

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).

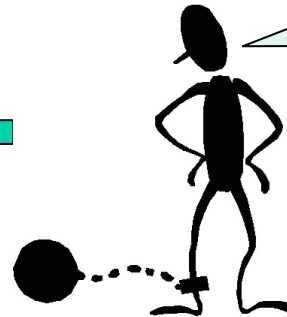
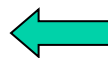
Problem Statement

- Previous lecture provided a rather clumsy treatment of an ensemble of spins.
- A system of N spins with wavefunctions $|\psi\rangle = c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$
($P_\alpha = |c_\alpha|^2$, $P_\beta = |c_\beta|^2$, $P_\alpha + P_\beta = 1$) 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):

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



Rather unwieldy
for large N !

- 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 known, 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 $|a_1|^2, |a_2|^2, \dots$ 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 no “average state vector”, it turns out there is 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 pure state.
 - 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 $\langle u_j | \psi(t) \rangle \langle \psi(t) | u_i \rangle = c_i^*(t) c_j(t)$

$$\underbrace{\hspace{10em}}_{\text{density operator: } \hat{\rho}_\psi(t) = |\psi(t)\rangle \langle \psi(t)|}$$

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 $c_i^*(t)c_j(t)$,

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

- Time evolution:

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_\psi(t) &= \frac{\partial}{\partial t} [|\psi(t)\rangle \langle \psi(t)|] = \cancel{\frac{\partial}{\partial t} |\psi(t)\rangle} \langle \psi(t)| + |\psi(t)\rangle \cancel{\frac{\partial}{\partial t} \langle \psi(t)|} \\ &= -i\hat{H}|\psi\rangle \langle \psi| + |\psi\rangle \langle \psi| i\hat{H} \\ &= -i[\hat{H}, \hat{\rho}_\psi(t)] \end{aligned} \quad \text{(remember } \hat{H} \text{ is Hermitian)}$$

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

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 $|\psi_n\rangle$: $\mathcal{P}_n(a_i) = \langle \psi_n | \hat{P}_i | \psi_n \rangle = \text{Tr} \left\{ \hat{\rho}_n \hat{P}_i \right\}$

$$\begin{array}{ccc} & |u_i\rangle\langle u_i| & |\psi_n\rangle\langle\psi_n| \\ & \swarrow & \swarrow \end{array}$$

... in general: $\mathcal{P}(a_i) = \sum_n p_n \mathcal{P}_n(a_i)$

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

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:

ensemble average

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

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).

$$\hat{H} = \hat{H}_l + \hat{H}_s + \hat{H}_i$$

lattice
spin
interaction term

- Assuming weak interaction between nuclear spin and the lattice:

$$\hat{H} \approx \hat{H}_l + \hat{H}_s \quad (\text{We'll revisit this when discussing relaxation theory})$$

- It then suffices to solve the Liouville equations independently.

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

lattice density operator

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

conventional notation for spin density operator

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

We'll just solve this one.

Hilbert Space vs Liouville Space

QM property

Hilbert Space

Liouville Space

System:

$$|\psi(t)\rangle \quad (\text{metric} = \text{inner product})$$

$$\hat{\sigma}(t) \quad (\text{metric} = \text{trace})$$

Time evolution:

$$\frac{\partial}{\partial t} |\psi\rangle = -i\hat{H}|\psi\rangle$$

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

Time independent \hat{H} :

$$|\psi(t)\rangle = \underbrace{e^{-i\hat{H}t}}_{\text{rotation in ket space}} |\psi(0)\rangle$$

$$\hat{\sigma}(t) = \underbrace{e^{-i\hat{H}t}}_{\text{rotation in operator space}} \hat{\sigma}(0)$$

Observables:
- pure state

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle$$

$$\langle \hat{A} \rangle = \text{Tr}\{\hat{\sigma}_\psi \hat{A}\}$$

- statistical ensemble

computable
but ugly

$$\overline{\langle \hat{A} \rangle} = \text{Tr}\{\hat{\sigma} \hat{A}\}$$

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.* $(\hat{B}_n | \hat{B}_m) = \text{Tr}(\hat{B}_n^\dagger \hat{B}_m) = \text{Tr}(\hat{B}_n \hat{B}_m) = \delta_{nm}$.

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

$\therefore \hat{\sigma} = \sum_n \overline{\langle \hat{B}_n \rangle} \hat{B}_n$ \rightarrow Coefficients of the expansion are the ensemble averages of the expected values of the respective operators!

- $\left. \begin{array}{l} \text{Tr}(\hat{I}_p \hat{I}_q) = \frac{1}{4} \delta_{pq} \\ \text{Tr}(\hat{I}_p \hat{E}) = 0 \end{array} \right\}$ for $p, q \in \{x, y, z\}$ \rightarrow $\{\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z\}$ form an orthogonal Hermitian basis set.

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



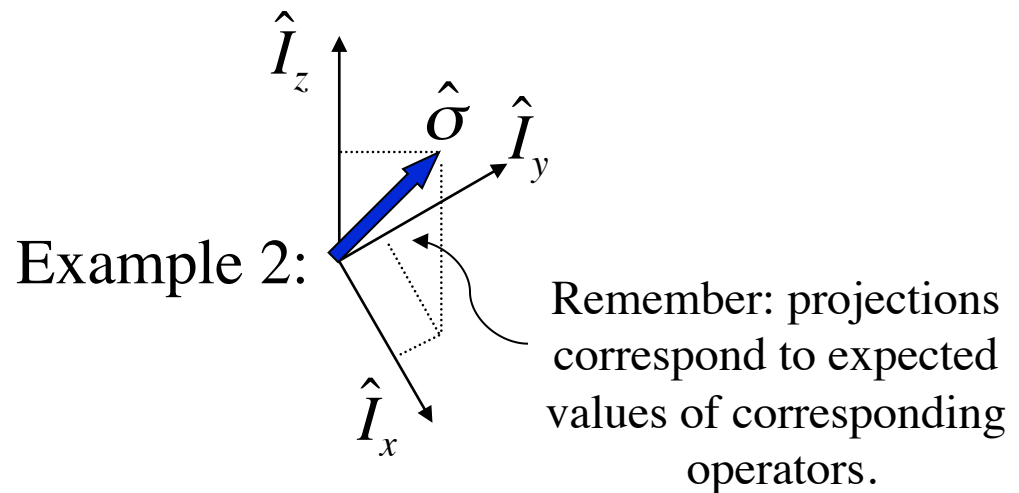
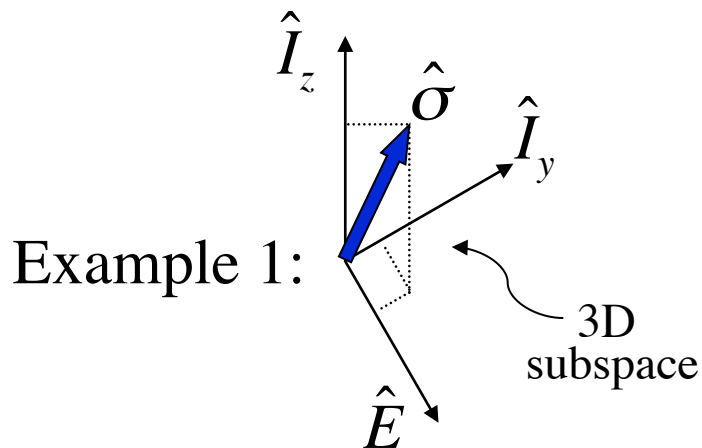
To what physical quantity does $\overline{\langle \hat{I}_x \rangle}$ correspond?

Geometric Picture

- $\hat{\mathcal{O}}$ is a “vector” in Liouville space (also called “operator” or “coherence” space).

Key idea: $\hat{\mathcal{O}}$ rotates around in coherence space.

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



Thermal Equilibrium Spin Density Operator

- 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:

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

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:

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

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

- As before, using the high temperature approximation:

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

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:

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

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

Solution: $\hat{\sigma}(t) = e^{-i\hat{H}t} \hat{\sigma}(0) = e^{-i\hat{H}t} \hat{\sigma}(0) e^{i\hat{H}t}$
(superoperator notation) (notation used in most texts)

- Case 2: Piecewise constant:

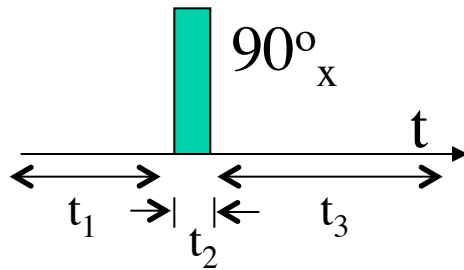
Solution: $\hat{\sigma}(0) \xrightarrow{\hat{H}_1 t_1} e^{-i\hat{H}_1 t_1} \hat{\sigma}(0) e^{i\hat{H}_1 t_1} \xrightarrow{\hat{H}_2 t_2} e^{-i\hat{H}_2 t_2} e^{-i\hat{H}_1 t_1} \hat{\sigma}(0) e^{i\hat{H}_1 t_1} e^{i\hat{H}_2 t_2} \dots$

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

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

A Simple NMR Experiment

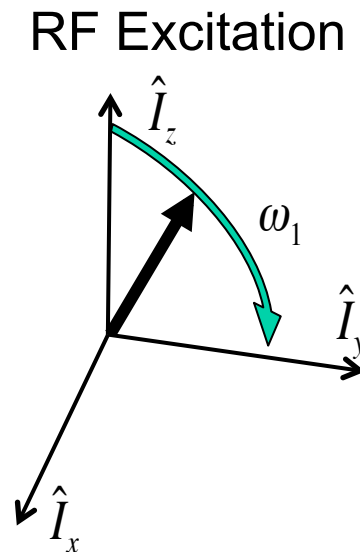
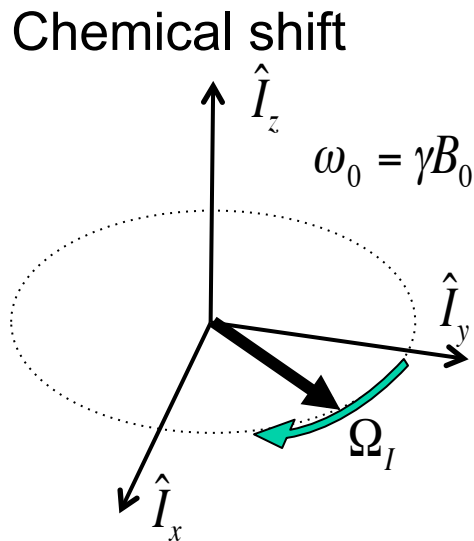
- Consider the following experiment:



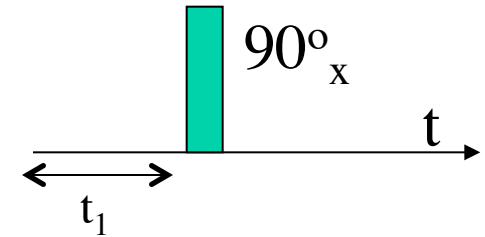
- Ignoring relaxation, what are $\hat{\sigma}(t)$, $M_x(t)$, $M_y(t)$, and $M_z(t)$ for the time intervals t_1 , t_2 , and t_3 ?

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...



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):

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

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

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

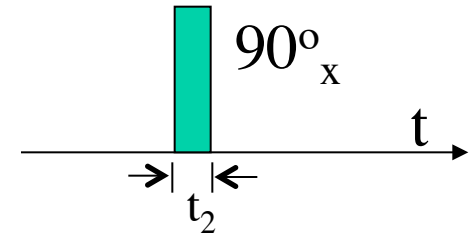
$$= \underbrace{\rho \gamma \hbar}_{\text{spins/volume}} \underbrace{\frac{1}{2} C}_{\text{normalization value for } \text{Tr}(\hat{I}_z^2)} = \rho \frac{\gamma^2 \hbar^2 B_0}{4kT}$$

- Time evolution:

$$\hat{\sigma}(t) = \underbrace{e^{-i\hat{H}t}}_{\text{time independent}} \hat{\sigma}(0) = C \underbrace{e^{i\gamma B_0 \hat{I}_z t}}_{\text{Rotation about } \hat{I}_z \text{ axis!}} \hat{I}_z = C \hat{I}_z \quad \rightarrow \quad \begin{matrix} M_z = \rho \frac{\gamma^2 \hbar^2 B_0}{4kT} = M_0 \\ M_x = M_y = 0 \end{matrix} \quad \text{for } t_0 < t < t_1$$

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).

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

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

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

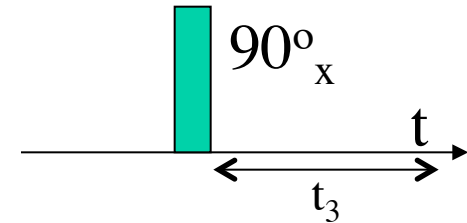
rotation about \hat{I}_x axis

Uses fact that spin operators commute cyclically

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

$$\rightarrow \begin{aligned} M_y &= M_0 \\ M_z &= M_x = 0 \end{aligned} \quad \text{for } t = t_1 + t_2$$

NMR in Liouville Space:



- Let's consider the case of being slightly off-resonance (on-resonance case is trivial)...
- Free precession (RF turned off): $\hat{H}' = -(\omega_0 - \omega)\hat{I}_z = -\Omega\hat{I}_z$

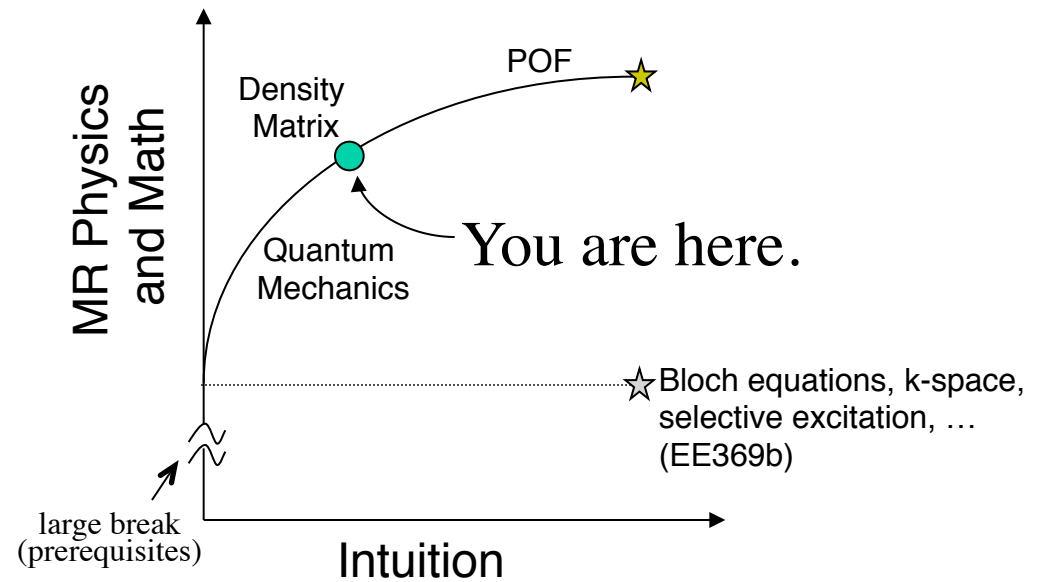
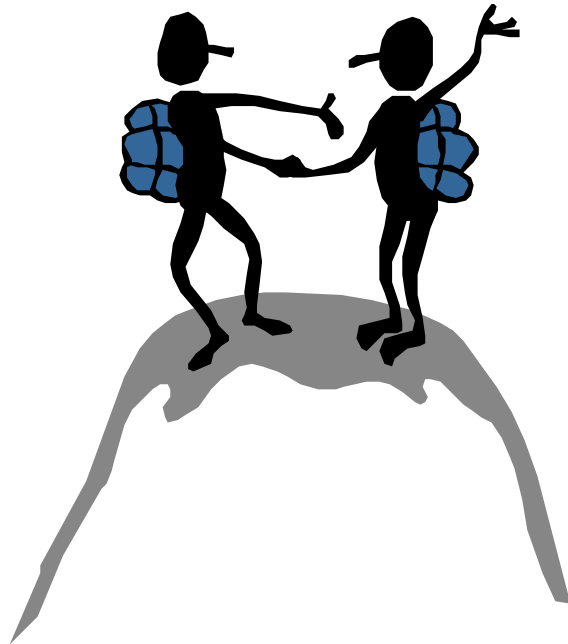
$$\hat{\sigma}'(t) = C \underbrace{e^{i\Omega t \hat{I}_z}}_{\text{rotation about } \hat{I}_z \text{ axis}} \hat{I}_y = C \left(\hat{I}_y \cos(\Omega t) + \hat{I}_x \sin(\Omega t) \right)$$

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

$$\rightarrow M_z = 0, \quad M_x = M_0 \sin(\Omega t), \quad M_y = M_0 \cos(\Omega t) \quad \text{for } t > t_1 + t_2$$

Larmor precession!

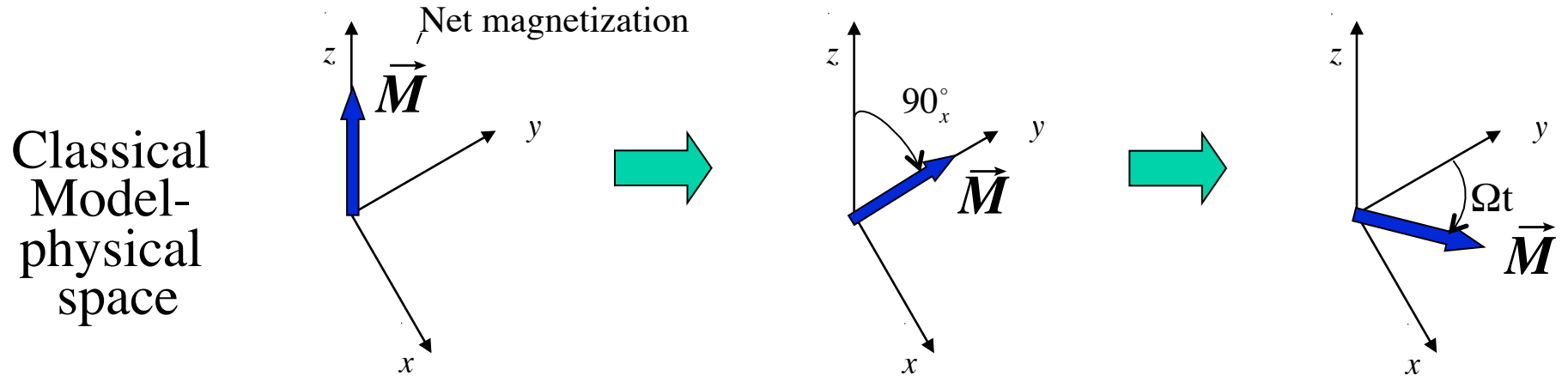
Congratulations!



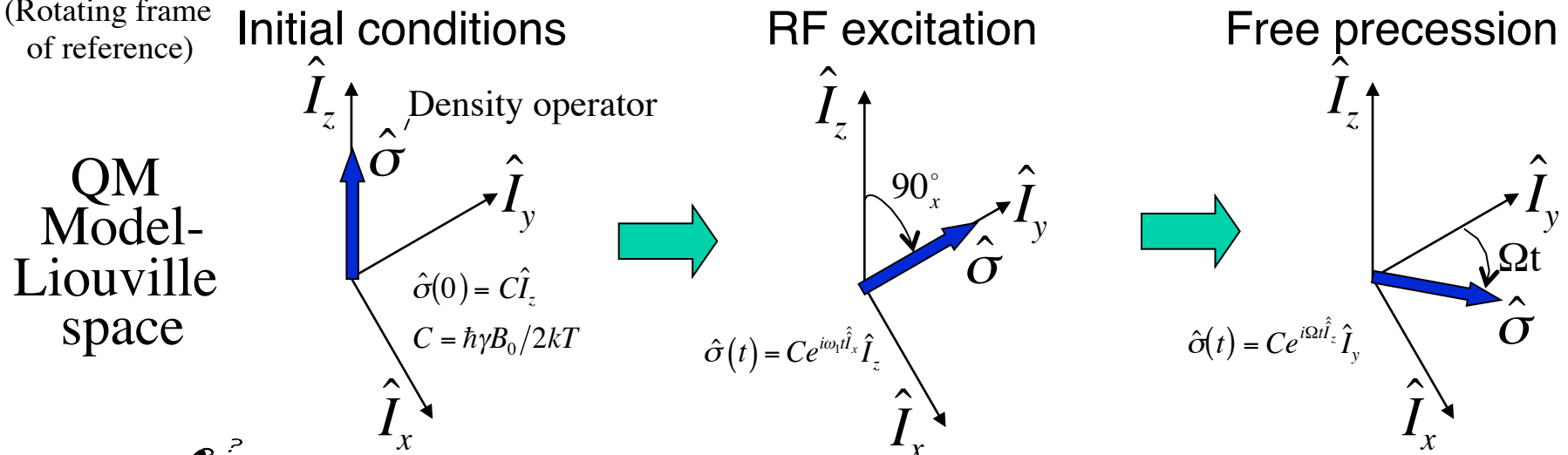
All the hard stuff is over.
(well almost)

A Comparison

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



(Rotating frame of reference)



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

Next lecture: Chemical shift and Coupling