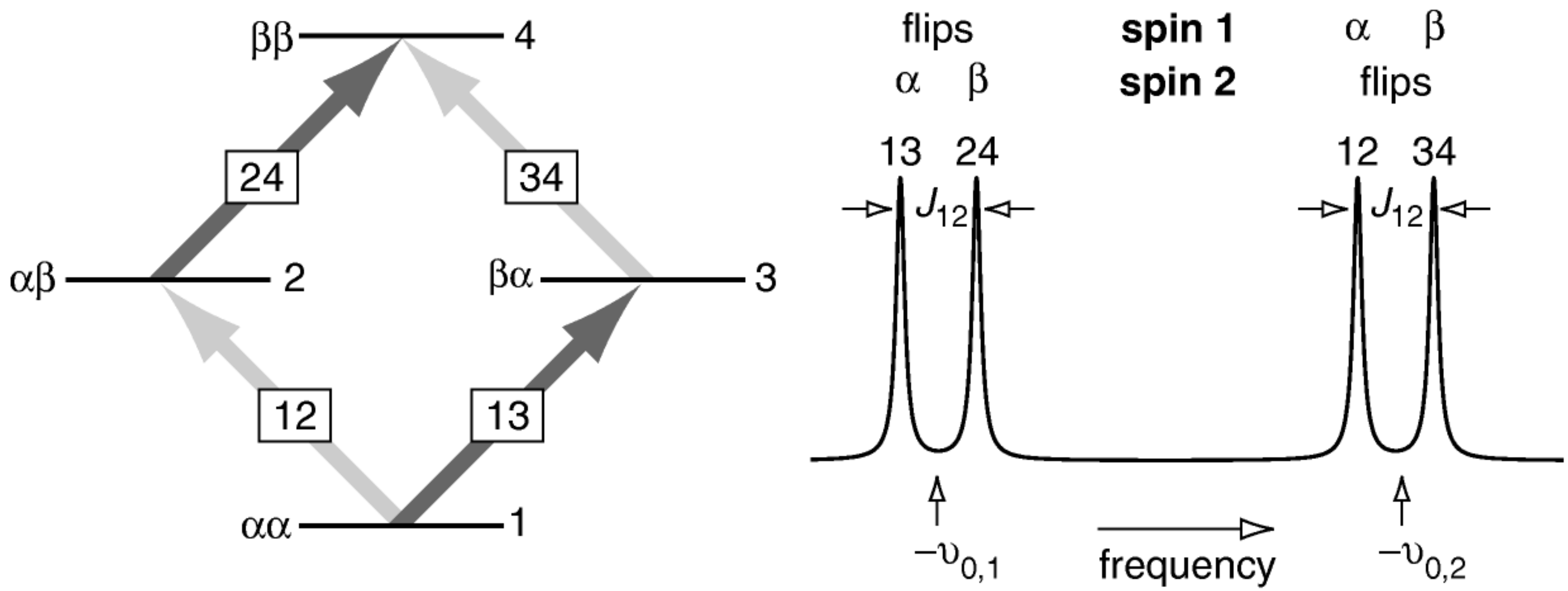
The energy levels of the two spins each with spin I=1/2 and J Coupling between them is then written as

$$E_{m_1,m_2} = \upsilon_{01} m_1 + \upsilon_{02} m_2 + J_{12} m_1 \times m_2 \quad \text{in Hz for the case } |\upsilon_{01} - \upsilon_{02}| >> J_{12}$$

m_1	m_2	state	Frequency Hz
+1/2	+1/2	$\alpha\alpha$	$(1/2)\upsilon_{01}+(1/2)\upsilon_{02}+(1/4)J_{12}$
+1/2	-1/2	$\alpha\beta$	$(1/2)\upsilon_{01}-(1/2)\upsilon_{02}-(1/4)J_{12}$
-1/2	+1/2	$\beta\alpha$	$-(1/2)\upsilon_{01}+(1/2)\upsilon_{02}-(1/4)J_{12}$
-1/2	-1/2	$\beta\beta$	$-(1/2)\upsilon_{01}-(1/2)\upsilon_{02}+(1/4)J_{12}$

Energy Levels
Two Spins I=1/2 and J Coupling

The energy level diagram directly predicts the NMR spectrum.

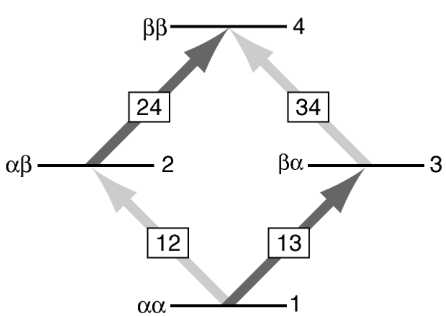


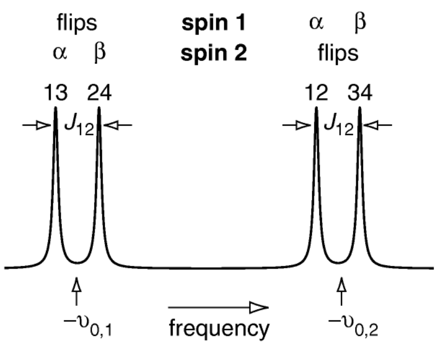
Left: Energy level diagram; dark arrows show spin 1 flip and its transitions and light arrow show flip of the spin 2 and its transitions. Right: The NMR spectrum resulting from the four transitions.

Energy Levels
Two Spins I=1/2 and J Coupling

The NMR spectrum has all the information of the energy levels or the Hamiltonian of the system.

Transition	Spin states	Frequency Hz
1→2	αα→αβ	$-\upsilon_{02}-(1/2)J_{12}$
3→4	βα→ββ	$-\upsilon_{02}+(1/2)J_{12}$
1→3	αα→βα	$-\upsilon_{01}-(1/2)J_{12}$
2→4	αβ→ββ	$-\upsilon_{01}+(1/2)J_{12}$





A Bit More of Quantum Mechanics

So far we saw that the energy of interaction of nuclear spins with magnetic field and with each other can be expressed by a Hamiltonian that in turn expressed in terms of the various components of the spin angular momentum. With this description we could calculate the transitions. We did not describe how we excite the transition and what happens during the NMR experiment such as one pulse experiment or spin echo experiment.

To understand the time course of a NMR experiment we have to follow the system as it evolves during the experiment. We have to understand how the spin system states are defined in quantum mechanics and how they change in an experiment and how we can observe the spin system state.

Wave Function: The state of the Spin

In quantum theory, we don not know a priori whether a spin (say I=1/2) is in the α state (+1/2) or in the β state (-1/2). So we write in general the state to be a superposition of the two possible state

$$|\psi(t)\rangle = C_\alpha(t)|\alpha\rangle + C_\beta(t)|\beta\rangle$$

The coefficients $C_\alpha(t)$ and $C_\beta(t)$ are numbers (complex numbers in general) and their phase can vary in time and their magnitudes give rise to the value of the observable quantities in NMR. This function $|\psi(t)\rangle$ is called a wave function and as it is a complex function we can also write its complex conjugate as

$$\langle\psi(t)| = \langle\alpha|C_\alpha^*(t) + \langle\beta|C_\beta^*(t)$$

Then

$$\langle\psi(t)|\psi(t)\rangle = \left(\langle\alpha|C_\alpha^*(t) + \langle\beta|C_\beta^*(t)\right)\left(C_\alpha(t)|\alpha\rangle + C_\beta(t)|\beta\rangle\right)$$

$$= C_\alpha^*(t)C_\alpha(t)\langle\alpha|\alpha\rangle + C_\alpha^*(t)C_\beta(t)\langle\alpha|\beta\rangle + C_\beta^*(t)C_\alpha(t)\langle\beta|\alpha\rangle + C_\beta^*(t)C_\beta(t)\langle\beta|\beta\rangle$$

$$= C_\alpha^*(t)C_\alpha(t) + C_\beta^*(t)C_\beta(t) \text{ is just a number}$$

Properties of Wave Function

We can then compute a number as a bra|ket product

$$\langle \psi(t) | \psi(t) \rangle = \left(\langle \alpha | C_\alpha^*(t) + \langle \beta | C_\beta^*(t) \right) \left(C_\alpha(t) | \alpha \rangle + C_\beta(t) | \beta \rangle \right)$$

$$= C_\alpha^*(t) C_\alpha(t) \langle \alpha | \alpha \rangle + C_\alpha^*(t) C_\beta(t) \langle \alpha | \beta \rangle + C_\beta^*(t) C_\alpha(t) \langle \beta | \alpha \rangle + C_\beta^*(t) C_\beta(t) \langle \beta | \beta \rangle$$

$$= C_\alpha^*(t) C_\alpha(t) + C_\beta^*(t) C_\beta(t) \text{ is just a number}$$

In this calculation we have used the fact that the spin states are orthogonal.

$$\langle \alpha | \alpha \rangle = 1$$

$$\langle \alpha | \beta \rangle = 0$$

$$\langle \beta | \alpha \rangle = 0$$

$$\langle \beta | \beta \rangle = 1$$

Expectation Values

Once we define the state of the system by a wave function, we can now ask what is the chance that we have a component of the spin angular momentum along z-axis and is given by the expectation value of the spin angular momentum operator along z-axis.

$$\left\langle \widehat{\boldsymbol{I}}_z \right\rangle = \frac{\left\langle \psi(t) \middle| \hat{\boldsymbol{I}}_z \middle| \psi(t) \right\rangle}{\left\langle \psi(t) \middle| \psi(t) \right\rangle}$$

Since the denominator is a number we can set it to equal to 1 saying the wave function is normalized, all we have to do is compute

$$\left\langle \widehat{\boldsymbol{I}}_z \right\rangle = \left\langle \psi(t) \middle| \hat{\boldsymbol{I}}_z \middle| \psi(t) \right\rangle$$

And we will use the fact that the state α and β are eigen states of I_z

$$\widehat{\boldsymbol{I}}_z \left| \alpha \right\rangle = +\frac{1}{2} \left| \alpha \right\rangle \quad \widehat{\boldsymbol{I}}_z \left| \beta \right\rangle = -\frac{1}{2} \left| \beta \right\rangle$$

Expectation Values

Then the expectation value of I_z is

$$\left\langle \widehat{\boldsymbol{I}}_z(t) \right\rangle = \frac{1}{2} C_\alpha^*(t) C_\alpha(t) - \frac{1}{2} C_\beta^*(t) C_\beta(t)$$

We have used the orthogonal property of the spin states α and β in evaluating the above value.

$$\left\langle \widehat{\boldsymbol{I}}_z(t) \right\rangle = \frac{1}{2}\left(C_\alpha^*(t) C_\alpha(t) - C_\beta^*(t) C_\beta(t) \right)$$

The above equation means that the average value of the component along z-axis is given by the difference in the probability of finding the spin in the +1/2 state or -1/2 state when many measurements are made.

Expectation Values

We can now see what happens to the spin angular momentum components in the transverse plane and using the fact that

$$\widehat{\boldsymbol{I}}_x|\alpha\rangle = +\frac{1}{2}|\beta\rangle \quad \widehat{\boldsymbol{I}}_x|\beta\rangle = \frac{1}{2}|\alpha\rangle \qquad \widehat{\boldsymbol{I}}_y|\alpha\rangle = +\frac{1}{2}i|\beta\rangle \quad \widehat{\boldsymbol{I}}_y|\beta\rangle = -\frac{1}{2}i|\alpha\rangle$$

$$\left\langle \widehat{\boldsymbol{I}}_x(t) \right\rangle = \frac{1}{2}\left(C_\alpha^*(t)C_\beta(t) + C_\beta^*(t)C_\alpha(t)\right) \quad \left\langle \widehat{\boldsymbol{I}}_y(t) \right\rangle = \frac{1}{2}i\left(C_\alpha^*(t)C_\beta(t) - C_\beta^*(t)C_\alpha(t)\right)$$

Again the expectation value for these components also depend on the coefficients that are probability functions.

Bulk Magnetization

We are now ready to arrive at the bulk magnetization that is induced when a collection such individual spins are exposed to a magnetic field. The bulk magnetization along z-axis then sum of the expectation value of the z-component of the individual spins.

$$M_z(t) = \gamma \sum_{i=1}^{N} \left\langle \hat{\boldsymbol{I}}_{iz}(t) \right\rangle = \sum_{i=1}^{N} \frac{1}{2} \left(C_{i\alpha}^{*}(t) C_{i\alpha}(t) - C_{i\beta}^{*}(t) C_{i\beta}(t) \right)$$

$$M_z(t) = \frac{1}{2} \gamma N \overline{\left(C_{\alpha}^{*}(t) C_{\alpha}(t) - C_{\beta}^{*}(t) C_{\beta}(t) \right)}$$

$$M_z(t) = \gamma N \overline{\left\langle \hat{\boldsymbol{I}}_z \right\rangle} \quad \text{where} \; \overline{\left\langle \hat{\boldsymbol{I}}_z \right\rangle} = \frac{1}{N} \sum_{1}^{N} \left\langle \hat{\boldsymbol{I}}_{iz} \right\rangle$$

The bar above the functions on the right hand side indicates sum over the ensemble of spins.

Populations

The probability difference that gives component along z- axis now can be interpreted as population difference in the two states that give rise to the z-magnetization

$$n_\alpha = N\left(\overline{C_\alpha^*(t)C_\alpha(t)}\right)$$

$$n_\beta = N\left(\overline{C_\beta^*(t)C_\beta(t)}\right)$$

and

$$M_z(t) = \frac{1}{2}\gamma\left(n_\alpha - n_\beta\right)$$

Bulk Magnetization – Transverse Plane

We can in the same way compute magnetization along x-axis and y-axis.

$$M_x(t) = \gamma N \overline{\langle \hat{\boldsymbol{I}}_x \rangle} = \frac{1}{2}\gamma N \overline{\left(C_\alpha^*(t) C_\beta(t) + C_\beta^*(t) C_\alpha(t) \right)}$$

$$M_y(t) = \gamma N \overline{\langle \hat{\boldsymbol{I}}_y(t) \rangle} = \frac{1}{2} i\gamma N \overline{\left(C_\alpha^*(t) C_\beta(t) - C_\beta^*(t) C_\alpha(t) \right)}$$

At equilibrium there is only z-magnetization and no magnetization in the transverse plane. This means that the ensemble average on the right goes to zero.

$$\overline{\left(C_\alpha^*(t) C_\beta(t) + C_\beta^*(t) C_\alpha(t) \right)} = 0 \qquad \overline{\left(C_\alpha^*(t) C_\beta(t) - C_\beta^*(t) C_\alpha(t) \right)} = 0$$

*This is called the **random phase approximation** or that there is no **coherence** between the spin states.*

Time Evolution in Quantum Mechanics

We discussed in the vector model how magnetization rotates in the presence of applied fields (both DC and RF). We wrote the equation of motion as the time derivative of the magnetic moment equal to the torque on the moment. In the same way, the motion of the spins can be expressed in terms of its state undergoing change effected by the interaction Hamiltonian.

$$\frac{d\left|\psi(t)\right\rangle}{dt} = -i\hat{\boldsymbol{H}}\left|\psi(t)\right\rangle$$

Suppose if we consider a single spin I=1/2 in the rotating frame then the Hamiltonian is

$$\hat{\boldsymbol{H}} = \Omega\hat{\boldsymbol{I}}_z$$

And

$$\left|\psi(t)\right\rangle = C_\alpha(t)\left|\alpha\right\rangle + C_\beta(t)\left|\beta\right\rangle$$

Time Evolution in Quantum Mechanics

Then,

$$\frac{d\left|\psi(t)\right\rangle}{dt} = -i\widehat{\boldsymbol{H}}\left|\psi(t)\right\rangle$$

$$\frac{d\left[C_\alpha(t)\left|\alpha\right\rangle + C_\beta(t)\left|\beta\right\rangle\right]}{dt} = -i\Omega\widehat{\boldsymbol{I}}_z\left[C_\alpha(t)\left|\alpha\right\rangle + C_\beta(t)\left|\beta\right\rangle\right]$$

$$\frac{dC_\alpha(t)}{dt}\left|\alpha\right\rangle + \frac{dC_\beta(t)}{dt}\left|\beta\right\rangle = -i\Omega C_\alpha(t)\widehat{\boldsymbol{I}}_z\left|\alpha\right\rangle - i\Omega C_\beta(t)\widehat{\boldsymbol{I}}_z\left|\beta\right\rangle$$

$$\boxed{\widehat{\boldsymbol{I}}_z\left|\alpha\right\rangle = \frac{1}{2}\left|\alpha\right\rangle} \quad \boxed{\widehat{\boldsymbol{I}}_z\left|\beta\right\rangle = -\frac{1}{2}\left|\beta\right\rangle}$$

By multiplying on either side by <α| and <β| and using <α| α > = <β| β > = 1, and <α| β > = <β| α > = 0, we can simply separate the above equation into two equations on the coefficients as

$$\frac{dC_\alpha(t)}{dt} = -i\Omega C_\alpha(t) \text{ and } \frac{dC_\beta(t)}{dt} = +i\Omega C_\beta(t)$$

Time Evolution in Quantum Mechanics

The solution of these two equations is straightforward,

$$\frac{dC_\alpha(t)}{dt} = -i\frac{1}{2}\Omega C_\alpha(t) \text{ and } \frac{dC_\beta(t)}{dt} = +i\frac{1}{2}\Omega C_\beta(t)$$

$$C_\alpha(t) = C_\alpha(0)e^{-i\frac{1}{2}\Omega t} \text{ and } C_\beta(t) = C_\beta(0)e^{i\frac{1}{2}\Omega t}$$

Since we know now the value of the coefficients C's at any time t we can evaluate the expectation values of the spin angular momentum components in the x, y, and axis

$$\left\langle \hat{\boldsymbol{I}}_x(t) \right\rangle = \frac{1}{2}\left(C_\alpha^*(t)C_\beta(t) + C_\beta^*(t)C_\alpha(t)\right) \quad \left\langle \hat{\boldsymbol{I}}_y(t) \right\rangle = \frac{1}{2}i\left(C_\alpha^*(t)C_\beta(t) - C_\beta^*(t)C_\alpha(t)\right)$$

$$\left\langle \hat{\boldsymbol{I}}_z(t) \right\rangle = \frac{1}{2}\left(C_\alpha^*(t)C_\alpha(t) - C_\beta^*(t)C_\beta(t)\right)$$

Time Evolution in Quantum Mechanics

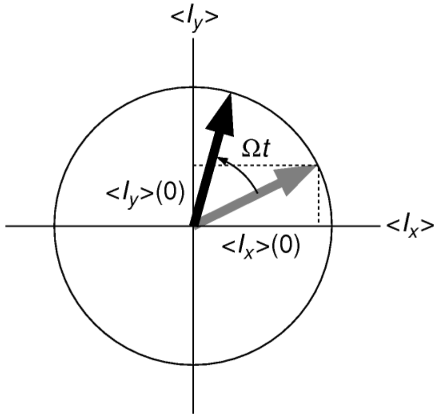
Let us just evaluate one of these in detail

$$\left\langle \hat{\boldsymbol{I}}_x(t) \right\rangle = \frac{1}{2}\left(C_\alpha^*(t)C_\beta(t) + C_\beta^*(t)C_\alpha(t)\right) = \frac{1}{2}C_\alpha^*(0)C_\beta(0)e^{i\Omega t} + \frac{1}{2}C_\beta^*(0)C_\alpha(0)e^{-i\Omega t}$$

$$= \frac{1}{2}C_\alpha^*(0)C_\beta(0)[\cos(\Omega t) + i\sin(\Omega t)] + \frac{1}{2}C_\beta^*(0)C_\alpha(0)[\cos(\Omega t) - i\sin(\Omega t)]$$

$$= \cos(\Omega t)\left[\frac{1}{2}C_\alpha^*(0)C_\beta(0) + \frac{1}{2}C_\beta^*(0)C_\alpha(0)\right] - \sin(\Omega t)\left[i\frac{1}{2}C_\beta^*(0)C_\alpha(0) - i\frac{1}{2}C_\alpha^*(0)C_\beta(0)\right]$$

$$\left\langle \hat{\boldsymbol{I}}_x(t) \right\rangle = \cos(\Omega t)\left\langle \hat{\boldsymbol{I}}_x(0) \right\rangle - \sin(\Omega t)\left\langle \hat{\boldsymbol{I}}_y(0) \right\rangle$$



Time Evolution in Quantum Mechanics

Similar calculations can be done for the other components and in summary we have

$$\left\langle \widehat{\boldsymbol{I}}_x(t) \right\rangle = \cos(\Omega t)\left\langle \widehat{\boldsymbol{I}}_x(0) \right\rangle - \sin(\Omega t)\left\langle \widehat{\boldsymbol{I}}_y(0) \right\rangle$$

$$\left\langle \widehat{\boldsymbol{I}}_y(t) \right\rangle = \cos(\Omega t)\left\langle \widehat{\boldsymbol{I}}_y(0) \right\rangle - \sin(\Omega t)\left\langle \widehat{\boldsymbol{I}}_x(0) \right\rangle$$

$$\left\langle \widehat{\boldsymbol{I}}_z(t) \right\rangle = \left\langle \widehat{\boldsymbol{I}}_z(0) \right\rangle$$

Free evolution does not affect the z-component. The x and y components rotate in the xy plane. These results are same as we got from the vector model.

Time Evolution of Bulk Magnetization in Quantum Mechanics

We know that the value of the bulk magnetizations are given by their respective expectation values and thus we can compute the state of the magnetization components at any time t.

$$M_x(t) = \gamma N\overline{\left\langle \hat{\boldsymbol{I}}_x(t) \right\rangle} = \cos(\Omega t)\gamma N\overline{\left\langle \hat{\boldsymbol{I}}_x(0) \right\rangle} - \sin(\Omega t)\gamma N\overline{\left\langle \hat{\boldsymbol{I}}_y(0) \right\rangle}$$

$$M_x(t) = \cos(\Omega t)M_x(0) - \sin(\Omega t)M_y(0)$$

$$M_y(t) = \gamma N\overline{\left\langle \hat{\boldsymbol{I}}_y(t) \right\rangle} = \cos(\Omega t)\gamma N\overline{\left\langle \hat{\boldsymbol{I}}_y(0) \right\rangle} + \sin(\Omega t)\gamma N\overline{\left\langle \hat{\boldsymbol{I}}_x(0) \right\rangle}$$

$$M_y(t) = \cos(\Omega t)M_y(0) + \sin(\Omega t)M_x(0)$$

$$M_z(t) = \gamma N\overline{\left\langle \hat{\boldsymbol{I}}_z(t) \right\rangle} = \gamma N\overline{\left\langle \hat{\boldsymbol{I}}_y(0) \right\rangle}$$

$$M_z(t) = M_z(0)$$

Time Evolution Due to RF Pulse in Quantum Mechanics

So far we worked with a rotating frame Hamiltonian corresponding to just the applied static magnetic field.

$$\widehat{\boldsymbol{H}} = \Omega \widehat{\boldsymbol{I}}_z$$

Now let us say we have an RF field also along x-axis and for simplicity let us also assume that we are on-resonance (Ω=0). So the new Hamiltonian in the rotating frame in the presence of RF along x-axis is

$$\widehat{\boldsymbol{H}} = \omega_1 \widehat{\boldsymbol{I}}_x$$

Where ω_1 is the amplitude of the RF in units of radians/sec. We can repeat the calculations in the same line as before and the results for the magnetization components can be given by analogy.

Time Evolution Due to RF Pulse in Quantum Mechanics

The effect of RF along x axis then,

$$M_x(t) = \gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_x(t) \right\rangle} = \gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_x(0) \right\rangle}$$

$$M_x(t) = M_x(0)$$

$$M_y(t) = \gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_y(t) \right\rangle} = \cos(\omega_1 t)\gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_y(0) \right\rangle} - \sin(\omega_1 t)\gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_z(0) \right\rangle}$$

$$M_y(t) = \cos(\omega_1 t)M_y(0) - \sin(\omega_1 t)M_z(0)$$

$$M_z(t) = \gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_z(t) \right\rangle} = \cos(\omega_1 t)\gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_z(0) \right\rangle} + \sin(\omega_1 t)\gamma N\overline{\left\langle \widehat{\boldsymbol{I}}_y(0) \right\rangle}$$

$$M_z(t) = \cos(\omega_1 t)M_z(0) + \sin(\omega_1 t)M_y(0)$$

Under x-pulse the magnetization precess in the zy plane as we saw in the vector model. For example if we set $\omega_1 t=\pi/2$ and at t=0 with magnetization only along +z axis, we will end up along –y axis.

Operator Formalism

We have collected so much knowledge in quantum frame work to describe the spins interacting with the magnetic field, RF, and among themselves and now we see that if we follow the evolution of the components of the spin angular momentum operator, we can predict the course of the magnetization of a spin in any NMR experiment. To facilitate that, we will describe the state of the spin system directly by these spin angular momentum operators. It is then said that we have described the system by a density operator (as opposed to describing the state by a wave function).

For a single isolated spin system, the arbitrary state can be given by the operator $\rho(t)$,

$$\widehat{\boldsymbol{\rho}}(t) = a_x(t)\widehat{\boldsymbol{I}}_x + a_y(t)\widehat{\boldsymbol{I}}_y + a_z(t)\widehat{\boldsymbol{I}}_z$$

Operator Formalism

Now we can write the time evolution of this density operator (Liouville-von Neumann equation) to describe the spin system.

$$\hat{\boldsymbol{\rho}}(t) = a_x(t)\hat{\boldsymbol{I}}_x + a_y(t)\hat{\boldsymbol{I}}_y + a_z(t)\hat{\boldsymbol{I}}_z$$

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}(t) = -i\left(\hat{\boldsymbol{H}}\hat{\boldsymbol{\rho}}(t) - \hat{\boldsymbol{\rho}}(t)\hat{\boldsymbol{H}}\right)$$

$$\hat{\boldsymbol{\rho}}(t) = e^{-i\hat{\boldsymbol{H}}t}\hat{\boldsymbol{\rho}}(0)e^{i\hat{\boldsymbol{H}}t}$$

Note that in the above the order in which the terms are written is important since

$$\hat{\boldsymbol{H}}\hat{\boldsymbol{\rho}}(t) \neq \hat{\boldsymbol{\rho}}(t)\hat{\boldsymbol{H}}$$

Operator Formalism – Rotations

Let us say at t=0 a_x=1 a_y=a_z=0, then

$$\hat{\boldsymbol{\rho}}(0) = \hat{\boldsymbol{I}}_x$$

Also Let us say the Hamiltonian is

$$\hat{\boldsymbol{H}} = \Omega \hat{\boldsymbol{I}}_z$$

Then

$$\hat{\boldsymbol{\rho}}(t) = e^{-i\hat{\boldsymbol{H}}t}\,\hat{\boldsymbol{\rho}}(0)\,e^{i\hat{\boldsymbol{H}}t} = e^{-i\Omega\hat{\boldsymbol{I}}_z t}\,\hat{\boldsymbol{I}}_x\,e^{-i\Omega\hat{\boldsymbol{I}}_z t}$$

$$\hat{\boldsymbol{\rho}}(t) = \hat{\boldsymbol{I}}_x \cos(\Omega t) + \hat{\boldsymbol{I}}_y \sin(\Omega t)$$

The whole calculation can be written in a notation as below

$$\hat{\boldsymbol{\rho}}(0) \xrightarrow{\hat{\boldsymbol{H}}t} \hat{\boldsymbol{\rho}}(t)$$

$$\hat{\boldsymbol{I}}_x \xrightarrow{\Omega\hat{\boldsymbol{I}}_z t} \hat{\boldsymbol{I}}_x \cos(\Omega t) + \hat{\boldsymbol{I}}_y \sin(\Omega t)$$

Operator Formalism – Rotations

Let us say the Hamiltonian is

$$\widehat{\boldsymbol{H}} = \omega_1 \widehat{\boldsymbol{I}}_x$$

Then

$$\widehat{\boldsymbol{\rho}}(t) = e^{-i\widehat{\boldsymbol{H}}t}\widehat{\boldsymbol{\rho}}(0)e^{i\widehat{\boldsymbol{H}}t} = e^{-i\omega_1\widehat{\boldsymbol{I}}_x t}\widehat{\boldsymbol{\rho}}(0)e^{i\omega_1\widehat{\boldsymbol{I}}_x t}$$

Using the notation we described before

$$\widehat{\boldsymbol{I}}_x \xrightarrow{\omega_1\widehat{\boldsymbol{I}}_x t} \widehat{\boldsymbol{I}}_x$$

$$\widehat{\boldsymbol{I}}_y \xrightarrow{\omega_1\widehat{\boldsymbol{I}}_x t} \widehat{\boldsymbol{I}}_y \cos(\omega_1 t) + \widehat{\boldsymbol{I}}_z \sin(\omega_1 t)$$

$$\widehat{\boldsymbol{I}}_z \xrightarrow{\omega_1\widehat{\boldsymbol{I}}_x t} \widehat{\boldsymbol{I}}_z \cos(\omega_1 t) - \widehat{\boldsymbol{I}}_y \sin(\omega_1 t)$$

Rotations -Summary

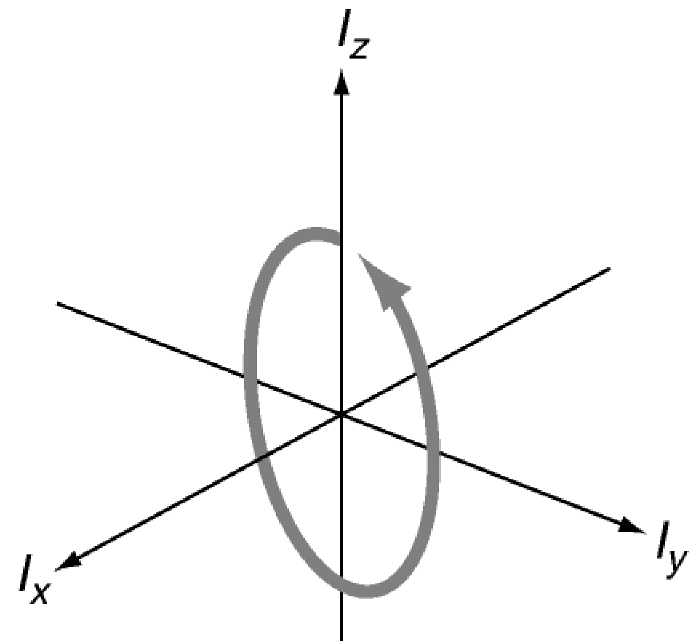
Let us now summarize the rotations under pulses about different axes and flip angles.

$$\hat{I}_y \xrightarrow{\frac{\pi}{2}\hat{I}_x} \hat{I}_z \qquad \hat{I}_y \xrightarrow{\pi\hat{I}_x} -\hat{I}_y$$

$$\hat{I}_z \xrightarrow{\frac{\pi}{2}\hat{I}_x} -\hat{I}_y \qquad \hat{I}_z \xrightarrow{\pi\hat{I}_x} -\hat{I}_z$$

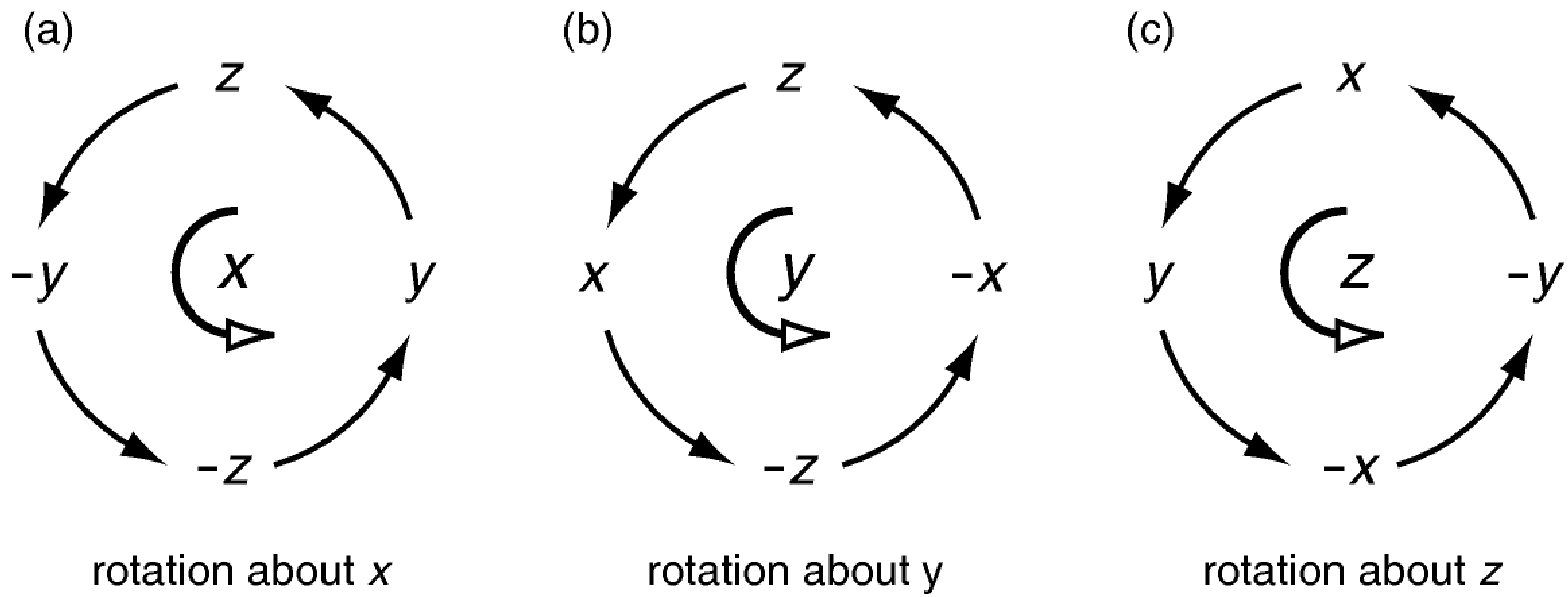
$$\hat{I}_x \xrightarrow{\frac{\pi}{2}\hat{I}_y} -\hat{I}_z \qquad \hat{I}_x \xrightarrow{\pi\hat{I}_y} -\hat{I}_x$$

$$\hat{I}_z \xrightarrow{\frac{\pi}{2}\hat{I}_y} \hat{I}_x \qquad \hat{I}_z \xrightarrow{\pi\hat{I}_y} -\hat{I}_z$$



Rotations -Summary

Positive rotations are counter-clockwise (as shown) and negative rotation is clockwise.



Operators – Two Spins

We can extend the same representation of the state of the system by operators to two spins I_1 and I_2.

$$\widehat{\boldsymbol{E}}_1 \;\; \widehat{\boldsymbol{I}}_{1x} \;\; \widehat{\boldsymbol{I}}_{1y} \;\; \widehat{\boldsymbol{I}}_{1z} \quad \widehat{\boldsymbol{E}}_2 \;\; \widehat{\boldsymbol{I}}_{2x} \;\; \widehat{\boldsymbol{I}}_{2y} \;\; \widehat{\boldsymbol{I}}_{2z}$$

The two unit operators E_1 and E_2 do not represent any observable. We need also the products of the spin operators of the two spins to describe the system. Noting that the products with the E operator is the same as the 8 operators above, we have

$$2\widehat{\boldsymbol{I}}_{1x}\widehat{\boldsymbol{I}}_{2x} \;\; 2\widehat{\boldsymbol{I}}_{1x}\widehat{\boldsymbol{I}}_{2y} \;\; 2\widehat{\boldsymbol{I}}_{1x}\widehat{\boldsymbol{I}}_{2z}$$

$$2\widehat{\boldsymbol{I}}y\widehat{\boldsymbol{I}}_{2x} \;\; 2\widehat{\boldsymbol{I}}_{1y}\widehat{\boldsymbol{I}}_{2y} \;\; 2\widehat{\boldsymbol{I}}_{1y}\widehat{\boldsymbol{I}}_{2z}$$

$$2\widehat{\boldsymbol{I}}_{1z}\widehat{\boldsymbol{I}}_{2x} \;\; 2\widehat{\boldsymbol{I}}_{1z}\widehat{\boldsymbol{I}}_{2y} \;\; 2\widehat{\boldsymbol{I}}_{1z}\widehat{\boldsymbol{I}}_{2z}$$

Hamiltonian for Two Spins

Let us recall the Hamiltonian for two spins I_1 and I_2

$$\hat{\boldsymbol{H}} = \upsilon_{01}\hat{\boldsymbol{I}}_{1\mathbf{z}} + \upsilon_{02}\hat{\boldsymbol{I}}_{2\mathbf{z}} + J_{12}\hat{\boldsymbol{I}}_{1\mathbf{z}}\hat{\boldsymbol{I}}_{2\mathbf{z}} \quad \text{in Hz for the case } \left|\upsilon_{01} - \upsilon_{02}\right| >> J_{12}$$

Let us convert the above in to the rotating frame Hamiltonian in angular frequency units.

$$\hat{\boldsymbol{H}} = \Omega_1\hat{\boldsymbol{I}}_{1\mathbf{z}} + \Omega_2\hat{\boldsymbol{I}}_{2\mathbf{z}} + 2\pi J_{12}\hat{\boldsymbol{I}}_{1\mathbf{z}}\hat{\boldsymbol{I}}_{2\mathbf{z}} \quad \text{in rad/sec for the case } \left|\Omega_1 - \Omega_2\right| >> 2\pi J_{12}$$

The time evolution of the two spin system is under the influence of the above Hamiltonian and can be calculated in separate steps.

$$\hat{\boldsymbol{\rho}}(0) \xrightarrow{\Omega_1 t\hat{\boldsymbol{I}}_{1\mathbf{z}}} \xrightarrow{\Omega_2 t\hat{\boldsymbol{I}}_{2\mathbf{z}}} \xrightarrow{2\pi J_{12} t\hat{\boldsymbol{I}}_{1\mathbf{z}}\hat{\boldsymbol{I}}_{2\mathbf{z}}} \hat{\boldsymbol{\rho}}(t)$$

We have already seen the evolution of single spin operators under the Zeemann term and RF pulses. For two spins the respective spin operators evolve separately with these terms as if they are independent. The evolution under the coupling part of the Hamiltonain is slightly more involved.

Evolution under Coupling-Two Spins

Let us now illustrate the evolution under the coupling part of the Hamiltonian

$$\widehat{\boldsymbol{H}}_J = 2\pi J_{12}\widehat{\boldsymbol{I}}_{1\boldsymbol{z}}\widehat{\boldsymbol{I}}_{2\boldsymbol{z}}$$

$$\widehat{\boldsymbol{I}}_{1x} \xrightarrow{2\pi J_{12}t\widehat{\boldsymbol{I}}_{1\boldsymbol{z}}\widehat{\boldsymbol{I}}_{2\boldsymbol{z}}} \widehat{\boldsymbol{I}}_{1x}\cos(\pi J_{12}t) + 2\widehat{\boldsymbol{I}}_{1y}\widehat{\boldsymbol{I}}_{2z}\sin(\pi J_{12}t)$$

This kind of evolution is called a bi-linear rotation as the rotation is about the product of two operators both along the z-direction. Note the second term on the right, it is also a product term in which the state of spin 1 is represented by its y-component which also senses the state of the z-component of the coupled second spin.

Evolution under Coupling-Two Spins

We can now illustrate all of such evolutions:

$$\hat{\boldsymbol{I}}_{1x} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z} \hat{\boldsymbol{I}}_{2z}} \hat{\boldsymbol{I}}_{1x} \cos(\pi J_{12} t) + 2\hat{\boldsymbol{I}}_{1y} \hat{\boldsymbol{I}}_{2z} \sin(\pi J_{12} t)$$

$$\hat{\boldsymbol{I}}_{1y} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z} \hat{\boldsymbol{I}}_{2z}} \hat{\boldsymbol{I}}_{1y} \cos(\pi J_{12} t) - 2\hat{\boldsymbol{I}}_{1x} \hat{\boldsymbol{I}}_{2z} \sin(\pi J_{12} t)$$

$$\hat{\boldsymbol{I}}_{1z} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z} \hat{\boldsymbol{I}}_{2z}} \hat{\boldsymbol{I}}_{1z}$$

$$\hat{\boldsymbol{I}}_{2x} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z} \hat{\boldsymbol{I}}_{2z}} \hat{\boldsymbol{I}}_{2x} \cos(\pi J_{12} t) + 2\hat{\boldsymbol{I}}_{2y} \hat{\boldsymbol{I}}_{1z} \sin(\pi J_{12} t)$$

$$\hat{\boldsymbol{I}}_{2y} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z} \hat{\boldsymbol{I}}_{2z}} \hat{\boldsymbol{I}}_{2y} \cos(\pi J_{12} t) - 2\hat{\boldsymbol{I}}_{2x} \hat{\boldsymbol{I}}_{1z} \sin(\pi J_{12} t)$$

$$\hat{\boldsymbol{I}}_{2z} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z} \hat{\boldsymbol{I}}_{2z}} \hat{\boldsymbol{I}}_{2z}$$

Evolution -Two Spins

Let us now see the physical meaning of the se terms that we have collected. Let us say at t=0 we have I_{1x} and I_{2x} and see the evolution. As one can see if we follow one spin through the evolution under various parts of the Hamiltonian we can write for the other spin by induction

$$\hat{\boldsymbol{I}}_{1x} \xrightarrow{\Omega_1 t \hat{\boldsymbol{I}}_{1z}} \hat{\boldsymbol{I}}_{1x}\cos(\Omega_1 t) + \hat{\boldsymbol{I}}_{1y}\sin(\Omega_1 t)$$

$$\cos(\Omega_1 t)\hat{\boldsymbol{I}}_{1x} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z}\hat{\boldsymbol{I}}_{2z}} \cos(\Omega_1 t)\left[\hat{\boldsymbol{I}}_{1x}\cos(\pi J_{12} t) + 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2z}\sin(\pi J_{12} t)\right]$$

$$\sin(\Omega_1 t)\hat{\boldsymbol{I}}_{1y} \xrightarrow{2\pi J_{12} t \hat{\boldsymbol{I}}_{1z}\hat{\boldsymbol{I}}_{2z}} \sin(\Omega_1 t)\left[\hat{\boldsymbol{I}}_{1y}\cos(\pi J_{12} t) - 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2z}\sin(\pi J_{12} t)\right]$$

However, We can detect only the I_x or I_y operators and not the product operators

Evolution -Two Spins

The observed signal of the spin 1 is thus come from the term

$$\hat{\boldsymbol{I}}_{1x}\cos(\Omega_1 t)\cos(\pi J_{12} t)+\hat{\boldsymbol{I}}_{1y}\sin(\Omega_1 t)\cos(\pi J_{12} t)$$

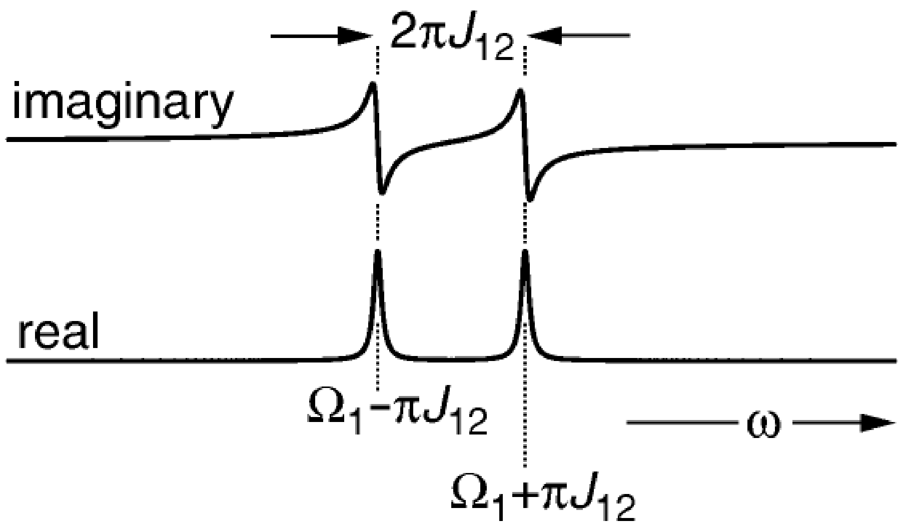
In the observed signal S(t) the x-component is the real part and the y-component is the imaginary part.

$$\begin{aligned}
S(t) &= [\cos(\Omega_1 t)\cos(\pi J_{12} t)+i\sin(\Omega_1 t)\cos(\pi J_{12} t)]\exp(-Rt) \\
&= \cos(\pi J_{12} t)\exp(i\Omega_1 t)\exp(-Rt) \\
&= \frac{1}{2}[\exp(i\pi J_{12} t)+\exp(-i\pi J_{12} t)]\exp(\Omega_1 t)\exp(-Rt) \\
&= \frac{1}{2}[\exp(i(\Omega_1+\pi J_{12})t)+\exp(i(\Omega_1-\pi J_{12})t)]\exp(-Rt)
\end{aligned}$$

Evolution -Two Spins

Fourier transform S(t) will then give real and imaginary part of the spectrum with lines at the two frequencies in the exponent.

$$S(t) = \frac{1}{2}\left[\exp\left(i\left(\Omega_1 + \pi J_{12}\right)t\right) + \exp\left(i\left(\Omega_1 - \pi J_{12}\right)t\right)\right]\exp(-Rt)$$

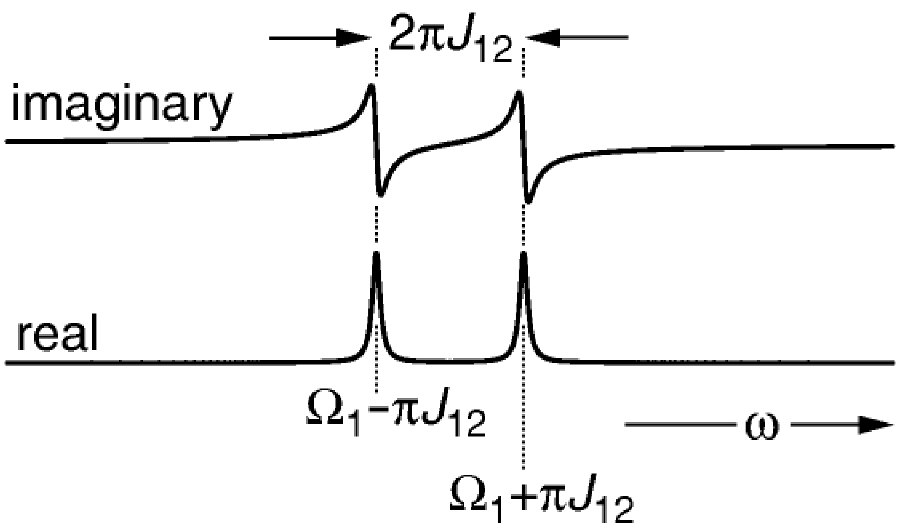


Note the horizontal axis in units of ω. The multiplets are in same phase with respect to each other in both the real and imaginary parts.

Evolution -Two Spins

Thus the evolution of I_{1x} under a two-spin Hamiltonian gives a in phase doublet spectrum

$$\widehat{\boldsymbol{I}}_{1x} \xrightarrow{\Omega_1 t \widehat{\boldsymbol{I}}_{1\mathbf{z}} + 2\pi J_{12} t \widehat{\boldsymbol{I}}_{1\mathbf{z}} \widehat{\boldsymbol{I}}_{2\mathbf{z}}}$$



Thus the operator I_{1x} is called the in-phase x operator.

Evolution -Two Spins

Suppose at t=0 if we have the operator $2I_{1x}I_{2z}$, then we can calculate the resulting spectrum in a similar way.

$$2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2z} \xrightarrow{\Omega_1 t\hat{\boldsymbol{I}}_{1z}} 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2z}\cos(\Omega_1 t) + 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2z}\sin(\Omega_1 t)$$

$$\cos(\Omega_1 t)2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2z} \xrightarrow{2\pi J_{12}t\hat{\boldsymbol{I}}_{1z}\hat{\boldsymbol{I}}_{2z}} \cos(\Omega_1 t)\left[2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2z}\cos(\pi J_{12}t) + \hat{\boldsymbol{I}}_{1y}\sin(\pi J_{12}t)\right]$$

$$\sin(\Omega_1 t)2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2z} \xrightarrow{2\pi J_{12}t\hat{\boldsymbol{I}}_{1z}\hat{\boldsymbol{I}}_{2z}} \sin(\Omega_1 t)\left[2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2z}\cos(\pi J_{12}t) - \hat{\boldsymbol{I}}_{1x}\sin(\pi J_{12}t)\right]$$

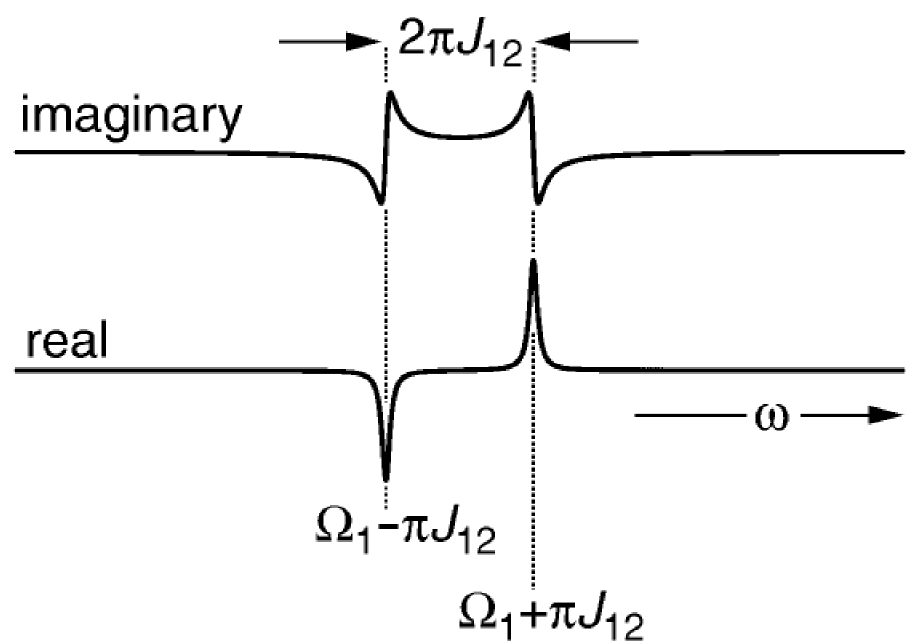
Noting again that we can only detect I_x or I_y components, the detected signal is

$$\begin{aligned}
S(t) &= \left[-\sin(\Omega_1 t)\sin(\pi J_{12}t) + i\cos(\Omega_1 t)\sin(\pi J_{12}t)\right]\exp(-Rt) \\
&= i\sin(\pi J_{12}t)\exp i(\Omega_1 t)\exp(-Rt) \\
&= i\frac{1}{2i}\left[\exp(i\pi J_{12}t) - \exp(-i\pi J_{12}t)\right]\exp(\Omega_1 t)\exp(-Rt) \\
&= \frac{1}{2}\left[\exp(i(\Omega_1 + \pi J_{12})t) - \exp(i(\Omega_1 - \pi J_{12})t)\right]\exp(-Rt)
\end{aligned}$$

Evolution -Two Spins

Up on Fourier transform the spectrum would be as below,

$$2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2z} \xrightarrow{\Omega_1 t \hat{\boldsymbol{I}}_{1z} + 2\pi J_{12} t \hat{\boldsymbol{I}}_{1z}\hat{\boldsymbol{I}}_{2z}}$$

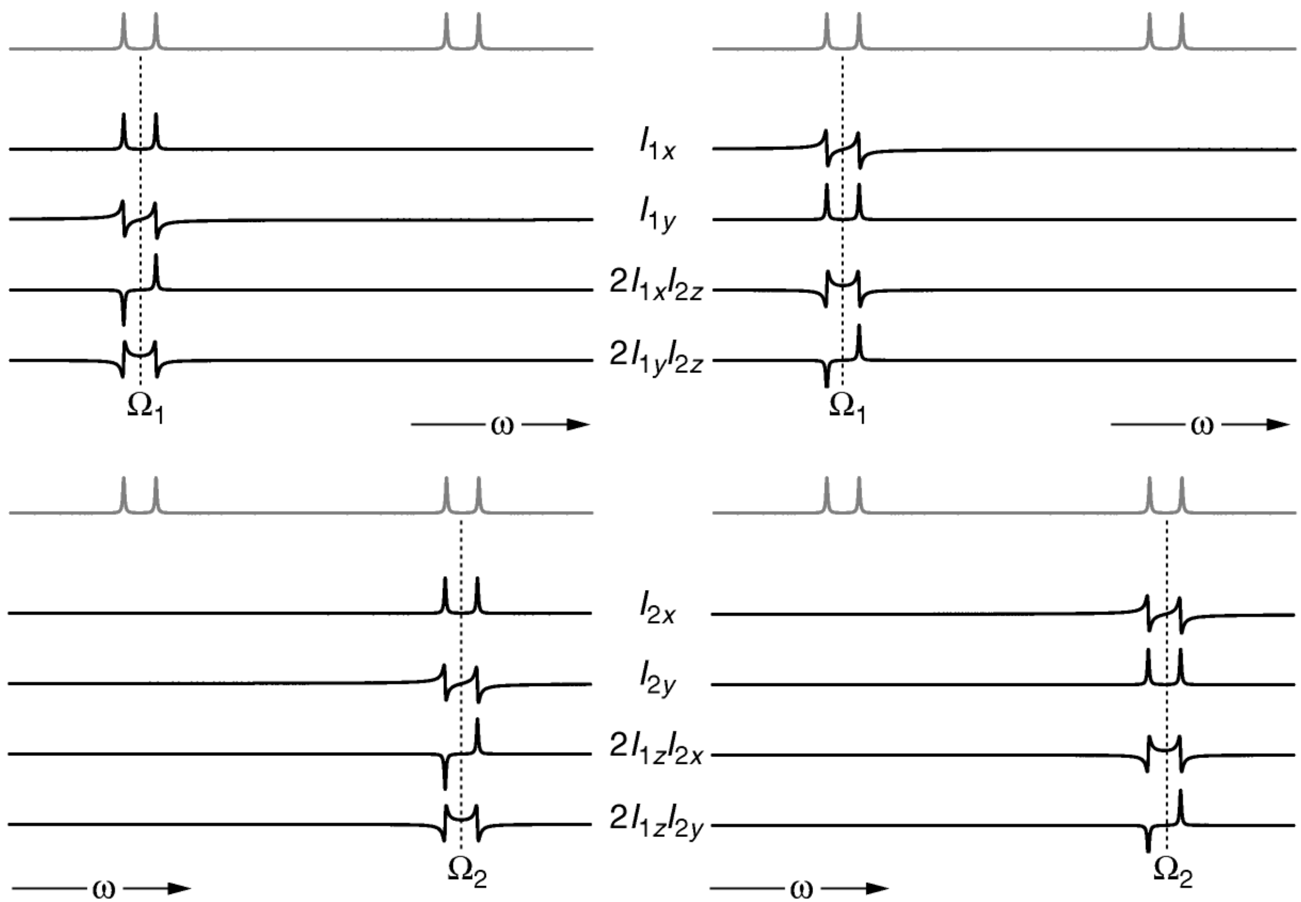


The mulitiplets are in opposite phase in both the real and imaginary part and so the operator $2I_{1x}I_{2z}$ is called anti-phase x component of the spin 1.

Summary of Physical Nature of Operators - Two Spins

x- is absorption

y- is absorption



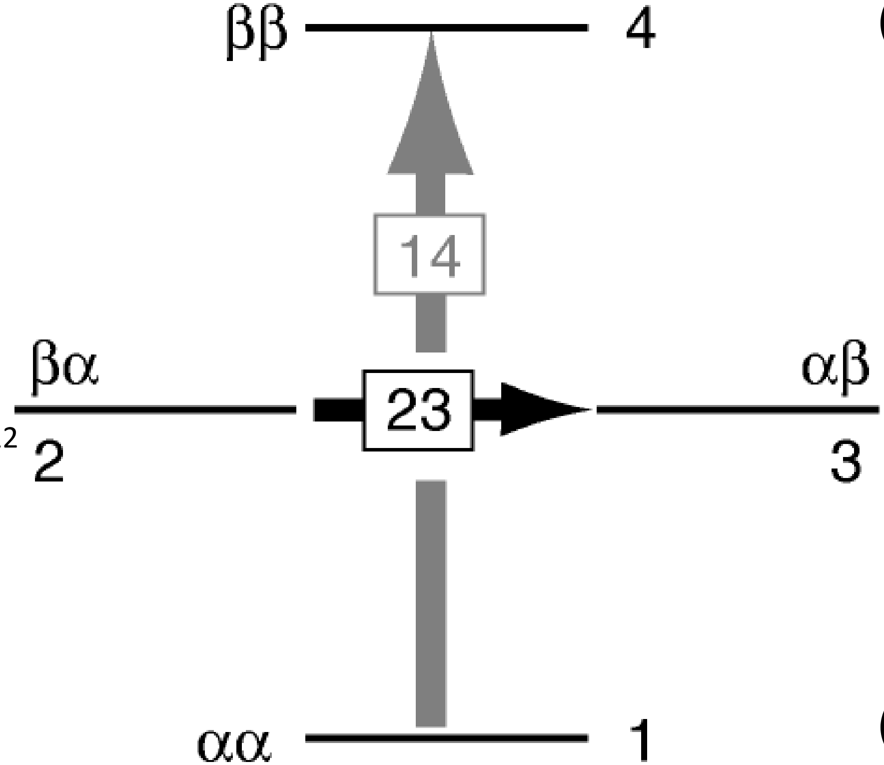
Summary of Physical Nature of Operators - Two Spins

z - magnetization on spin 1	$\hat{\boldsymbol{I}}_{\boldsymbol{1z}}$
in - phase x - and y - magnetization on spin 1	$\hat{\boldsymbol{I}}_{\boldsymbol{1}x}, \hat{\boldsymbol{I}}_{\boldsymbol{1}y}$
z - magnetization on spin 2	$\hat{\boldsymbol{I}}_{2\boldsymbol{z}}$
in - phase x - and y - magnetization on spin 2	$\hat{\boldsymbol{I}}_{2x}, \hat{\boldsymbol{I}}_{2y}$
anti - phase x - and y - magnetization on spin 1	$2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2\boldsymbol{z}}, 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2\boldsymbol{z}}$
anti - phase x - and y - magnetization on spin 2	$2\hat{\boldsymbol{I}}_{2x}\hat{\boldsymbol{I}}_{2\boldsymbol{z}}, 2\hat{\boldsymbol{I}}_{2y}\hat{\boldsymbol{I}}_{2\boldsymbol{z}}$
multiple quantum coherences	$2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2x}, 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2y}, 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2y}, 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2x}$
non - equlibrium population	$2\hat{\boldsymbol{I}}_{1z}\hat{\boldsymbol{I}}_{2z}$

Multiple Quantum Coherences

$(1/2)\upsilon_{01}+(1/2)\upsilon_{02}+(1/4)J_{12}$

$-(1/2)\upsilon_{01}+(1/2)\upsilon_{02}-(1/4)J_{12}$



$(1/2)\upsilon_{01}-(1/2)\upsilon_{02}-(1/4)J_{12}$

$(1/2)\upsilon_{01}+(1/2)\upsilon_{02}+(1/4)J_{12}$

$$\text{Double Quantum - x } (DQ_x) = 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2x} - 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2y}$$

$$\text{Double Quantum - y } (DQ_y) = 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2y} + 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2x}$$

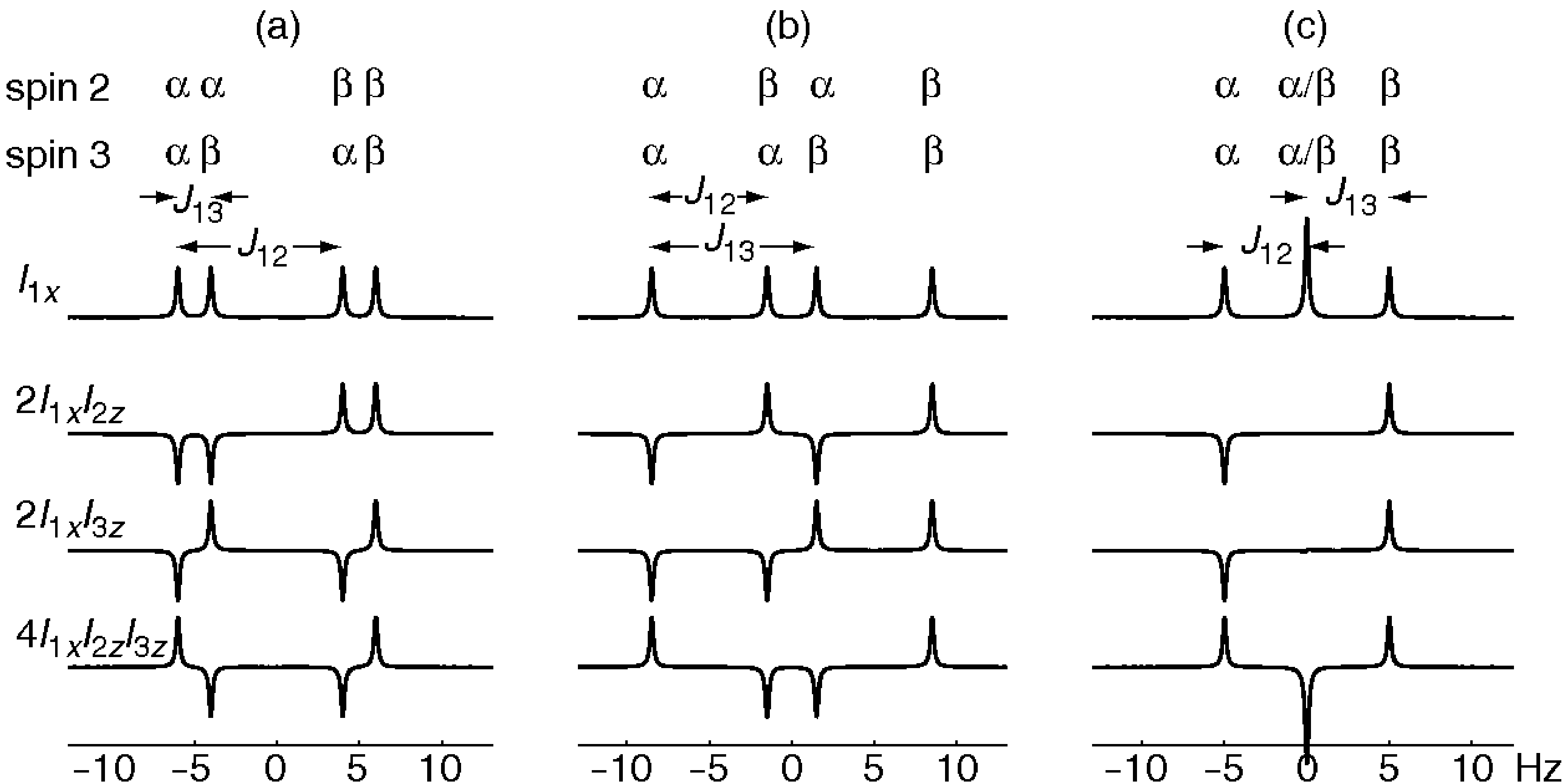
$$\text{Zero Quantum - x } (ZQ_x) = 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2x} + 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2y}$$

$$\text{Zero Quantum - y } (ZQ_y) = 2\hat{\boldsymbol{I}}_{1x}\hat{\boldsymbol{I}}_{2y} - 2\hat{\boldsymbol{I}}_{1y}\hat{\boldsymbol{I}}_{2x}$$

$$\upsilon(DQ) = \upsilon_{01} + \upsilon_{02}$$

$$\upsilon(ZQ) = \upsilon_{01} - \upsilon_{02}$$

Summary of Physical Nature of Operators - Three Spins



(a) J_{12}=10Hz, J_{13}=2Hz, *(b) J_{12}=7Hz, J_{13}=10Hz,* *(c) J_{12}=5Hz, J_{13}=5Hz*