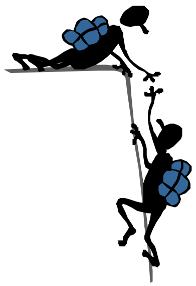
Lecture #7
NMR in Liouville Space



- Topics
  – Statistical Mixture of Quantum States
  – The Density Operator
  – NMR in Liouville Space
- Handouts and Reading assignments
  – van de Ven, section 1.10: pp 45-48.
  – Miller, Chapter 14, pp 335-353 (optional).

Problem Statement

- Previous lecture provided a rather clumsy treatment of an ensemble of spins.
- A system of N spins with wavefunctions $|\psi\rangle = c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$ $\left(P_\alpha = |c_\alpha|^2,\ P_\beta = |c_\beta|^2,\ P_\alpha + P_\beta = 1\right)$ could contain spins in many different states since $\angle c_1$ and $\angle c_2$ are arbitrary.

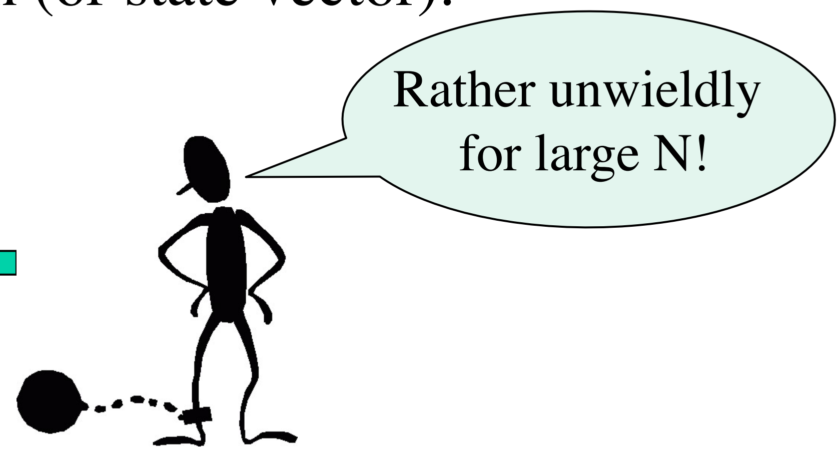
- In practice, the state of the system is almost never perfectly determined ($i.e.$ not all $|\psi_i\rangle$ precisely known).

- Question: How can we best incorporate the partial information we have about a system in order to make optimal predictions and calculations?

A Collection of Spins

- In a typical experiment, the number of nuclear spins, N, can be very large, e.g. 10^{20}.
- For independent spins, the complete quantum state is described by the wavefunction (or state vector):

$$|\psi\rangle = \sum_{n=1}^{N} a_n |\psi_n\rangle$$



- We rarely, if ever, know $|\psi\rangle$ precisely. Rather, we typically have only a statistical model for the state of the system.

Statistical Mixture of States

- Given a system such that the state is $|\psi_1\rangle$ with probability p_1 or $|\psi_2\rangle$ with probability p_2, etc. ($\sum p_i = 1$), then the system is said to consist of a statistical mixture of states.

- $|\psi_i\rangle$ s need not be orthogonal, but can be chosen to be normalized.

- Probabilities enter at two fundamentally different levels.
  - The system state vector is not perfectly well know, rather we only have a statistical model for being in a given state.
  - Even if the state vector *were* perfectly well known, the probabilistic predictions arising from the QM postulates regarding the measurement process still apply.

- A system described by a statistical mixture of states is *not* the same as a system whose state vector $|\psi\rangle$ is a linear superposition of states:

$$|\psi\rangle = \sum_i a_i |\psi_i\rangle$$

“Average State Vector”?

- Consider a system with state vector: $|\psi\rangle = \sum_i a_i |\psi_i\rangle$
  - Measurements of this system involve computing $\langle\psi|\hat{O}|\psi\rangle$ which contains not only terms such as $|a_1|^2$, $|a_2|^2$, … but also cross terms of the form $a_i a_j^*$ representing interference effects.
  - Such cross terms are very important! For example, in MR these are the terms which give rise to transverse magnetization.
- Let p_i be the probability of the system being in state $|\psi_i\rangle$. In this statistical mixture of states, measurements are of the form:

$$\sum_i p_i \langle\psi_i|\hat{O}|\psi_i\rangle \Longrightarrow \text{no } a_i a_j^* \text{ cross terms!}$$

- While there is <u>*no*</u> “average state vector”, it turns out there <u>*is*</u> an “average operator” which can adequately describe a statistical mixture of states.

“average operator” = density operator

Density Operator for a Pure State

- A system with a perfectly know state (*i.e.* all p_i=0 except one) is said to be in a <u>pure</u> <u>state</u>.
  - Consider a system in a pure state with normalized state vector

    $$|\psi(t)\rangle = \sum_i c_i(t)|u_i\rangle$$ where $\{|u_i\rangle\}$ form an orthonormal basis.
  - Time evolution: $\frac{\partial}{\partial t}|\psi(t)\rangle = -i\hat{H}(t)|\psi(t)\rangle$
  - Expectation of observable $\hat{A}$: $\langle\hat{A}\rangle = \langle\psi(t)|\hat{A}|\psi(t)\rangle = \sum_{i,j} c_i^*(t)c_j(t)A_{ij}$

    $A_{ij} = \langle u_i|\hat{A}|u_j\rangle$ (matrix elements of $\hat{A}$ in the $\{|u_i\rangle\}$ basis)

- Noting that $\langle u_j \underbrace{|\psi(t)\rangle\langle\psi(t)|}_{} u_i\rangle = c_i^*(t)c_j(t)$

  density operator: $\hat{\rho}_\psi(t) = |\psi(t)\rangle\langle\psi(t)|$

Density Operator for a Pure State

- We now need to:

  1) show $\langle \hat{A} \rangle$ can be computed from $\hat{\rho}_\psi(t)$.

  an arbitrary observable

  2) find the time evolution of $\hat{\rho}_\psi(t)$.

- Using the expressions for A_{ij} and $c_i^*(t)c_j(t)$,

$$\left\langle \hat{A} \right\rangle(t) = \sum_{i,j} \left\langle u_j \middle| \hat{\rho}_\psi(t) \middle| u_i \right\rangle \left\langle u_i \middle| \hat{A} \middle| u_j \right\rangle = \sum_j \left\langle u_j \middle| \hat{\rho}_\psi(t)\, \hat{A} \middle| u_j \right\rangle = \underline{\underline{\mathrm{Tr}\left\{ \hat{\rho}_\psi(t) \hat{A} \right\}}}$$

- Time evolution:

$$\frac{\partial}{\partial t}\hat{\rho}_\psi(t) = \frac{\partial}{\partial t}\Big[|\psi(t)\rangle\langle\psi(t)| \Big] = \overbrace{\frac{\partial}{\partial t}|\psi(t)\rangle}^{-i\hat{H}|\psi\rangle}\langle\psi(t)| + |\psi(t)\rangle \overbrace{\frac{\partial}{\partial t}\langle\psi(t)|}^{i\langle\psi|\hat{H}}$$

(remember $\hat{H}$ is Hermitian)

$$= -i\Big[\hat{H}, \overbrace{|\psi(t)\rangle\langle\psi(t)|}^{\hat{\rho}_\psi(t)} \Big]$$

$\therefore$ in superoperator notation : $\underline{\underline{\dfrac{\partial}{\partial t}\hat{\rho}_\psi = -i\hat{\hat{H}}\hat{\rho}_\psi}}$

Density Operator: Statistical Mixture

- Consider a system consisting of a statistical mixture of states $|\psi_i\rangle$ with associated probabilities p_i.
- Let a_i be an eigenvalue of $\hat{A}$ with associated eigenket $|u_i\rangle$.

… if the state vector were $|\psi_n\rangle$: $\mathcal{P}_n(a_i) = \langle\psi_n|\underbrace{\hat{P}_i}_{|u_i\rangle\langle u_i|}|\psi_n\rangle = \mathrm{Tr}\{\underbrace{\hat{\rho}_\mathrm{n}}_{|\psi_n\rangle\langle\psi_n|}\hat{P}_i\}$

… in general:

$$\mathcal{P}(a_i) = \sum_n p_n \mathcal{P}_n(a_i)$$

$$= \sum_n p_n \mathrm{Tr}\{\hat{\rho}_n \hat{P}_i\} = \mathrm{Tr}\left\{\sum_n p_n \hat{\rho}_n \hat{P}_i\right\} = \mathrm{Tr}\{\hat{\rho}\hat{P}_i\}$$

where $\hat{\rho} = \sum_n p_n \hat{\rho}_n$ is, by definition, the density operator for the system.

- It is then easy to show that:

$$\overset{\text{ensemble average}}{\overline{\langle \hat{A} \rangle}} = \mathrm{Tr}\{\hat{\rho}\hat{A}\} \quad \text{and} \quad \boxed{\frac{\partial}{\partial t}\hat{\rho} = -i\hat{\hat{H}}\hat{\rho} \quad \underline{\text{(Liouville-von Neuman equation)}}}$$

Spin Density Operator:
Spin-Lattice Disconnect

- Complete QM description of a molecule involves lots of terms in the Hamiltonian (nuclear spin, molecular motion, electron-nucleus interactions, etc).

$$\hat{H} = \underbrace{\hat{H}_l}_{\text{lattice}} + \underbrace{\hat{H}_s}_{\text{spin}} + \underbrace{\hat{H}_i}_{\text{interaction term}}$$

- Assuming weak interaction between nuclear spin and the lattice:

$$\hat{H} \approx \hat{H}_l + \hat{H}_s$$

(We'll revisit this when discussing relaxation theory)

- It then suffices to solve the Liouville equations independently.

$$\frac{\partial}{\partial t}\hat{\rho}_l = -i\hat{\hat{H}}_l\hat{\rho}_l$$

$\hat{\rho}_l$: lattice density operator

$$\frac{\partial}{\partial t}\hat{\sigma} = -i\hat{\hat{H}}_s\hat{\sigma}$$

$\hat{\sigma}$: conventional notation for spin density operator

We'll just solve this one.

- For any spin operator: $\overline{\langle \hat{A}_s \rangle} = \mathrm{Tr}(\hat{\sigma}\hat{A}_s)$

Hilbert Space vs Liouville Space

QM property	Hilbert Space	Liouville Space
System:	$\lvert\psi(t)\rangle$ (metric = inner product)	$\hat{\sigma}(t)$ (metric = trace)
Time evolution:	$\frac{\partial}{\partial t}\lvert\psi\rangle = -i\hat{H}\lvert\psi\rangle$	$\frac{\partial}{\partial t}\hat{\sigma} = -i\hat{\hat{H}}\hat{\sigma}$
Time independent $\hat{H}$:	$\lvert\psi(t)\rangle = \underbrace{e^{-i\hat{H}t}}_{\text{rotation in ket space}}\lvert\psi(0)\rangle$	$\hat{\sigma}(t) = \underbrace{e^{-i\hat{\hat{H}}t}}_{\text{rotation in operator space}}\hat{\sigma}(0)$
Observables: - pure state	$\langle\hat{A}\rangle = \langle\psi\lvert\hat{A}\rvert\psi\rangle$	$\langle\hat{A}\rangle = \mathrm{Tr}\{\hat{\sigma}_\psi\hat{A}\}$
- statistical ensemble	computable but ugly	$\overline{\langle\hat{A}\rangle} = \mathrm{Tr}\{\hat{\sigma}\hat{A}\}$

Observations about $\hat{\sigma}$, $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$

- Let $\hat{\sigma} = \sum_n b_n \hat{B}_n$ where $\hat{B}_n$ are an orthonormal set of Hermitian basis operators, *i.e.* $\left(\hat{B}_n \,|\, \hat{B}_m\right) = \mathrm{Tr}\left(\hat{B}_n^\dagger \hat{B}_m\right) = \mathrm{Tr}\left(\hat{B}_n \hat{B}_m\right) = \delta_{nm}$.

$$\overline{\left\langle \hat{B}_n \right\rangle} = \mathrm{Tr}\left(\hat{\sigma}\hat{B}_n\right) = \sum_m b_m \mathrm{Tr}\left(\hat{B}_m \hat{B}_n\right) = b_n$$

$$\therefore \hat{\sigma} = \sum_n \overline{\left\langle \hat{B}_n \right\rangle} \hat{B}_n$$

Coefficients of the expansion are the ensemble averages of the expected values of the respective operators!

- $$\left.\begin{aligned} \mathrm{Tr}\left(\hat{I}_p \hat{I}_q\right) &= \tfrac{1}{4}\delta_{pq} \\ \mathrm{Tr}\left(\hat{I}_p \hat{E}\right) &= 0 \end{aligned}\right\} \text{ for } p,q \in \{x,y,z\}$$

$\left\{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\right\}$ form an orthogonal Hermitian basis set.

- Hence, in any expansion of $\hat{\sigma}$ in terms of $\left\{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\right\}$, the expansion coefficients will be directly proportional to the expected values of the respective spin operators (would be equal if operators were normalized).

To what physical quantity does $\overline{\left\langle \hat{I}_x \right\rangle}$ correspond?

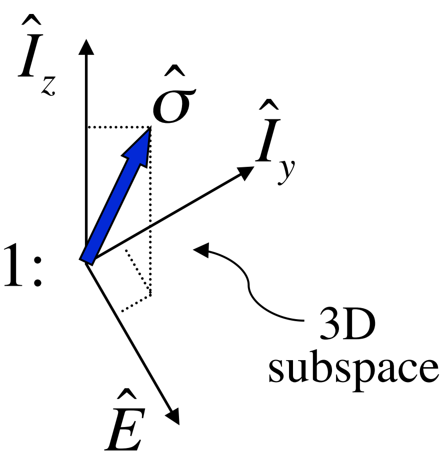
Geometric Picture

- $\hat{\sigma}$ is a "vector" in Liouville space (also called "operator" or "coherence" space).

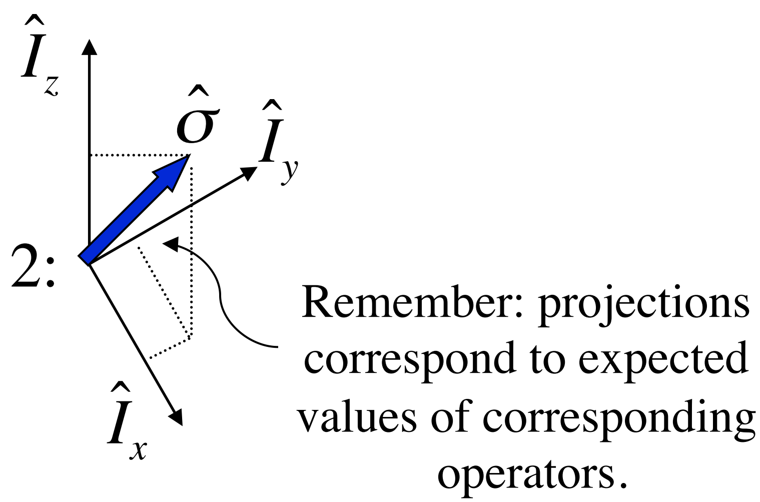
$$\boxed{\text{Key idea: } \hat{\sigma} \text{ rotates around in coherence space.}}$$

- Consider $\left\{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\right\}$ basis:

Example 1:



Example 2:



Thermal Equilibrium Spin Density Operator

eigenkets of $\hat{H}$

- Following the Hilbert Space formulation, $|\psi(0)\rangle = \sum_i c_i e^{-i\phi_i} |u_i\rangle$, the spin density matrix has elements:

$$\sigma_{ij}(0) = \overline{c_i c_j e^{-i(\phi_i - \phi_j)}} = \overline{c_i^2}\delta_{ij} = P_i \delta_{ij}$$

Kronecker delta function

In general: $\underline{\sigma} = \begin{pmatrix} P_1 & C_{1,2} & \cdots & C_{1,n} \\ C_{2,1} & P_2 & \ddots & \vdots \\ \vdots & \ddots & \ddots & C_{n-1,n} \\ C_{n,1} & \cdots & C_{n,n-1} & P_n \end{pmatrix}$

Off-diagonal elements called "coherences" (= 0 at thermal equilibrium).

Diagonal elements called "populations"

- Using the Boltzmann distribution one can verify:

$$\hat{\sigma}(0) = \tfrac{1}{Z} e^{-\hbar \hat{H}_0 / kT} \quad \text{where} \quad Z = \mathrm{Tr}(e^{-\hbar \hat{H}_0 / kT}).$$

remember $\hat{H}$ defined as $E/\hbar$

- As before, using the high temperature approximation:

$$\boxed{\hat{\sigma}(0) \approx \tfrac{1}{2}(\hat{E} - \tfrac{\hbar}{kT}\hat{H}_0) \quad \text{(spin 1/2 particles)}}$$

Solving the Liouville-von Neuman Eqn

- Let $\hat{\sigma}$ be the spin density operator for a system consisting of a statistical ensemble of states. The time evolution of $\hat{\sigma}$ is given by:

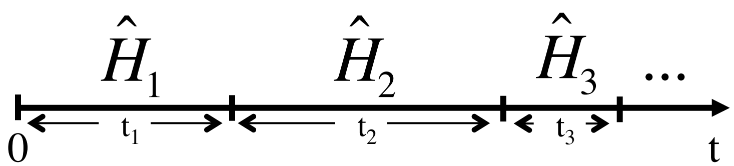
$$\frac{\partial}{\partial t}\hat{\sigma}(t) = -i\hat{\hat{H}}(t)\hat{\sigma}(t).$$

- Case 1: $\hat{H}$ independent of time.

$$\text{Solution: } \hat{\sigma}(t) = e^{-i\hat{\hat{H}}t}\hat{\sigma}(0) = e^{-i\hat{H}t}\hat{\sigma}(0)e^{i\hat{H}t}$$

(superoperator notation) (notation used in most texts)

- Case 2: Piecewise constant:



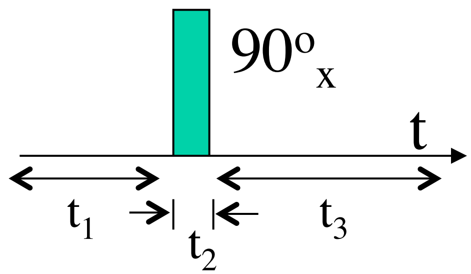
$$\text{Solution: } \hat{\sigma}(0) \xrightarrow{\hat{H}_1 t_1} \overbrace{e^{-i\hat{H}_1 t_1}\hat{\sigma}(0)e^{i\hat{H}_1 t_1}}^{\hat{\sigma}(t_1)} \xrightarrow{\hat{H}_2 t_2} \overbrace{e^{-i\hat{H}_2 t_2}e^{-i\hat{H}_1 t_1}\hat{\sigma}(0)e^{i\hat{H}_1 t_1}e^{i\hat{H}_2 t_2}}^{\hat{\sigma}(t_1 + t_2)} \quad \cdots$$

denotes "evolves under" $\hat{H}_1 t_1$

Numerical simulations most often use the matrix version of this formulation.

A Simple NMR Experiment

- Consider the following experiment:

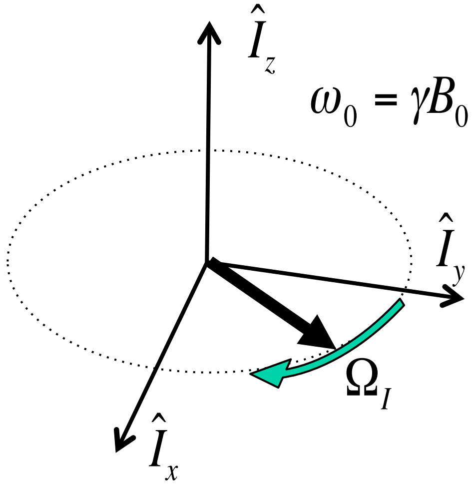


- Ignoring relaxation, what are $\hat{\sigma}(t)$, $M_x(t)$, $M_y(t)$, and M_z(t) for the time intervals t_1, t_2, and t_3?

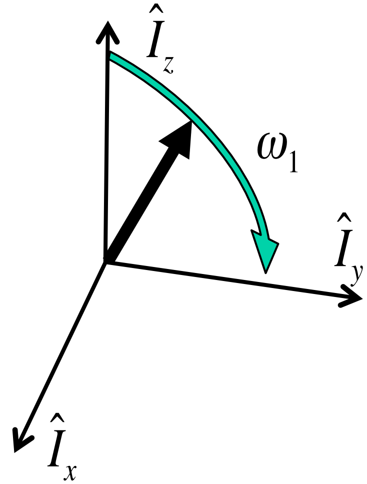
Sign Conventions

- Many MRS texts define $\omega_0 \equiv -\gamma B_0$.
- For this class, $\omega_0 \equiv \gamma B_0$ (consistent with most MRI texts and Bloch!).
- Leads to the following sign conventions...

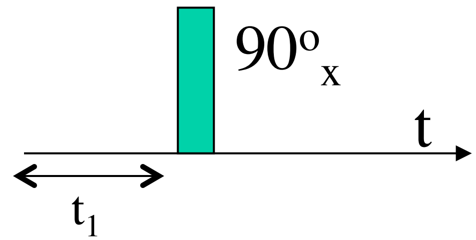
Chemical shift



RF Excitation



NMR in Liouville Space:



- At thermal equilibrium, $\hat{\sigma}(0) = \frac{1}{2}(\hat{E} + \frac{\hbar\gamma B_0}{kT}\hat{I}_z)$. (note: $\hat{H}_0 = -\gamma B_0 \hat{I}_z$)

  - Since $\hat{E}$ is invariant under rotations and orthogonal to $\hat{I}_x, \hat{I}_y$, and $\hat{I}_z$ (Why?), we can ignore this term (*i.e.* let's just work in a 3D subspace):

$$\hat{\sigma}_0 = C\hat{I}_z \quad \text{where} \quad C = \frac{\hbar\gamma B_0}{2kT} \quad \Longrightarrow \quad \text{matrix form: } \underline{\sigma}_0 = C\begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$$

- Question: What are the equilibrium values of M_x, M_y, and M_z?

$$\hat{\sigma}_0 = 0 \cdot \hat{I}_x + 0 \cdot \hat{I}_y + C\hat{I}_z \quad \Longrightarrow \quad M_x = M_y = 0, \quad M_z = \rho\gamma\hbar\overline{\langle \hat{I}_z \rangle}$$

$$= \rho\gamma\hbar\frac{1}{2}C = \rho\frac{\gamma^2\hbar^2 B_0}{4kT}$$

spins/volume

normalization value for $\mathrm{Tr}(\hat{I}_z^2)$

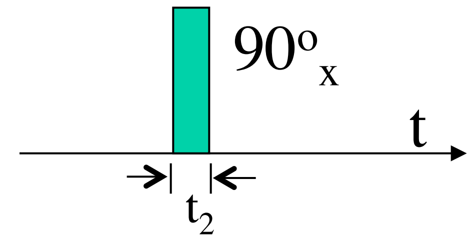
- Time evolution:

$$\hat{\sigma}(t) = e^{-i\hat{\hat{H}}t}\hat{\sigma}(0) = \underline{Ce^{i\gamma B_0\hat{\hat{I}}_z t}}\hat{I}_z = C\hat{I}_z \quad \Longrightarrow \quad \begin{matrix} M_z = \rho\frac{\gamma^2\hbar^2 B_0}{4kT} = M_0 \\ M_x = M_y = 0 \end{matrix} \quad \text{for } t_0 < t < t_1$$

time independent

Rotation about $\hat{I}_z$ axis!

NMR in Liouville Space:



- RF excitation: $\hat{H}(t) = -\gamma B_0 \hat{I}_z - \gamma B_1(\hat{I}_x \cos\omega t - \hat{I}_y \sin\omega t)$
  - $\hat{H}$ is now time-varying. Solve by switching to the rotating frame (hereafter we'll do almost everything in the rotating frame).

$$\hat{H}' = e^{-i\omega t\hat{\hat{I}}_z}\hat{H} \quad \text{and} \quad \hat{\sigma}' = e^{-i\omega t\hat{\hat{I}}_z}\hat{\sigma}$$

$$\Rightarrow \frac{\partial}{\partial t}\hat{\sigma}' = -i\hat{\hat{H}}_{eff}\hat{\sigma}' \text{ where } \hat{H}_{eff} = -(\omega_0 - \omega)\hat{I}_z - \omega_1\hat{I}_x$$

- On resonance: $\hat{\sigma}'(t) = Ce^{-i\hat{\hat{H}}_{eff}t}\hat{I}_z = \underline{Ce^{i\omega_1 t\hat{\hat{I}}_x}}\hat{I}_z = C\left(\hat{I}_z\cos(\omega_1 t) + \hat{I}_y\sin(\omega_1 t)\right)$

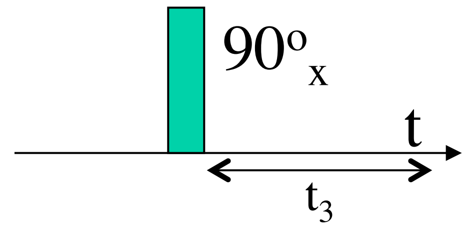
rotation about $\hat{I}_x$ axis

Uses fact that spin operators commute cylically

- Following a 90° pulse: $\hat{\sigma}'(t) = C\hat{I}_y$

$$\Rightarrow \begin{matrix} M_y = M_0 \\ M_z = M_x = 0 \end{matrix} \quad \text{for } t = t_1 + t_2$$

NMR in Liouville Space:



- Let's consider the case of being slightly off-resonance (on-resonance case is trivial)…

- Free precession (RF turned off): $\hat{H}' = -(\omega_0 - \omega)\hat{I}_z = -\Omega\hat{I}_z$

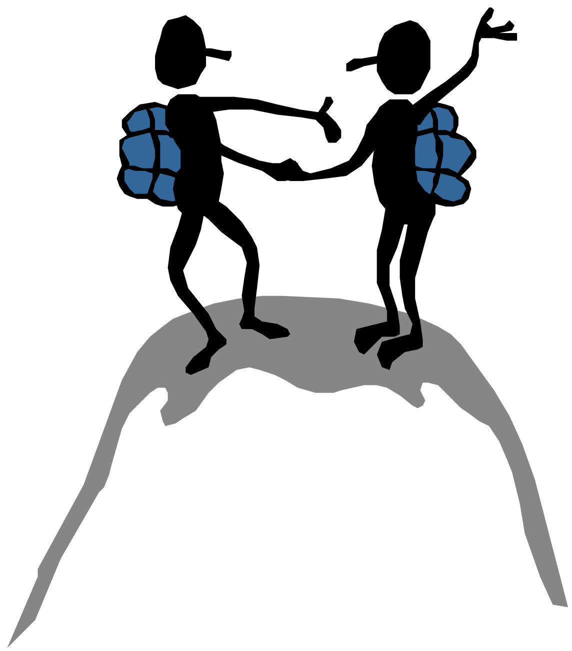
$$\hat{\sigma}'(t) = \underbrace{Ce^{i\Omega t\hat{\hat{I}}_z}}_{\text{rotation about } \hat{I}_z \text{ axis}}\hat{I}_y \quad = C\left(\hat{I}_y\cos(\Omega t) + \hat{I}_x\sin(\Omega t)\right)$$

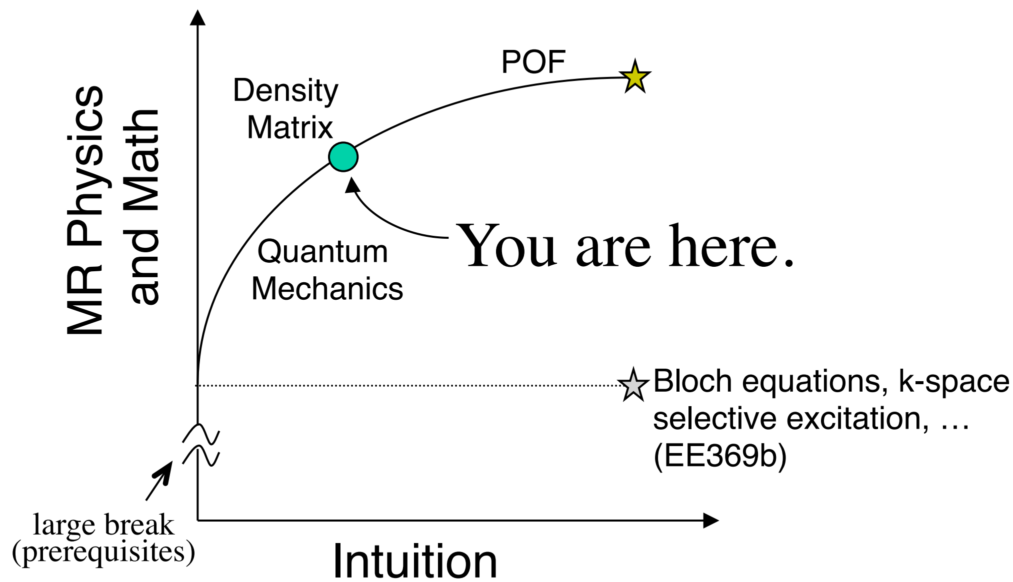
$\Rightarrow$ $\overline{\langle \hat{I}_x \rangle} = \frac{1}{2}C\sin(\Omega t), \quad \overline{\langle \hat{I}_y \rangle} = \frac{1}{2}C\cos(\Omega t), \quad \overline{\langle \hat{I}_z \rangle} = 0$

$\Rightarrow$ $M_z = 0, \; M_x = M_0\sin(\Omega t), \; M_y = M_0\cos(\Omega t) \;$ for $\; t > t_1 + t_2$

$\boxed{\text{Larmor precession!}}$

Congratulations!





All the hard stuff is over.
(well almost)

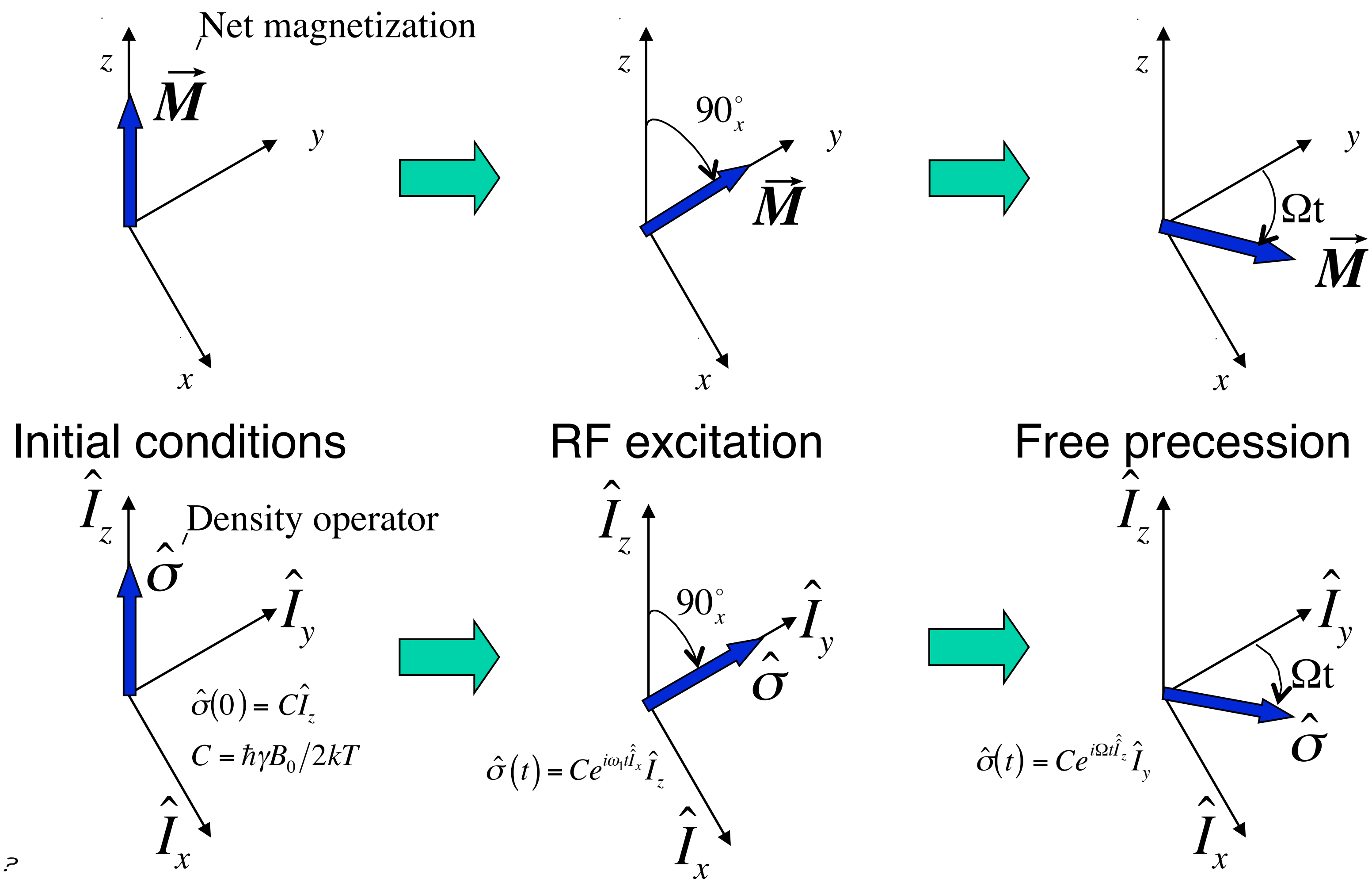
A Comparison

Given: Ensemble of independent spins slightly off resonance ($\omega_0 - \omega = \Omega$)

Classical Model-physical space

(Rotating frame of reference)

QM Model-Liouville space



For independent spin 1/2 particles, Liouville space is 4D.
What happened to the fourth dimension?

Next lecture: Chemical shift and Coupling