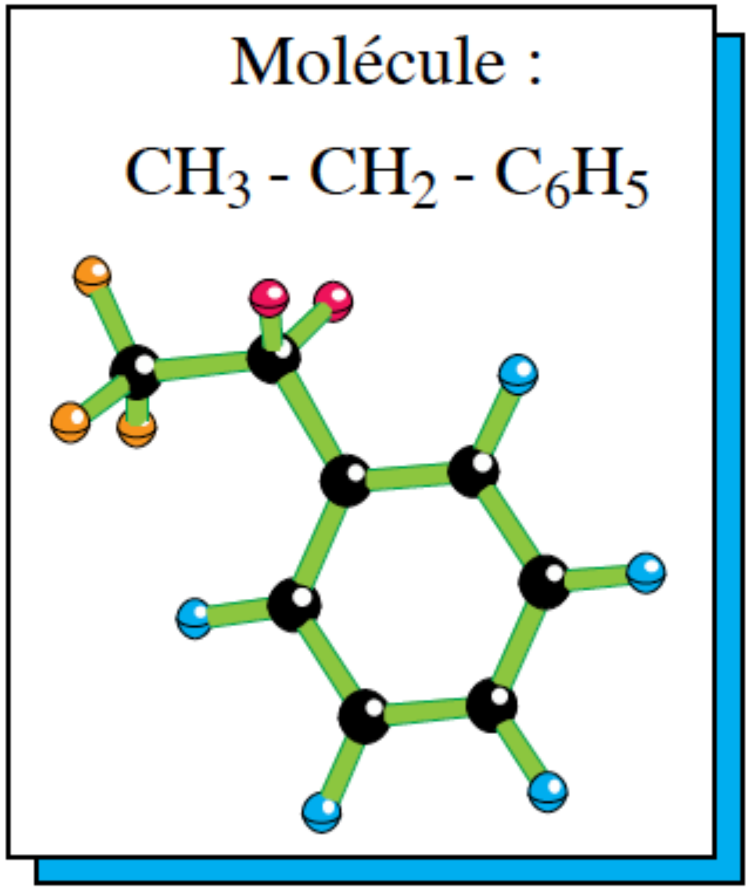
Advanced NMR & Imaging

Week 5: **Part II** - A Quantum Mechanical Description of Pulsed NMR Spectroscopy

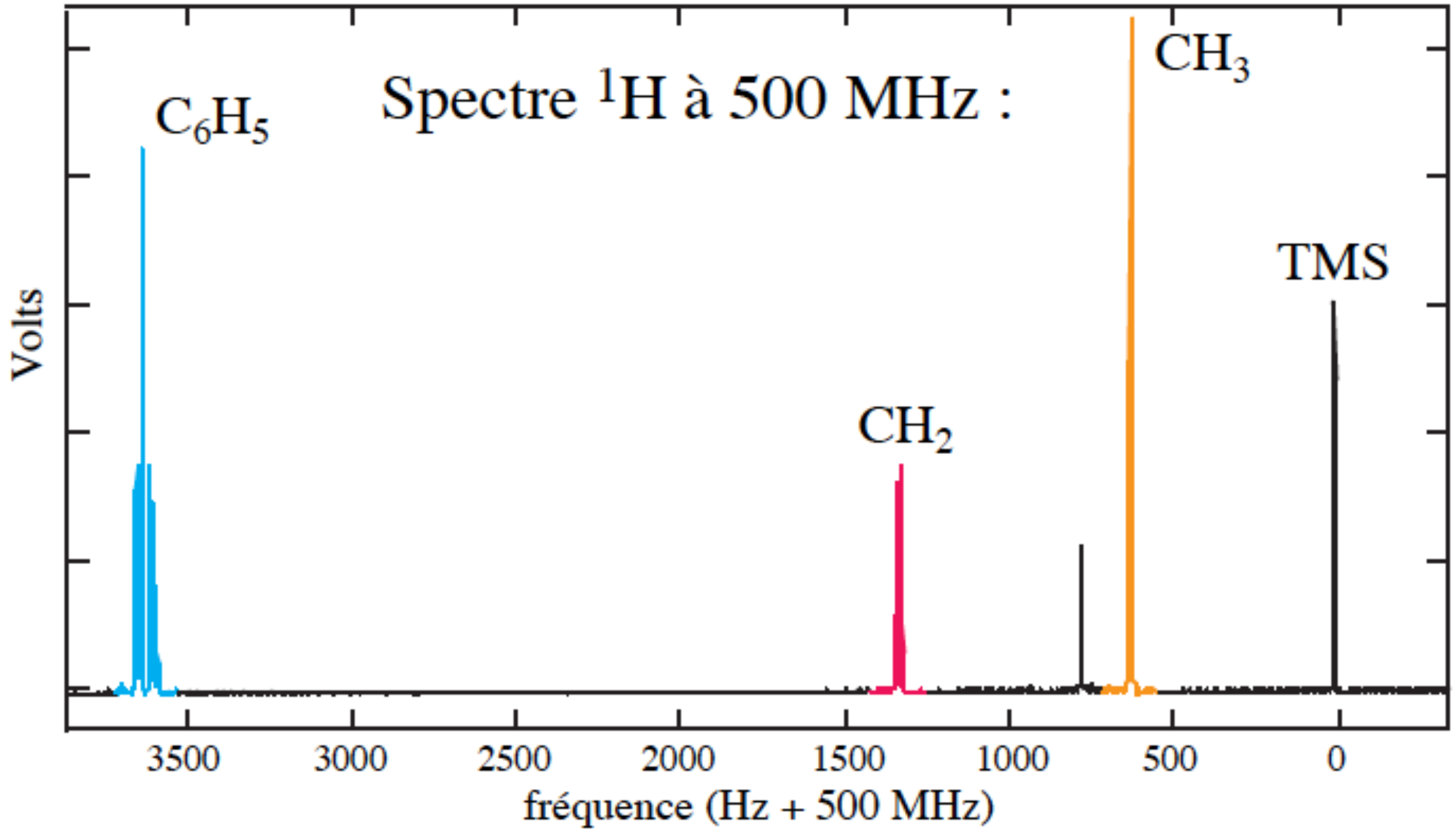
Objectives

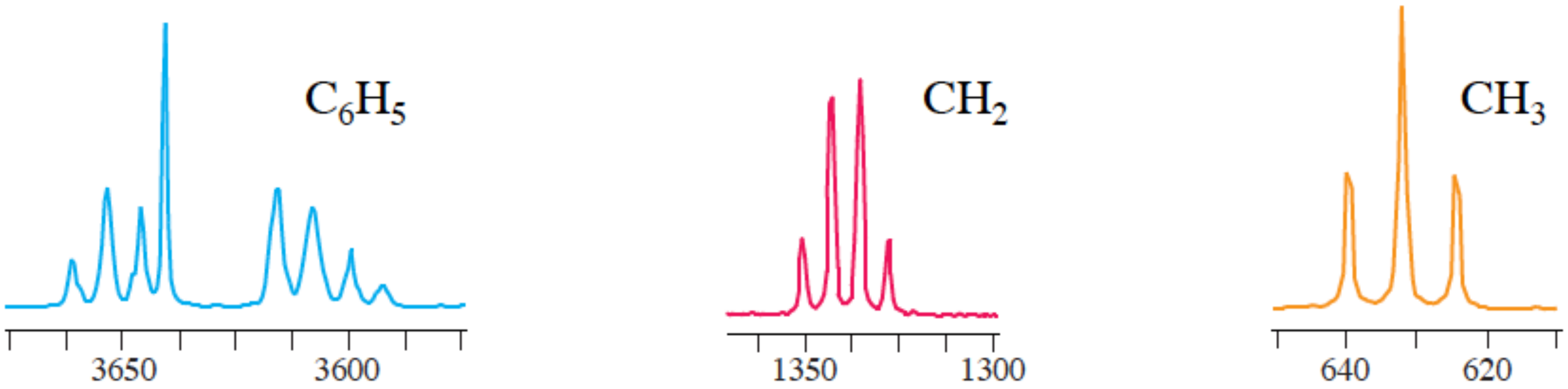
- Understand the quantum description of time-domain NMR spectroscopy

We understand this?

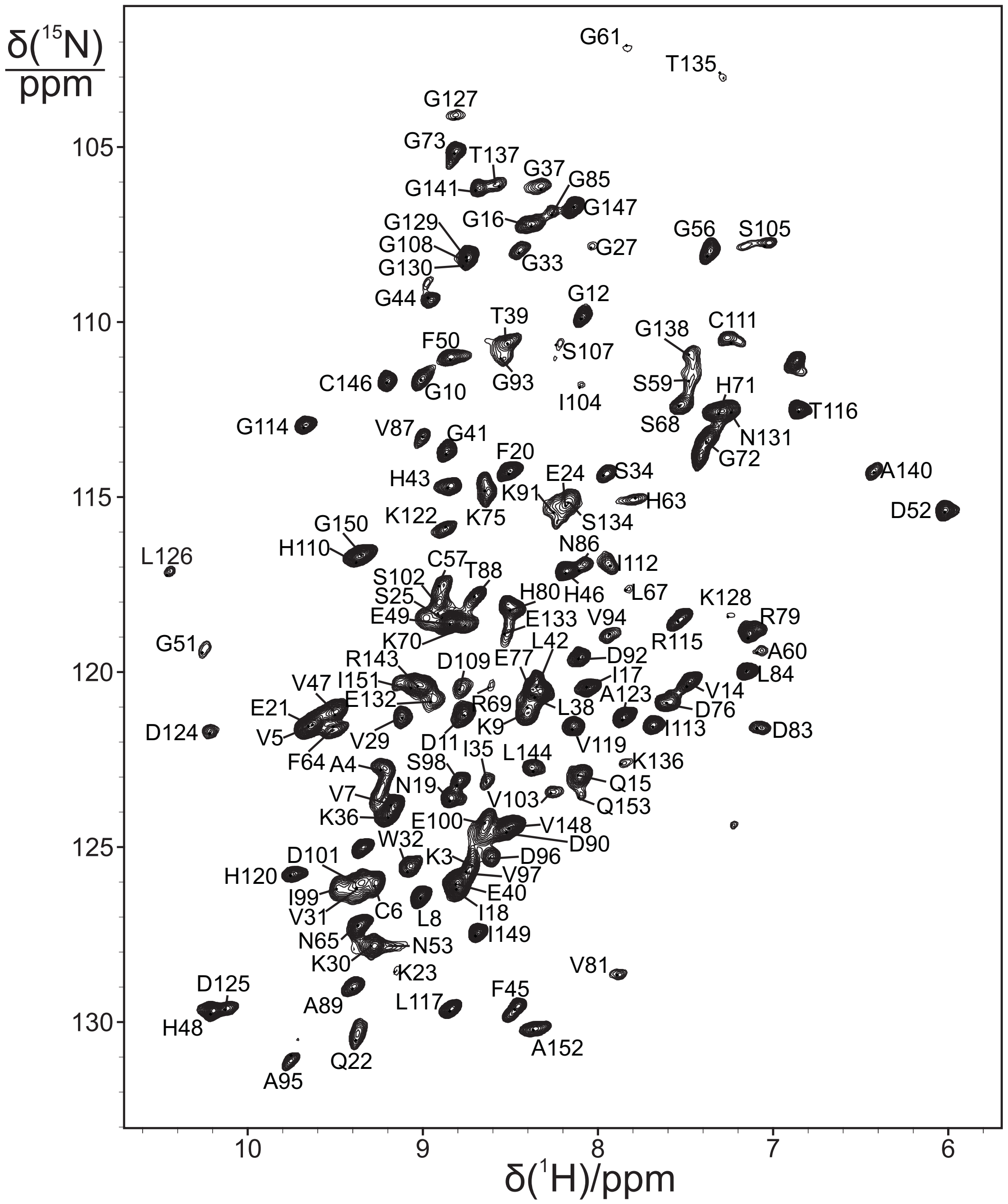

Molécule :

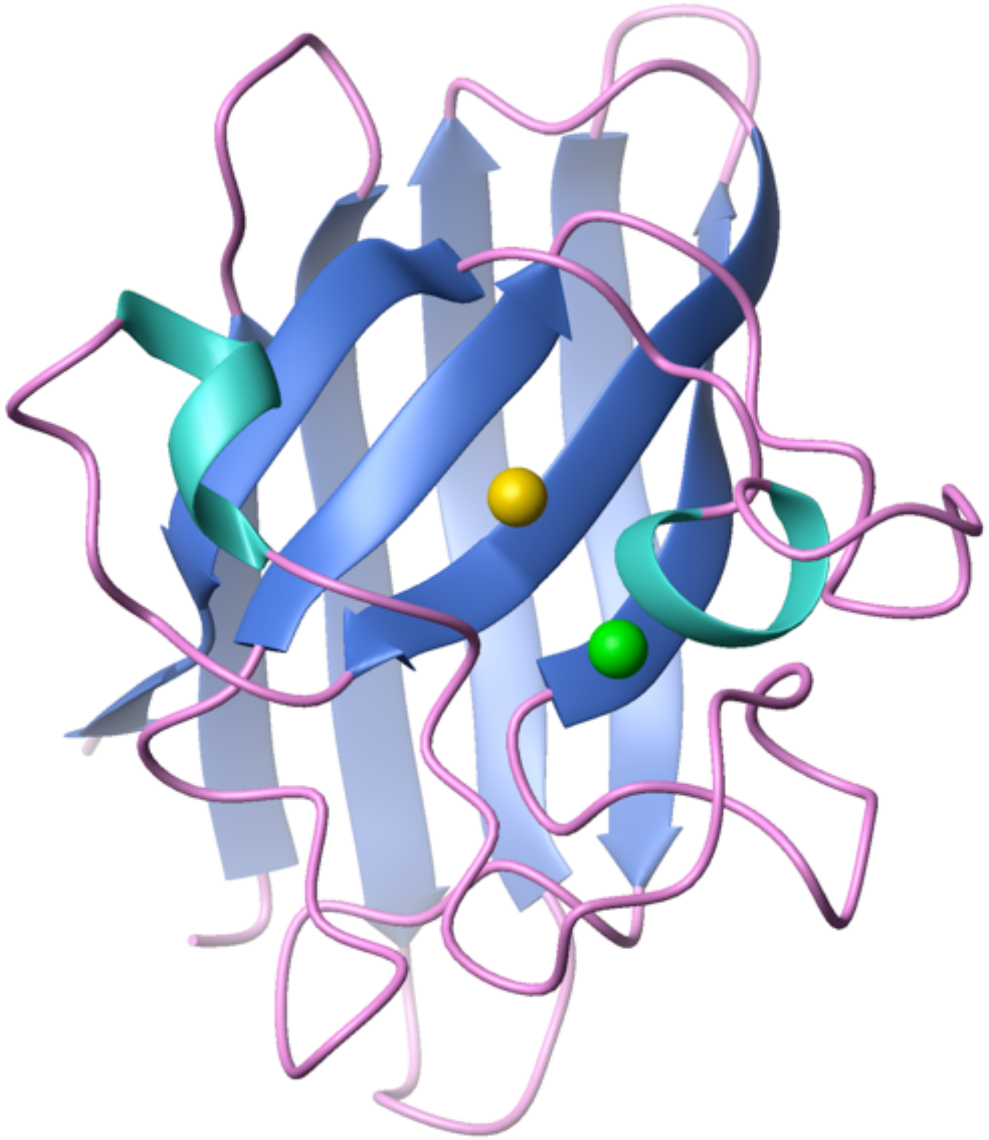
$CH_3 - CH_2 - C_6H_5$





But do we understand this?





Bibliography

M. Goldman *A Quantum Description of NMR in Liquids*; Clarendon Press: Oxford, 1988.

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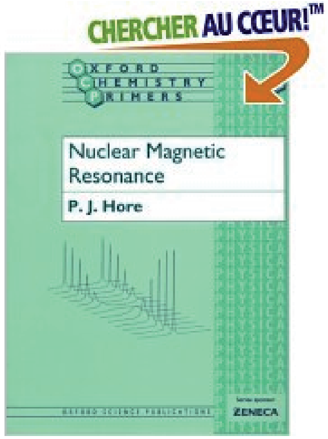

Nuclear Magnetic Resonance (Broché)

de P. J. Hore (Auteur) "Molecules are inconveniently small-too small to be observed and studied directly ..." (plus)

Aucun commentaire client existant. Soyez le premier.

Prix : EUR 14,72 LIVRAISON GRATUITE Voir les détails

Disponibilité : Habituellement expédié sous 2 à 4 semaines. Expédié et vendu par **Amazon.fr**. Emballage cadeau disponible.

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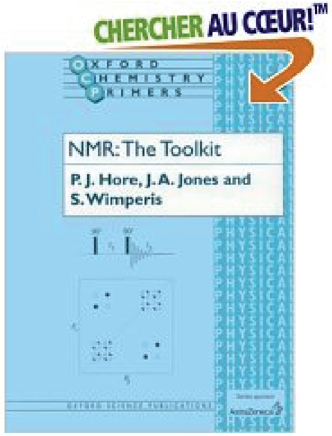

Nmr: The Toolkit (Broché)

de Peter Hore (Auteur), Jonathan Jones (Auteur), Stephen Wimperis (Auteur) "The so-called vector model of NMR spectroscopy is an essential weapon in the armoury of every practising NMR spectroscopist because it provides the sort of..." (plus)

Aucun commentaire client existant. Soyez le premier.

Prix : EUR 16,63 LIVRAISON GRATUITE Voir les détails

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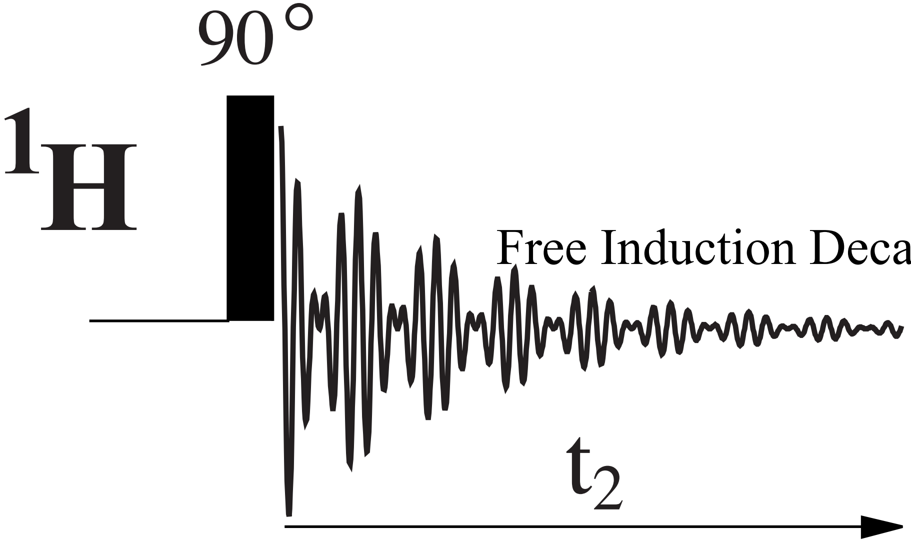
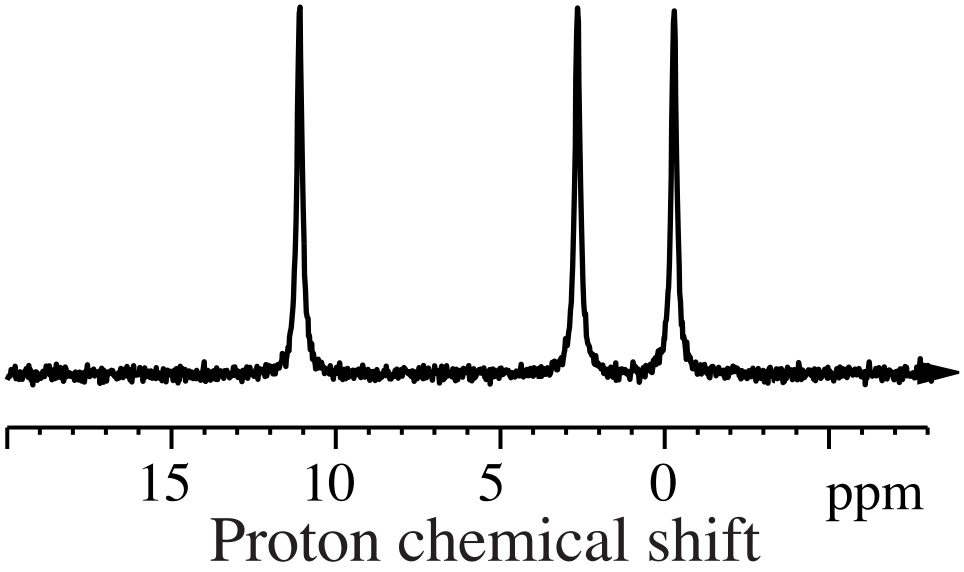
Pulsed Fourier Transform NMR

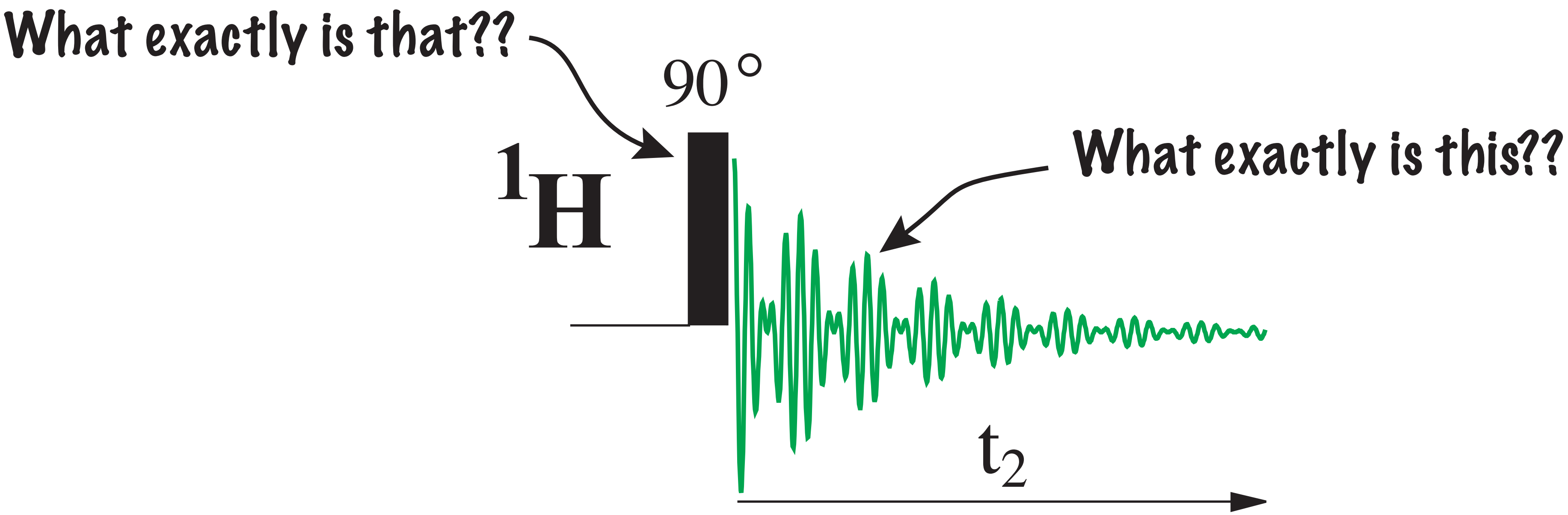


Fourier Transformation

$$I(\omega) = \int S(t)\exp\{-i\omega t\}dt$$



Pulsed Fourier Transform NMR



NMR experiments observe the voltage induced in a detection coil by *oscillating bulk magnetic moments* as they return to equlibrium.

The oscillations are induced by *perturbing* the system with a radio-frequency pulse. (Since the system is time-dependent, it must be out of equilibrium)

In following we will investigate the origin of these dynamic nuclear magnetic moments.

Magnetic Moments

NMR is concerned solely with the motion of nuclear magnetic moments: that is what is detected in the experiment. The nucleus possesses an intrinsic magnetic moment of classical energy

$$E = -\mu \cdot B, \tag{1.1}$$

where μ is the magnetic moment and B an external magnetic field. The corresponding Hamiltonian in quantum mechanics is the Zeeman Hamiltonian

$$\hbar\mathcal{H} = -\mu \cdot B. \tag{1.2}$$

This Zeeman Hamiltonian is added to the purely nuclear Hamiltonian and it turns out that

$$\mu = \gamma\hbar I, \tag{1.3}$$

where γ is the magnetogyric ratio and where I is the operator corresponding to spin. Thus we obtain in a static external magnetic field: $B = \left(0,0,B_0\right)$

$$\mathcal{H}_Z = -\gamma B_0 I_z. \tag{1.4}$$

Thus, to understand NMR we need to understand the properties and dynamics of spin operators. For a more detailed methodic treatment see, for example, Goldman.

Magnetic Moments

why we need to do quantum mechanics

The Schrodinger Equation of Motion

$$\frac{d}{dt}\left|\square\right\rangle = \left|\dot{\square}\right\rangle = \square i\mathcal{H}\left|\square\right\rangle$$

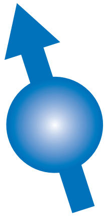
the motion of the state

the system Hamiltonian

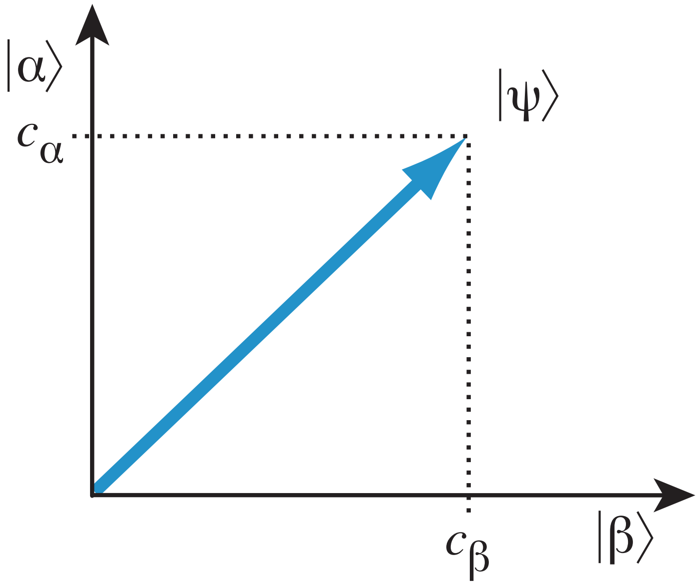
the state

how do we represent the state of the system?

Magnetic Moments



$|\psi\rangle =$ *the state of a single spin*

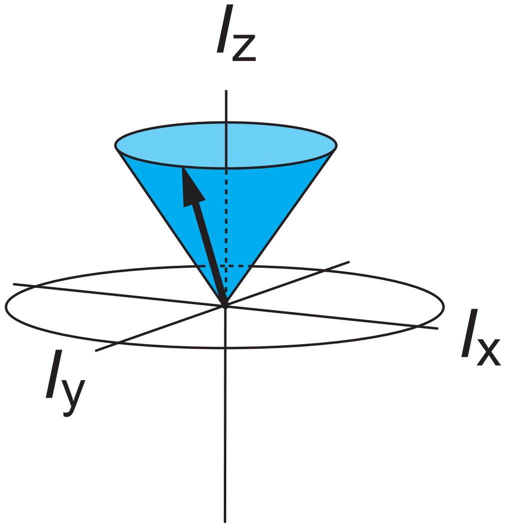


$$|\psi\rangle = c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$$

(For a single spin I = 1/2, any state of the system can be represent as a linear combination of the two basis states, and drawn as vector. (Here directly in the state space (Hilbert space))

Magnetic Moments

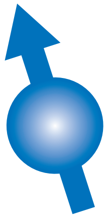
$|\psi\rangle =$ *the state of a single spin*



$$|\psi\rangle = a_x I_x + a_y I_y + a_z I_z$$

(An alternative basis set is the three components of angular momentum, and and 𝟙. (Liouville space))

Magnetic Moments



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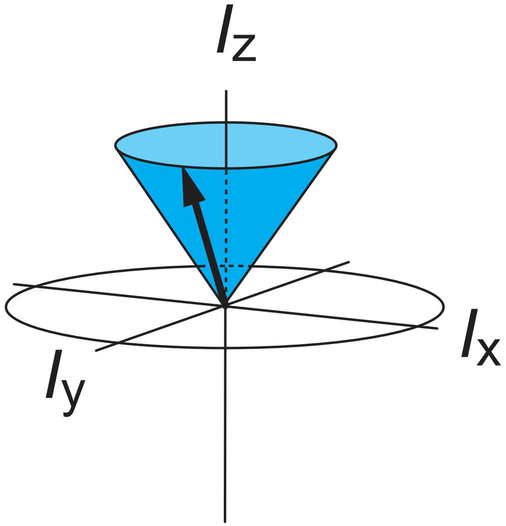
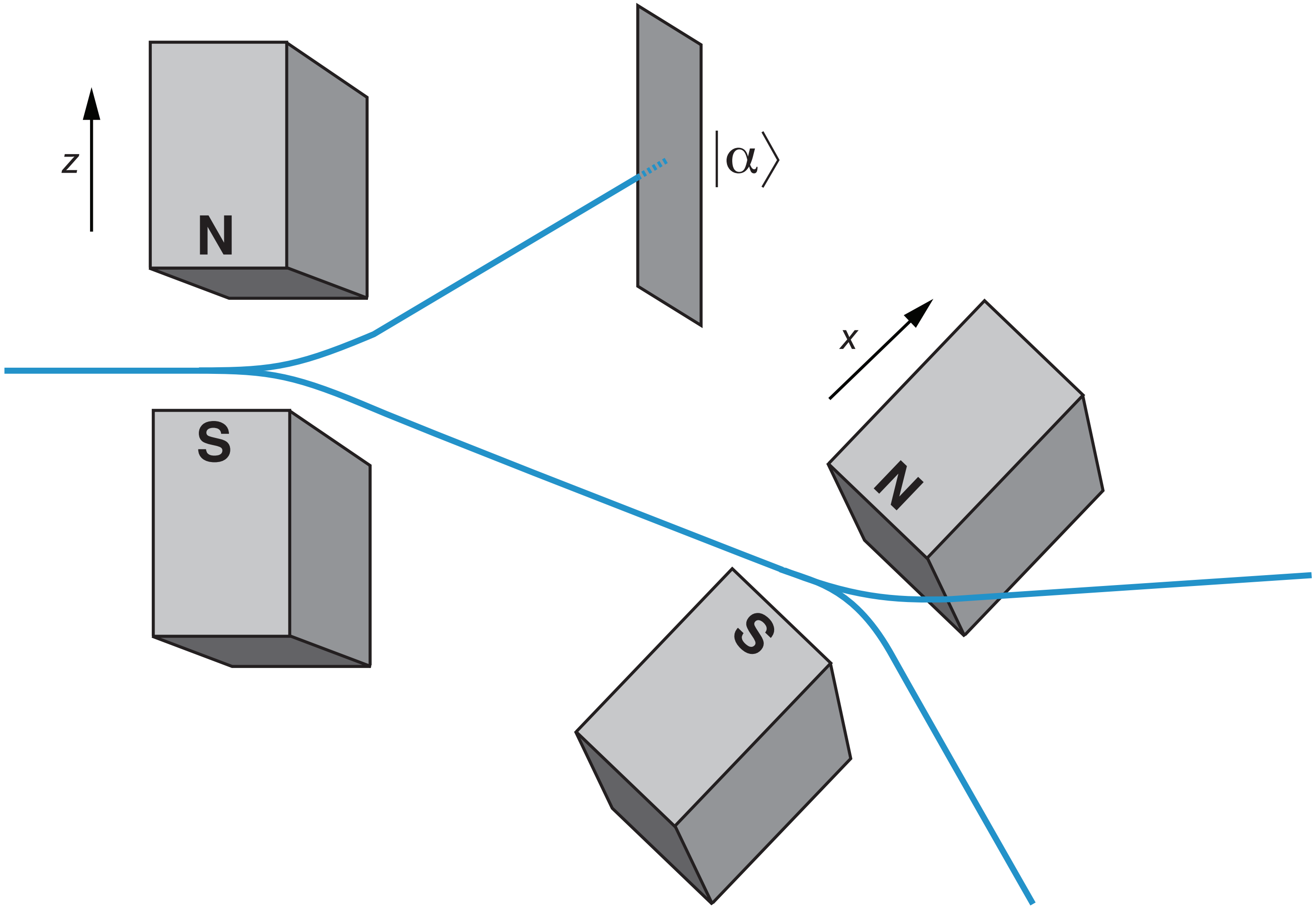


$$|\psi\rangle = a_x I_x + a_y I_y + a_z I_z$$

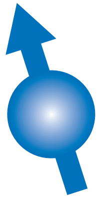
(An alternative basis set is the three components of angular momentum, and and $\mathbb{1}$. (Liouville space))

an NMR sample contains about 10^{21} spins....

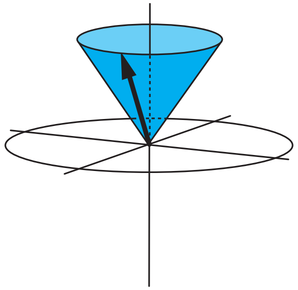
Stern Gerlach



The Density Matrix

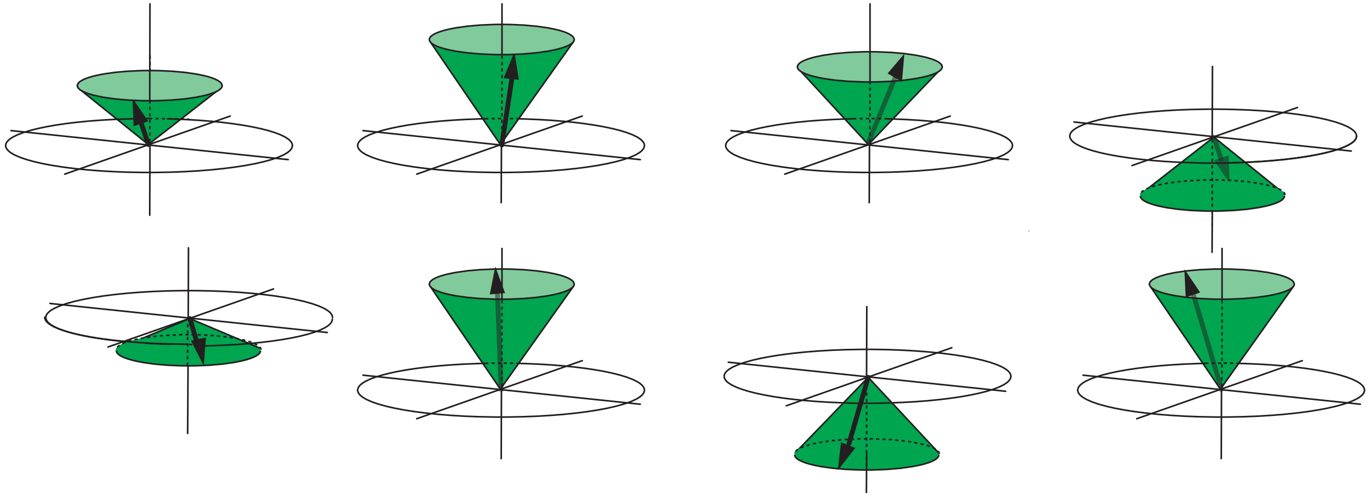


$|\psi\rangle =$ *the state of a single spin*



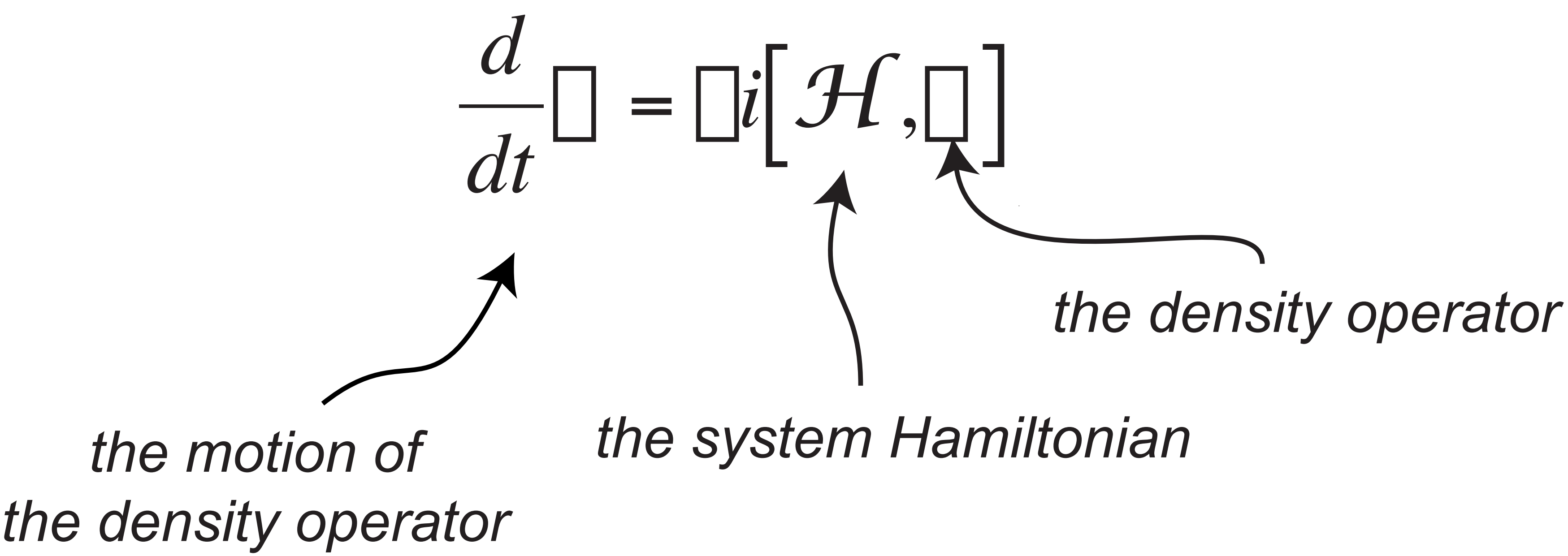
$$\sigma = \int P(\psi)|\psi\rangle\langle\psi|\,d\tau$$

The density operator: *the average state of a statistical ensemble of spins.*



Equation of Motion

The Schrodinger Equation of Motion of the Density Operator



$$\frac{d}{dt}\square = \square i\left[\mathcal{H},\square\right]$$

the motion of
the density operator

the system Hamiltonian

the density operator

The Liouville - von Neumann Equation

Equation of Motion

The Liouville - von Neumann equation:

$$\frac{d}{dt}\rho = -i\left[\mathcal{H},\rho\right]$$

The solution for a time independent Hamiltonian:

$$\rho(t) = \exp\left(-i\mathcal{H}t\right)\rho(0)\exp\left(+i\mathcal{H}t\right)$$

the state at
a given time

the system Hamiltonian

the initial state

Spin Dynamics

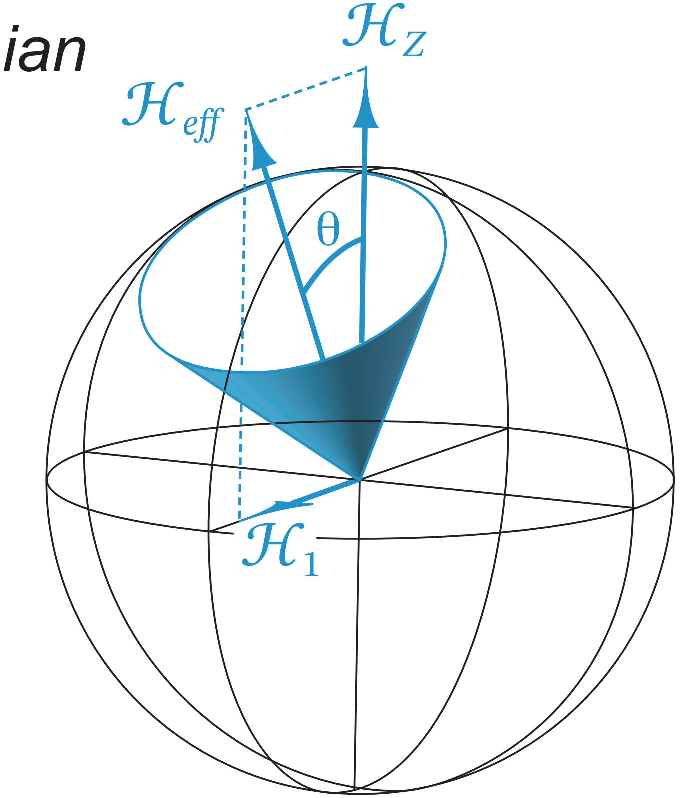
$$\sigma\left(t\right) = \exp\left(-i\mathcal{H}t\right)\sigma\left(0\right)\exp\left(+i\mathcal{H}t\right)$$

the state at a given time

the system Hamiltonian

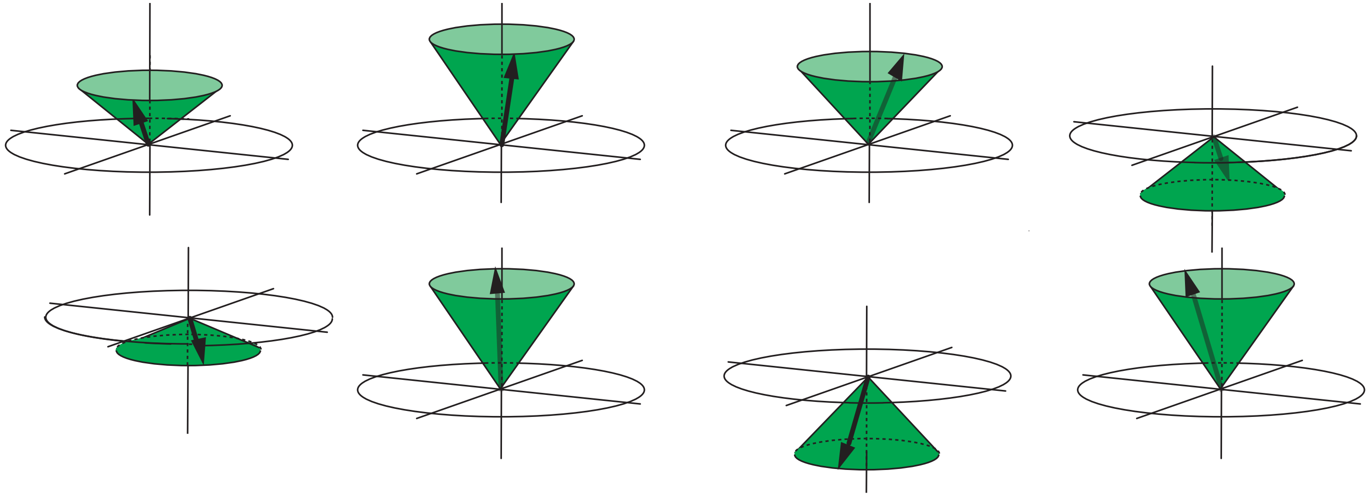
the initial state

The motion of the ensemble magnetic moment (bulk magnetization, polarisation), is a rotation around an axis defined by the Hamiltonian

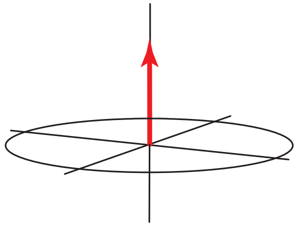


The Initial State at Equilibrium

The density operator: *the average state of a statistical ensemble of spins.*



In an ordinary ensemble, there is no phase coherence, and thus there is no net transverse component



At thermal equilibrium

$$\sigma_{eq} \propto I_z$$

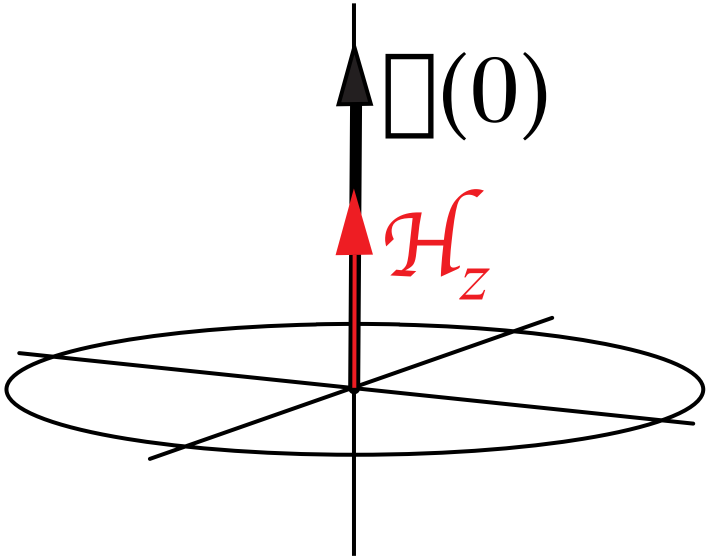
The Vector Model of Magnetic Resonance

$$\sigma(t) = \exp\{-i\omega_0 I_z t\} I_z \exp\{+i\omega_0 I_z t\}$$

the state at a given time

the system Hamiltonian

the initial state



1. Equilibrium. The net magnetization is aligned along the direction of the main field (z-axis).

Conclusions: Part I

- NMR spectroscopy detects transitions between different nuclear spin states. The principal interaction is the Zeeman Interaction

- The Zeeman interaction is modified (perturbed) by the scalar coupling and the chemical shift.

- Nuclear magnetic moments are proportional to the spin operator.

- The dynamics of spin operators are governed by the Schrodinger equation of motion.

Conclusions: Part I

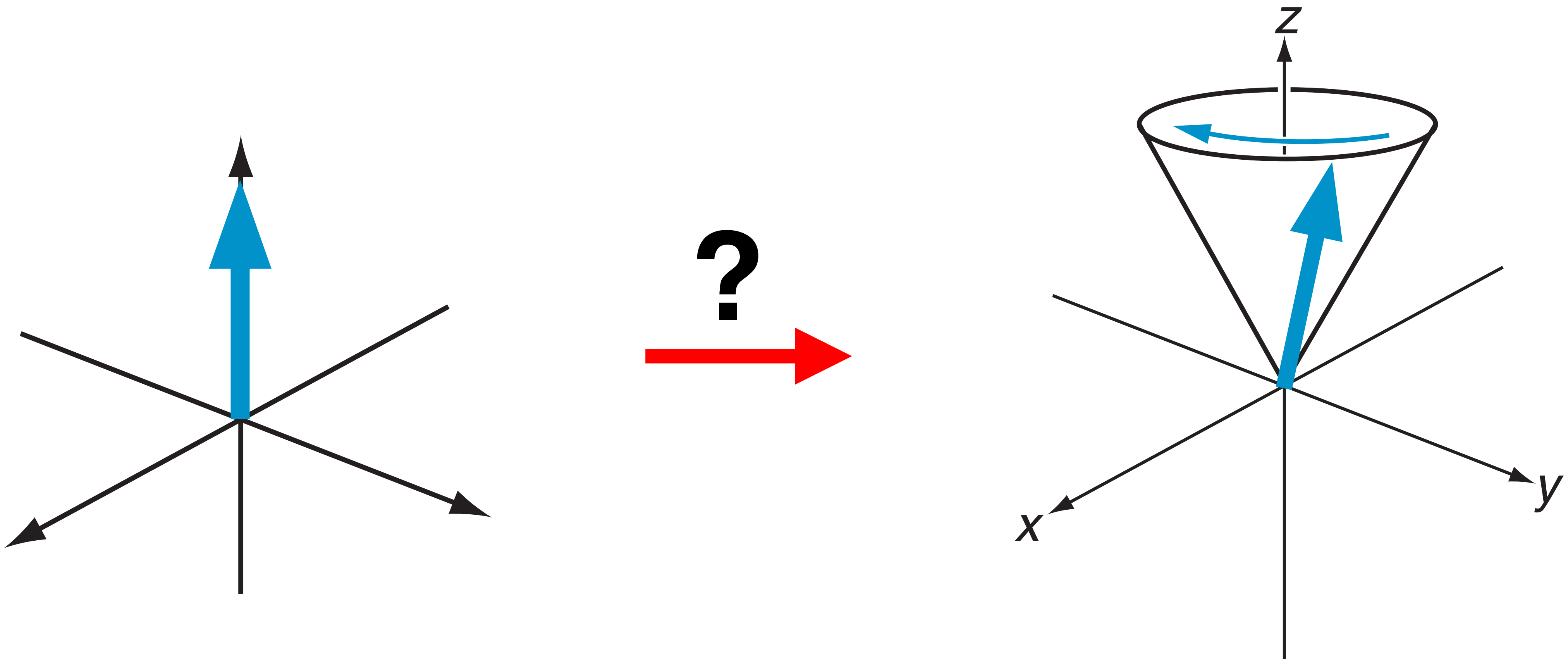
- The density operator describes the quantum state of an ensemble of spins.

- The equation of motion of the density operator is a rotation around an axis defined by the Hamiltonian for the system, at a frequency given by the magnitude of the Hamiltonian.

Pulsed FTNMR

How can we make the spins move?

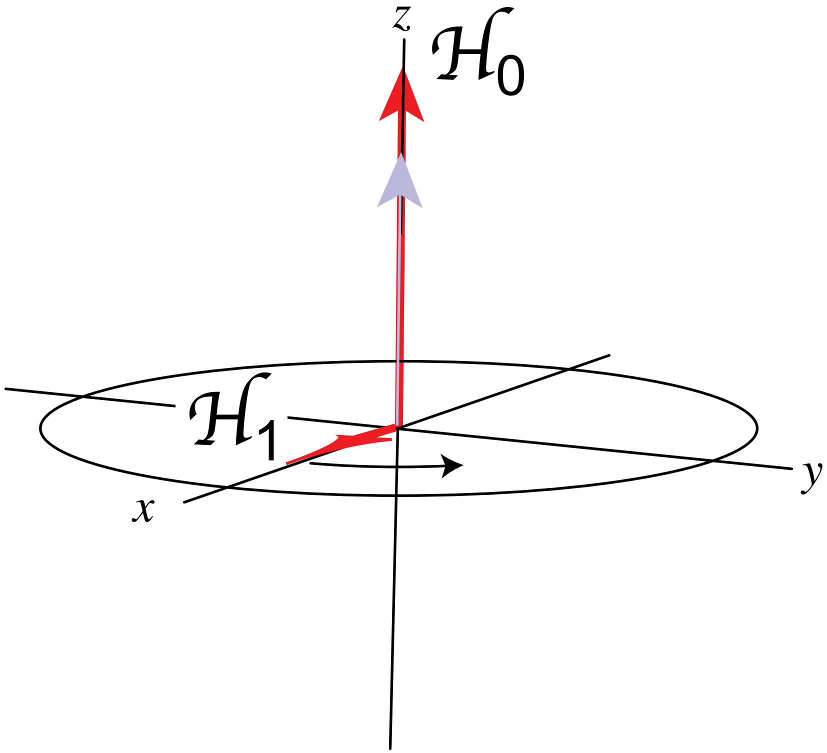
How can we tip the magnetization out of equilibrium?



Perturbing the Spins

2. Magnetic Resonance

$$\mathcal{H} = -\gamma B_0 I_Z - \gamma B_1 (I_x \cos(\omega t) + I_y \sin(\omega t))$$



Adding a small oscillating field perpendicular to the main field can cause resonance effects, even for $B_1 \ll B_0$.

Perturbing the Spins

2. Magnetic Resonance

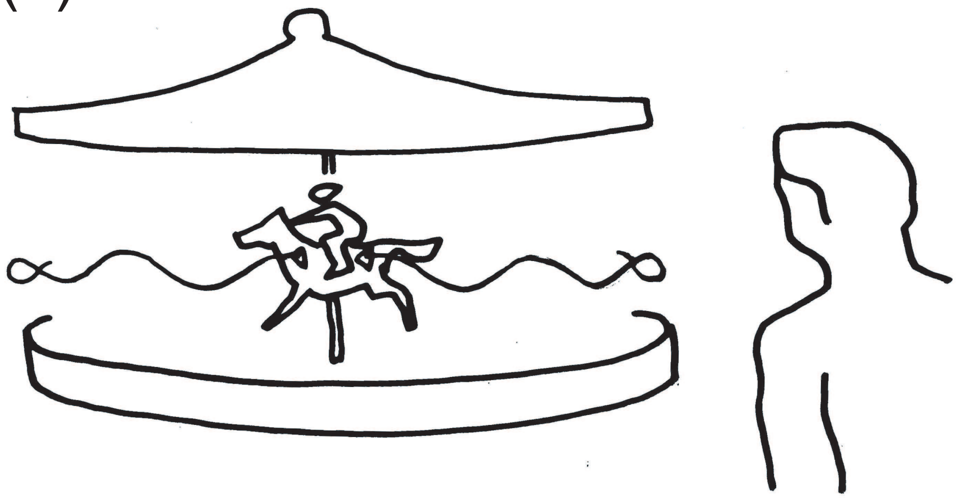
$$\mathcal{H} = -\gamma B_0 I_Z - \gamma B_1(I_x \cos(\omega t) + I_y \sin(\omega t))$$

to study the effect of this time dependent Hamiltonian
the most enlightening method is to remove the time dependence by
transforming to a rotating frame.

This can be understood geometrically (visually)
or mathematically....

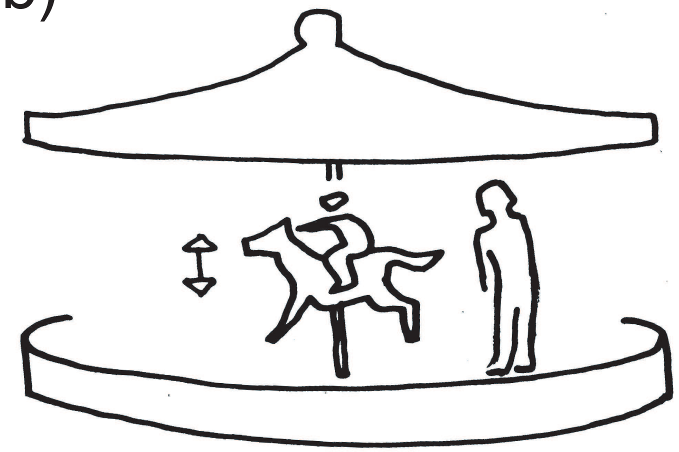
The Rotating Frame

(a)



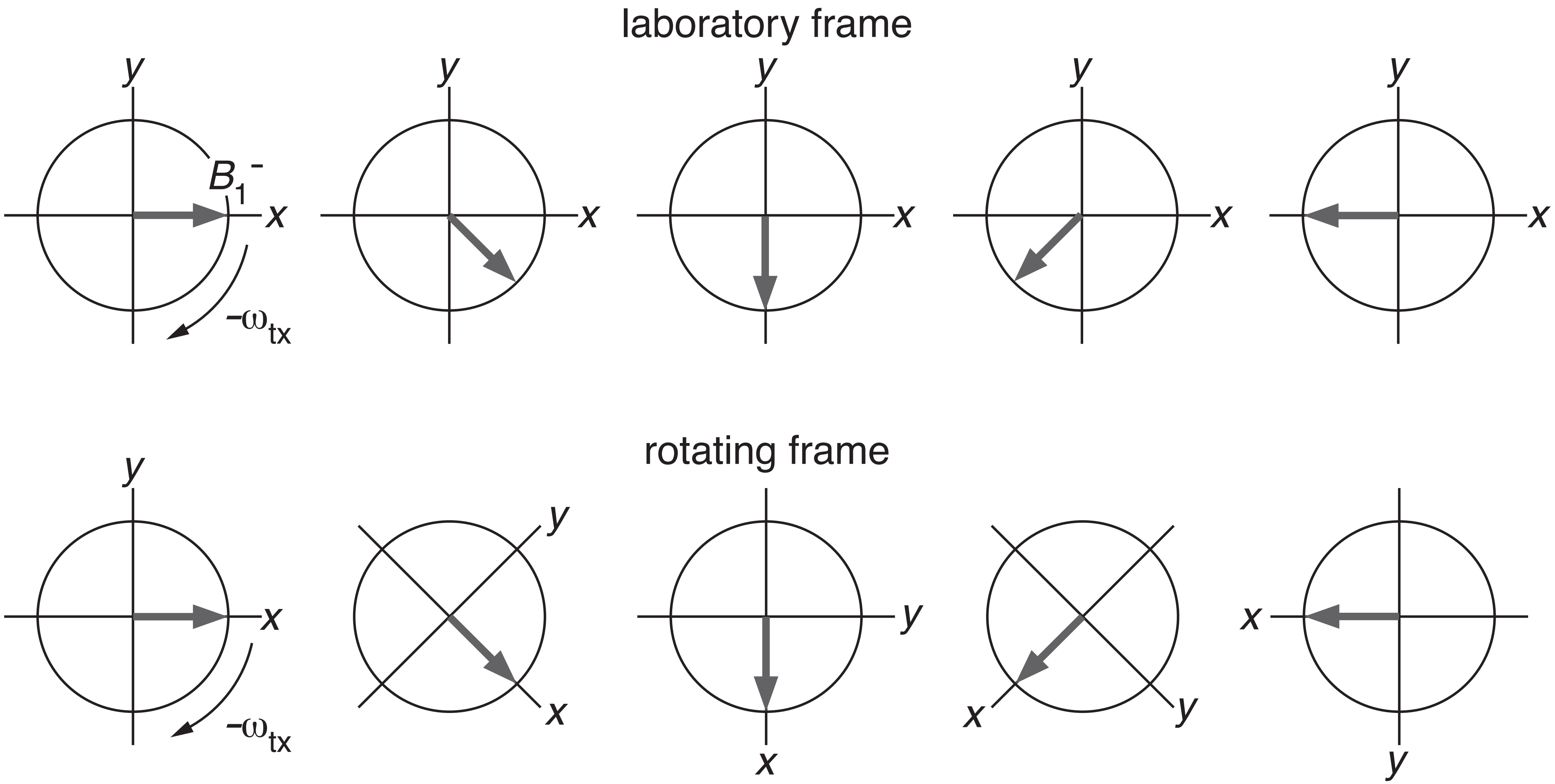
A child riding on a merry-go-round executes a complex motion as seen by a fixed observer.

(b)



If the observer stands on the merry-go-round the child appears to be executing a simple up–down motion.

The Rotating Frame



In a reference frame rotating at the Larmor frequency, transverse magnetisation appears static (here fixed on the x axis).

(Of course the precession has not really stopped, it is just that we are viewing it differently.)

The Rotating Frame

In order to render $\mathcal{H}$ time independent we use a change of representation. Starting with

$$\frac{d}{dt}\sigma = i\left[\mathcal{H},\sigma\right].$$

a change of representation goes as follows: given an operator Q we can associate it to another operator $\tilde{Q}$ where

$$\tilde{Q} = U(t)QU^{\dagger}(t) \quad (1.51)$$

where $U(t)$ is defined by the equation

$$\frac{d}{dt}U(t) = iAU(t)$$

with A a Hermitian operator which could be time dependent.

The Rotating Frame

Thus for $\tilde{\sigma}$ we have

$$\begin{aligned}\frac{d}{dt}\tilde{\sigma} &= \frac{d}{dt}U\sigma U^{\dagger}\\ &= \dot{U}\sigma U^{\dagger} + U\dot{\sigma}U^{\dagger} + U\sigma\dot{U}^{\dagger}\end{aligned}$$

and by substitution of $\dot{U}, \dot{\sigma}, \dot{U}^{\dagger}$

$$\frac{d}{dt}\tilde{\sigma} = iAU\sigma U^{\dagger} - U\left[\mathcal{H},\sigma\right]U^{\dagger} - iU\sigma U^{\dagger}A.$$

Since U is unitary it follows that

$$U\left[\mathcal{H},\sigma\right]U^{\dagger} = \left[U\mathcal{H}U^{\dagger}, U\sigma U^{\dagger}\right] = \left[\tilde{\mathcal{H}},\tilde{\sigma}\right]$$

and we obtain

$$\frac{d}{dt}\tilde{\sigma} = -i\left[\left(\tilde{\mathcal{H}} - A\right),\tilde{\sigma}\right]. \qquad (1.56)$$

In the new representation, defined by equation (1.51), the evolution of $\tilde{\sigma}$ is the same as if the system were subjected to an *effective Hamiltonian*

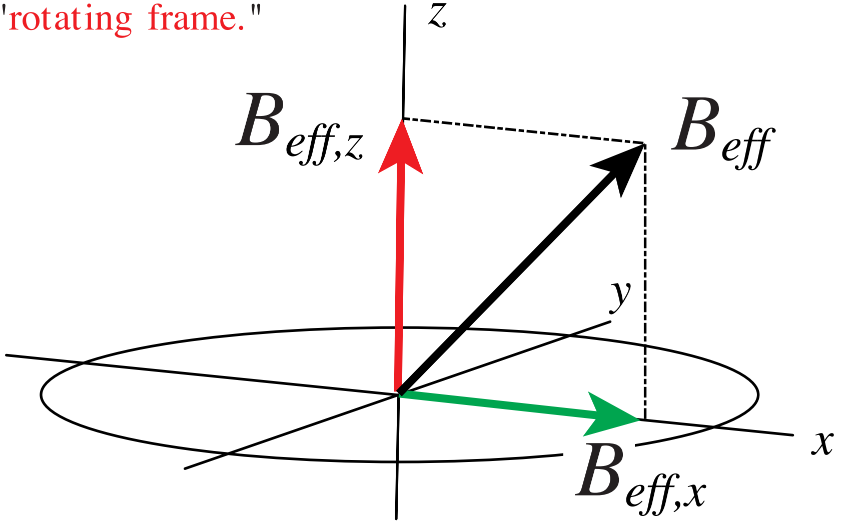
$$\mathcal{H}_{eff} = \tilde{\mathcal{H}} - A. \qquad (1.57)$$

The Rotating Frame

Returning to the problem we chose

$$A = \omega I_z$$

in equation (1.52) and we have $U = \exp(iAt) = \exp(i\omega I_z t)$. This change of representation corresponds to a rotation around z at a frequency $-\omega$, hence the name "rotating frame."



The time-dependent term in $\mathcal{H}$ can be written

$$\begin{aligned} I_x \cos\omega t + I_y \sin\omega t &= \exp(-i\omega I_z t) I_x \exp(i\omega I_z t) \\ &= U^\dagger(t) I_x U(t) \end{aligned}$$

The effective Hamiltonian in the rotating frame is therefore

$$\mathcal{H}_{eff} = (\omega_0 - \omega) I_z + \omega_1 U U^\dagger I_x U U^\dagger = (\omega_0 - \omega) I_z + \omega_1 I_x.$$

This Hamiltonian is time-independent. It is of the form of the Zeeman interaction with an effective field B_{eff} with components

$$B_z = -(\omega_0 - \omega)/\gamma \text{ and } B_x = B_1.$$

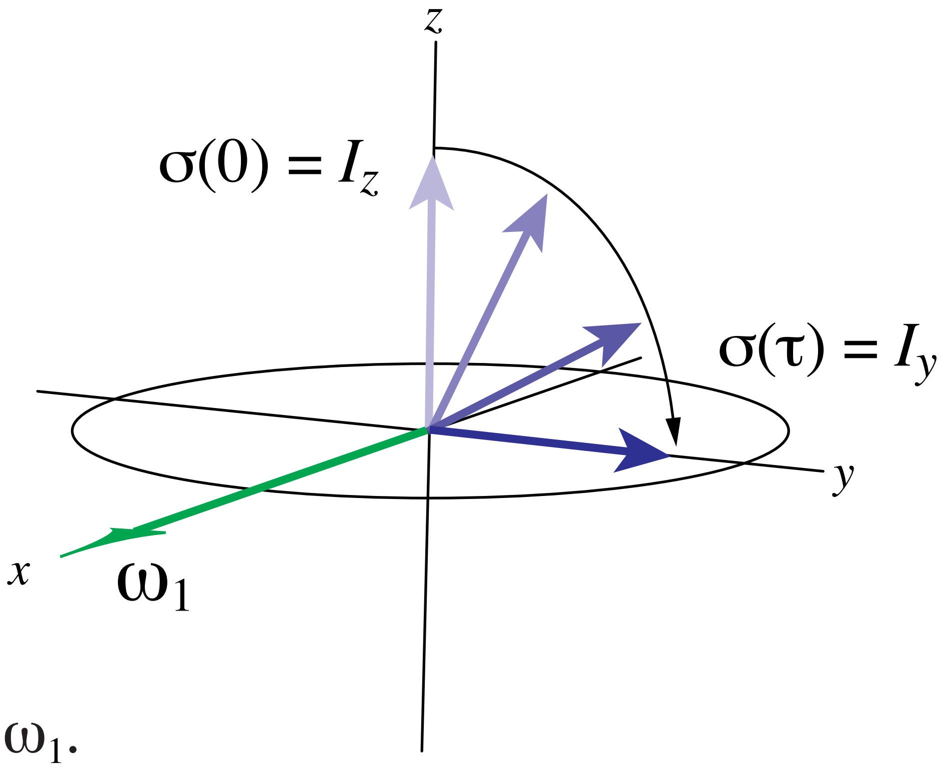
When $\omega_0 = \omega$ the effective field is purely transverse and the magnetization precesses around the x axis with a frequency ω_1 corresponding to the magnitude of the applied magnetic field. If the irradiation is applied for a time τ, such that $\omega_1 \tau = \pi/2$, I_z *will be converted into pure* I_y

The Rotating Frame: *Resonance*

This Hamiltonian is time-independent. It is of the form of the Zeeman interaction with an effective field B_{eff} with components

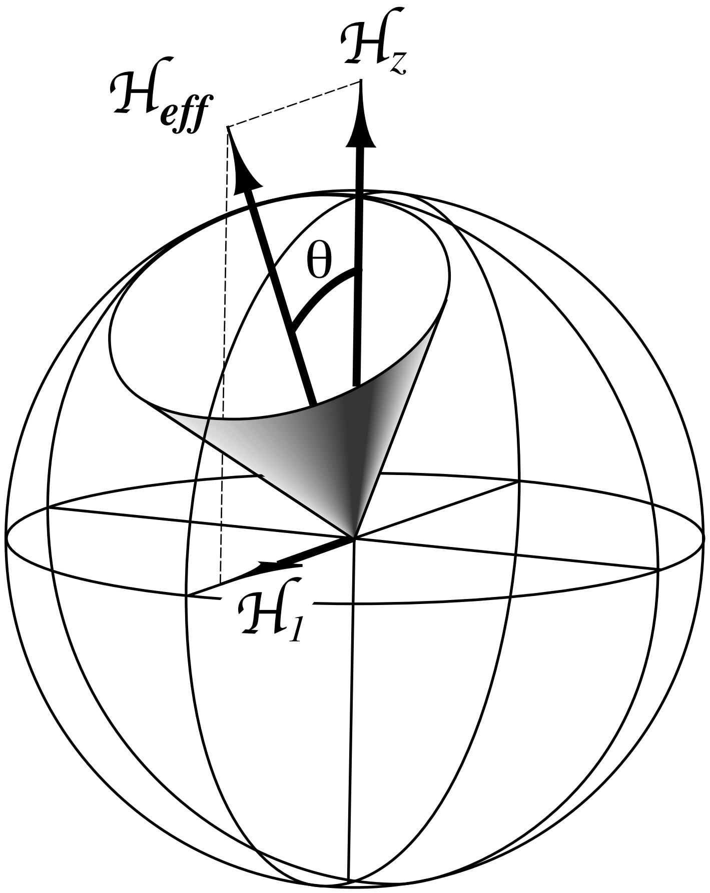
$$B_z = -(\omega_0 - \omega)/\gamma \text{ and } B_x = B_1.$$

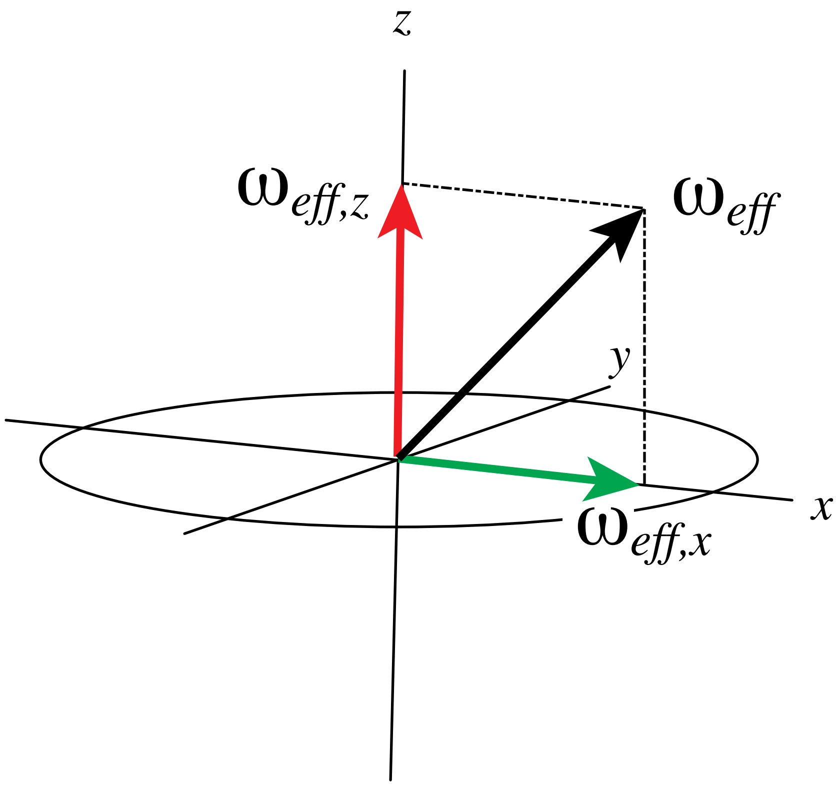
When $\omega_0 = \omega$ the effective field is purely transverse and the magnetization precesses around the *x* axis with a frequency ω_1 corresponding to the magnitude of the applied magnetic field. If the irradiation is applied for a time τ, such that $\omega_1\tau = \pi/2$, *I_z will be converted into pure I_y*



For any value of ω_1.

Radiofrequency Irradiation & Effective Field





$$\omega_{eff,z} = \omega_0 - \omega_{rf}$$

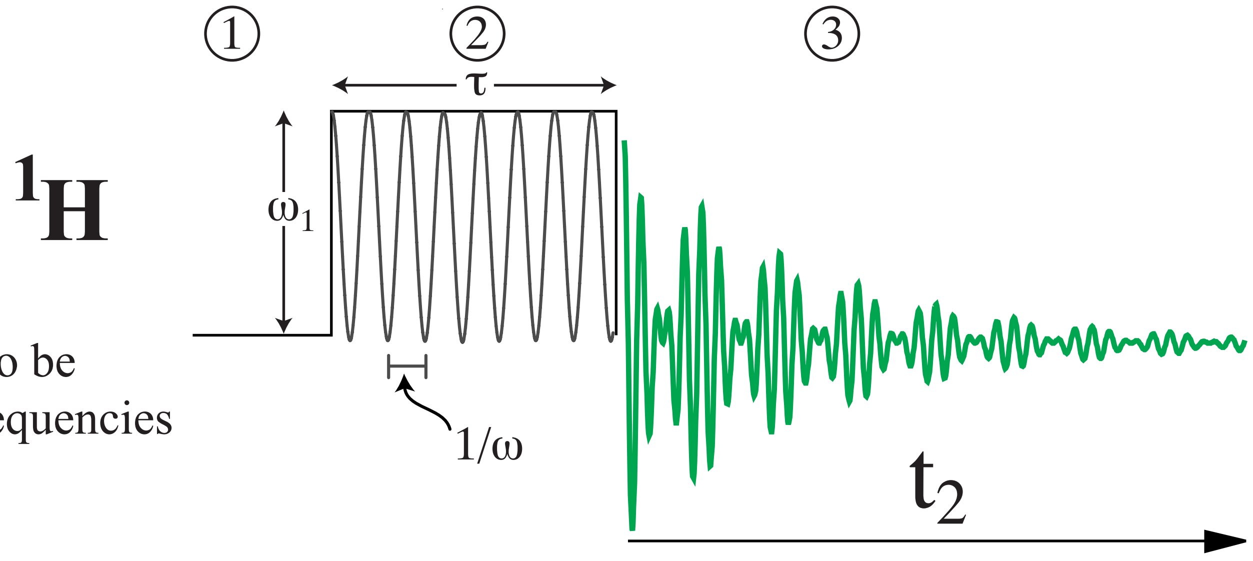
$$\omega_{eff,x} = \omega_1 = \gamma B_1$$

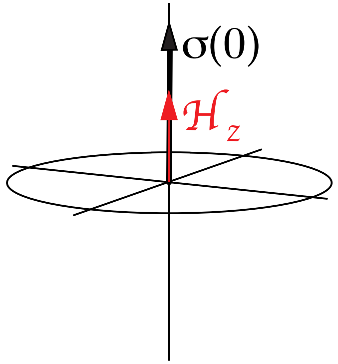
Pulsed FTNMR Spectroscopy

$\omega_1 = -\gamma B_1$

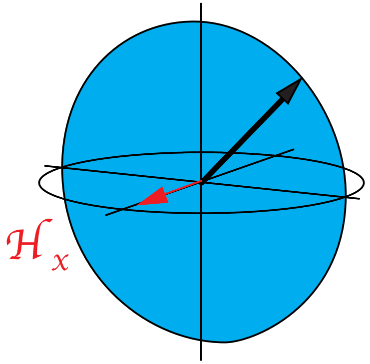
$\omega_1 \tau = \pi/2$

ω = carrier frequency,
chosen by the operator to be
near to the resonance frequencies

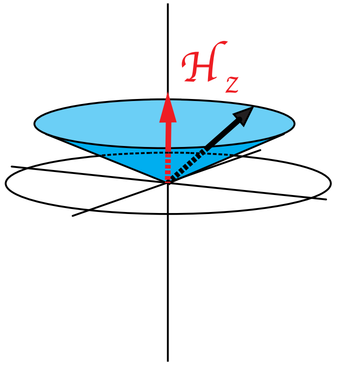




1. Equilibrium. The net magnetization is aligned along the direction of the main field (z-axis).

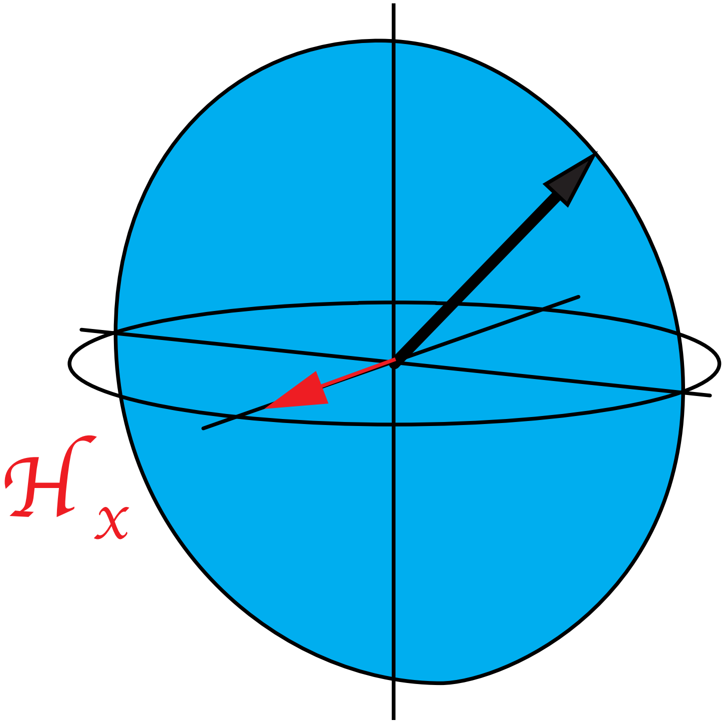


2. A field is applied in the transverse plane. The magnetization of the ensemble precesses around the field.



3. The field is removed leaving a net transverse component of the ensemble magnetization. This ***coherence*** then starts to precess around the main field.

Dances with Spins

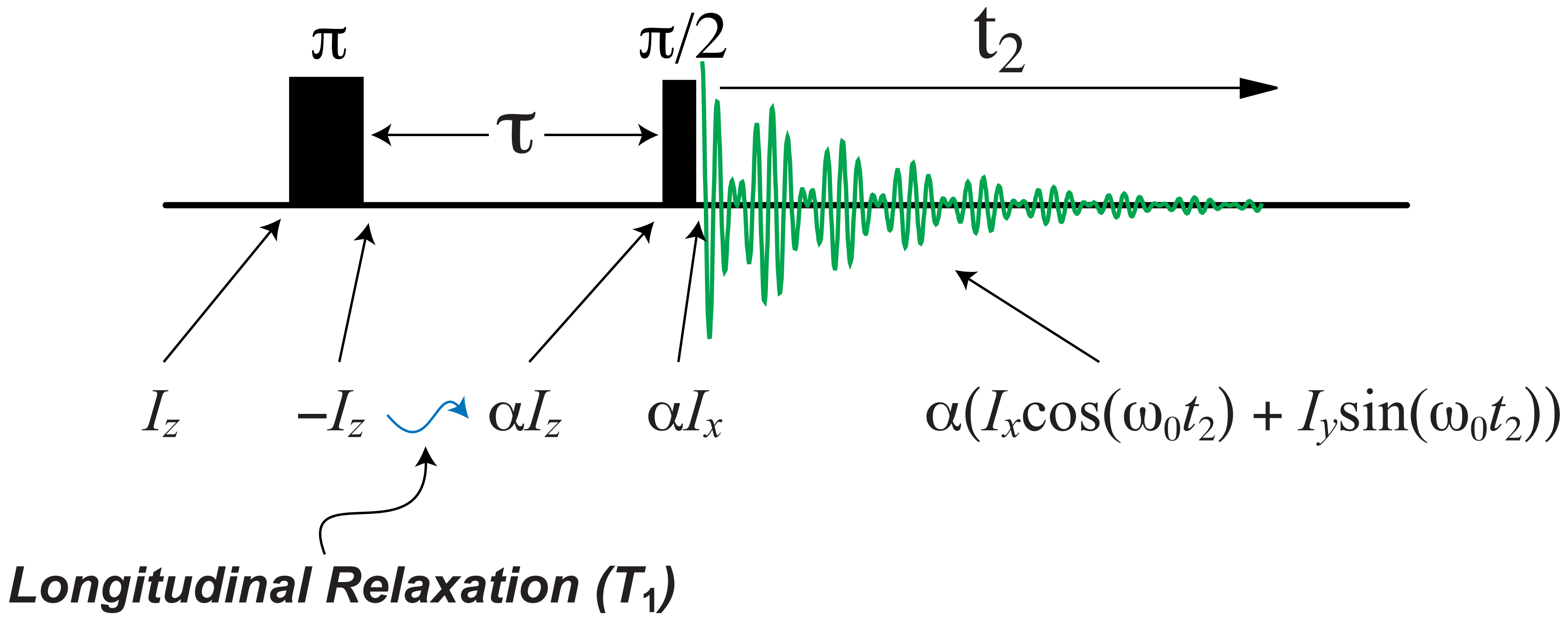


Spin Inversion: $\omega_1\tau = \pi$

(*size of signal? state of polarisation?*)

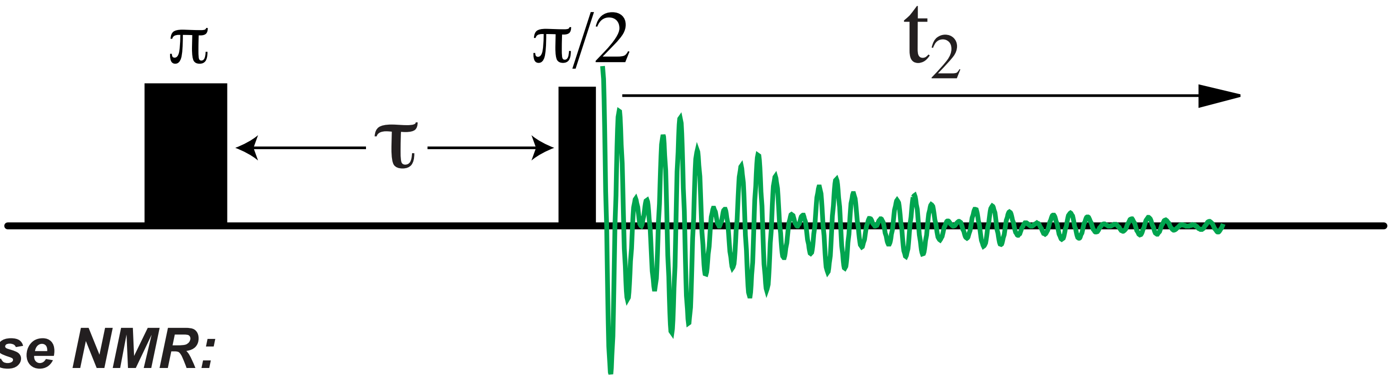
"Self-Induced Transparency" $\omega_1\tau = 2\pi$

Dances with Spins: Inversion-Recovery

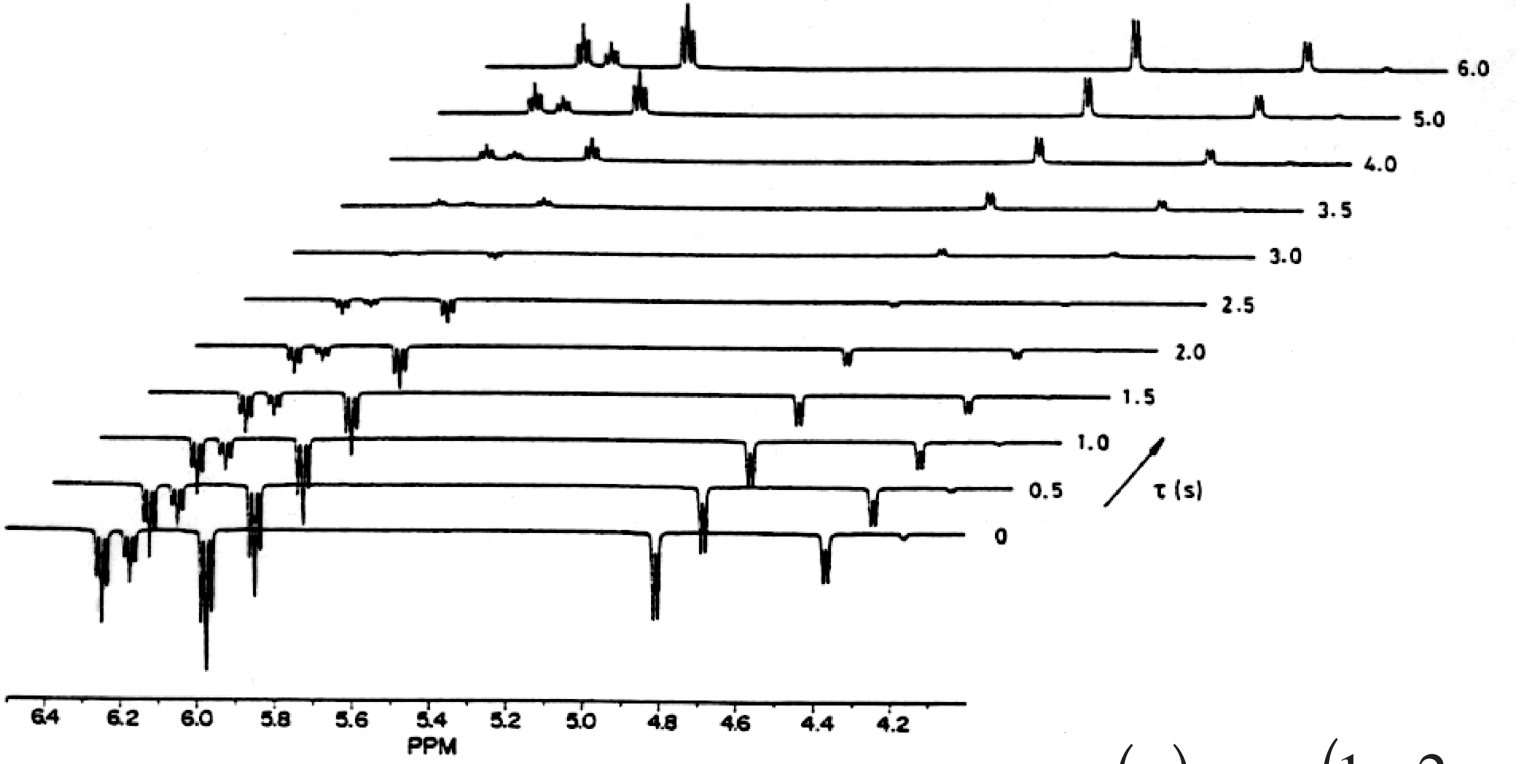


$$\alpha(\tau) = \alpha_0\left(1 - 2\exp(\tau/T_1)\right)$$

Dances with Spins: Inversion-Recovery



Multiple-Pulse NMR:
Measurement of Longitudinal Relaxation Rates (T_1)



$$\alpha(\tau) = \alpha_0\left(1 - 2\exp\left(\tau / T_1\right)\right)$$

Conclusions: Part II

- *The equation of motion of the density operator is a rotation around an axis defined by the Hamiltonian for the system, at a frequency given by the magnitude of the Hamiltonian.*

- The system can be perturbed from equilibrium by the application of weak resonant (radiofrequency) fields in the transverse plane.

- An on-resonance pulse induces a rotation perpendicular to the direction of the applied field in the rotating frame.

- *A “π/2 pulse” is induced by an on-resonant transverse field of duration* $\omega_1\tau = \pi/2$.

Conclusions: Part II

- *After a pulse, the transverse component of the density operator will oscillate around the z-axis (B_0) at the Larmor frequency.*
- *This oscillating magnetic moment will induce a current in a detection coil. This is the free induction decay.*
- *Population inversion (a 180° pulse) is achieved by an on-resonant transverse field of duration $\omega_1\tau = \pi$.*
- Signals can be acquired after multiple pulses and delays.
- The inversion-recovery pulse sequence allows measurement of T_1.

Homework

Learn the course material
(use the other resources when needed)

If it helps, review the lecture on the vector (classical)
model of NMR from Basic NMR
(available on this week's Moodle for ANMR)

(Don't Panic!)