Lecture #6
NMR in Hilbert Space

• Topics
  – Review of spin operators
  – Single spin in a magnetic field: longitudinal and transverse magnetization
  – Ensemble of spins in a magnetic field
  – RF excitation

• Handouts and Reading assignments
  – van de Ven, section 1.10, Appendices B.1 and C.
  – Miller, Chapter 12: pp 297-310 (optional).
Isolated Spin in a Magnetic Field

- Goal: Find the appropriate wavefunction $|\psi(t)\rangle$ that describes a system consisting of a nucleus (spin = 1/2) in a uniform magnetic field.

- Procedure:
  - Given: Schrödinger’s Equation: $\frac{\partial}{\partial t} |\psi(t)\rangle = -i\hat{H}(t)|\psi(t)\rangle$
  - Find $\hat{H}(t)$.
  - Solve for $|\psi\rangle$.
  - Compute quantities of interest: e.g. components of magnetic moment $\langle \hat{\mu}_x \rangle$, $\langle \hat{\mu}_y \rangle$, and $\langle \hat{\mu}_z \rangle$.

Later we’ll show these correspond to the familiar quantities $M_x$, $M_y$, and $M_z$. 
Review: Spin, Angular Momentum, and Magnetic Moment

- Spin, angular momentum, and magnetic moment operators are linearly related.

\[ \hat{\mu}_p = \gamma \hat{L}_p = \gamma \hbar \hat{I}_p, \quad p = \{x, y, z\} \]

- Spin 1/2 particle: \( \hat{I}_z |\alpha\rangle = + \frac{1}{2} |\alpha\rangle \) and \( \hat{I}_z |\beta\rangle = - \frac{1}{2} |\beta\rangle \)

- Matrix representation in \( \{|\alpha\rangle, |\beta\rangle\} \) basis:

\[
\begin{align*}
L_x &= \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
L_y &= \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\
L_z &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\end{align*}
\]
Spin Operators

• General case (based on properties of angular momentum):

\[ [\hat{I}_x, \hat{I}_y] = i\hat{I}_z \quad [\hat{I}_y, \hat{I}_z] = i\hat{I}_x \quad [\hat{I}_z, \hat{I}_x] = i\hat{I}_y \]

from which it follows that \( \hat{I}_x \), \( \hat{I}_y \), and \( \hat{I}_z \) commute cyclically:

\[
(\hat{I}_p)^n \hat{I}_q = \begin{cases} 
[\hat{I}_p, \hat{I}_q], & n \text{ odd} \\
\hat{I}_q, & n \text{ even}
\end{cases}
\]

superoperation notation

\( p, q = x, y, z; \ p \neq q \)

• Let’s also define a new operator \( \hat{I}^2 \) corresponding to the total angular momentum (magnitude).

\[
\hat{I}^2 = \hat{I}_x \hat{I}_x + \hat{I}_y \hat{I}_y + \hat{I}_z \hat{I}_z
\]

which is easily shown to satisfy

\[
\begin{align*}
[\hat{I}^2, \hat{I}_x] &= [\hat{I}^2, \hat{I}_y] = [\hat{I}^2, \hat{I}_z] = 0
\end{align*}
\]
Spin Operators

• From the commutator relations, one can derive the corresponding eigenkets and eigenvalues of $\hat{I}^2$ and $\hat{I}_z$ (note, since operators commute, they have a common set of eigenkets).

  Spectrum of $\hat{I}^2 = I(I+1)$ for $I$ integer multiple of 1/2

  Spectrum of $\hat{I}_z = m$ for $m = -I, -I+1, \ldots, I-1, I$

  $\Rightarrow$ $I$ is known as the spin quantum number.

  $\Rightarrow$ $m$ is known as the magnetic quantum number.

• Hence, spin/angular momentum/magnetic moment of elementary particles (e.g. electrons, protons, etc) are quantized in magnitude and along a projection onto any one axis.

• Formally, eigenkets of $\hat{I}_z$ are written as: $|I,m\rangle$

  where for $I = \frac{1}{2}$: $|\alpha\rangle = |\frac{1}{2}, +\frac{1}{2}\rangle \equiv |+\rangle$ and $|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle \equiv |-\rangle$. 

shorthand notation
Space quantization

- In a magnetic field $\mathbf{B} = B_0 \mathbf{\hat{z}}$, magnetic moment is quantized in $z$ (remember Stern-Gerlach experiment).

- Pictorial drawings for spin 1/2 nuclei (e.g. $^1\text{H}$, $^{31}\text{P}$, $^{13}\text{C}$)

**Picture 1:** “cones” (used by de Graaf)

<table>
<thead>
<tr>
<th>Spin Down</th>
<th>Spin Up</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta = 125.3^\circ$, $I = \frac{1}{2}$, $m = -\frac{1}{2}$</td>
<td>$\theta = 54.7^\circ$, $I = \frac{1}{2}$, $m = \frac{1}{2}$</td>
</tr>
<tr>
<td>$\mu_z = -\frac{1}{2} \gamma \hbar$, $</td>
<td>\mu</td>
</tr>
</tbody>
</table>

Angle between spin and magnetic field:

$$\theta = \cos^{-1}\left(\frac{m}{\sqrt{I(I+1)}}\right)$$

/ discrete!

**Picture 2:** “polarization” (used by Levitt)

- Single spin

Arrow depicts the direction for which magnetic moment is well defined, i.e. $= \frac{1}{2} \gamma \hbar$ with probability 1.0

- $|\alpha\rangle$
- $|\beta\rangle$

Note: $|\beta\rangle \neq -|\alpha\rangle$

What’s missing from these drawings?

If you were to measure $I_x$, $I_y$, and $I_z$ for an individual spin, what would you get?
The Hamiltonian

- Total energy of the system is given by the expected value of $\hat{H}(t)$.
  \[ \mathcal{E} = \hbar \langle \hat{H} \rangle = \hbar \langle \psi | \hat{H} | \psi \rangle \] (remember, we defined $\hat{H}$ as energy/\(\hbar\))

- Classically, the potential energy of a dipole in a magnetic field is:
  \[ \mathcal{E} = -\vec{\mu} \cdot \vec{B} = -\mu_z B_0 \] (assumes field is in z direction)

- Substituting the operator corresponding to $\mu_z$, yields the quantum mechanical Hamiltonian operator.
  \[ \hat{H} = -\gamma B_0 \hat{I}_z = -\omega_0 \hat{I}_z \]

- Thus, the spectrum of $\hat{H}$ is discrete with eigenvalues $\pm \frac{1}{2} \omega_0$ and eigenkets $|\alpha\rangle$ and $|\beta\rangle$. 

\[ \Delta\mathcal{E} = \hbar \omega_0 \quad \text{Zeeman splitting} \]
Solving Schrödinger’s Equation

- $\hat{H} = -\gamma B_0 \hat{I}_z$, hence $\hat{H}(t)$ is time independent.

Schrödinger’s Equation: $\frac{\partial}{\partial t} |\psi(t)\rangle = -i\hat{H}|\psi(t)\rangle$

- Solution:

$$|\psi(t)\rangle = e^{-it\hat{H}} |\psi(0)\rangle$$

$$|\psi(t)\rangle = \left( \hat{E} + (-i\hat{H}) + \frac{(-i\hat{H})^2}{2!} + \frac{(-i\hat{H})^3}{3!} + \ldots \right) |\psi(0)\rangle$$

Above equation implies expanding $|\psi\rangle$ in terms of eigenkets of $\hat{H}$ would be helpful. Most general solution then given by:

$$|\psi(t)\rangle = c_\alpha e^{i(\phi_\alpha + \gamma B_0 t/2)} |\alpha\rangle + c_\beta e^{i(\phi_\beta - \gamma B_0 t/2)} |\beta\rangle$$

$c_\alpha, c_\beta, \phi_\alpha,$ and $\phi_\beta$ real constants where $c_\alpha^2 + c_\beta^2 = 1$. 
Longitudinal Magnetization

- Wavefunction is $|\psi(t)\rangle = c_\alpha e^{i(\phi_\alpha + \gamma B_o t / 2)} |\alpha\rangle + c_\beta e^{i(\phi_\beta - \gamma B_o t / 2)} |\beta\rangle$.
- Longitudinal magnetization

$$\langle \hat{\mu}_z \rangle = \hbar \gamma \langle \psi | \hat{I}_z | \psi \rangle$$

$$= \frac{\hbar \gamma}{2} (c_\alpha^2 - c_\beta^2)$$

$$= \frac{\hbar \gamma}{2} (P_\alpha - P_\beta)$$

where $\begin{Bmatrix} P_\alpha \\ P_\beta \end{Bmatrix}$ probability finding the system in state $\begin{Bmatrix} |\alpha\rangle \\ |\beta\rangle \end{Bmatrix}$.

How do we find $P_\alpha$ and $P_\beta$?
Boltzmann Distribution

• Probability $P_n$ of finding a system in a specific state $|n\rangle$ is dependent on the energy $E_n$ as given by the Boltzmann distribution

$$P_n = \frac{1}{Z} e^{-E_n / kT}$$

where $Z = \sum_i e^{-E_i / kT}$.

• NMR Energies ($E_n = \mp \hbar \omega_0 / 2$) much smaller than $kT$. Thus

$$e^{-E_n / kT} \approx 1 - E_n / kT \quad \text{high temperature approximation}$$

Hence

$$\langle \hat{u}_z \rangle = \frac{\hbar \gamma}{2} \left( P_\alpha - P_\beta \right) = \frac{\hbar \gamma}{2} \left( \frac{\hbar \omega_0}{2kT} \right) = \frac{\hbar^2 \gamma^2 B_0}{4kT}$$

(factor of two from Z term)
Transverse Magnetization

- Some useful equations:
  \[ \hat{I}_x |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad \hat{I}_y |\alpha\rangle = \frac{i}{2} |\beta\rangle \]
  \[ \hat{I}_x |\beta\rangle = \frac{1}{2} |\alpha\rangle \quad \hat{I}_y |\beta\rangle = -\frac{i}{2} |\alpha\rangle \]

- Letting \( \Delta \phi = \phi_\beta - \phi_\alpha \), yields (after some algebra)
  \[ \langle \hat{\mu}_x \rangle = \hbar \gamma \langle \psi | \hat{I}_x |\psi\rangle = \frac{\hbar \gamma}{2} \left( c_\alpha c_\beta e^{-i(\omega_0 t + \Delta \phi)} + c_\beta c_\alpha e^{+i(\omega_0 t + \Delta \phi)} \right) \]
  \[ = \hbar \gamma c_\alpha c_\beta \cos(\omega_0 t + \Delta \phi) \]
  Similarly...
  \[ \langle \hat{\mu}_y \rangle = \hbar \gamma \langle \psi | \hat{I}_y |\psi\rangle = -\hbar \gamma c_\alpha c_\beta \sin(\omega_0 t + \Delta \phi) \]

- Aren't \( \phi_\alpha \) and \( \phi_\beta \) arbitrary?
**Ensemble of Identical Spins**

- Consider an ensemble of $N$ independent spins with $\phi_\alpha$ and $\phi_\beta$ (and by extension $\Delta \phi$) randomly distributed.

  \[ \langle \hat{\mu}_x \rangle = \langle \hat{\mu}_y \rangle = 0 \]

- Physical pictures for a collection of spins in states $|\alpha\rangle$ and $|\beta\rangle$:

  - "Cones"
  - "Polarization"
RF Excitation

• In order to get transverse magnetization, we need to establish some phase relationship (coherence) among spins.

• In the presence of a rotating magnetic field, the Hamiltonian is:
  \[ \hat{H}(t) = -\omega_0 \hat{I}_z - \omega_1 \left( \hat{I}_x \cos \omega t - \hat{I}_y \sin \omega t \right) \]
  where \( \omega_1 = \gamma B_1 \).

• \( \hat{H}(t) \) is periodic \( \Rightarrow \) change to rotating frame of reference.

\[ |\psi'\rangle = e^{-i\omega t \hat{I}_z} |\psi\rangle \text{ and } \hat{H}' = e^{-i\omega t \hat{I}_z} \hat{H} e^{i\omega t \hat{I}_z} = e^{-i\omega t \hat{I}_z} \hat{H} \]
  (Change of basis)

• Using Schrödinger’s equation and the chain rule for differentiation:

\[ \frac{\partial}{\partial t} |\psi'\rangle = -i \hat{H}_{\text{eff}} |\psi'\rangle \text{ where } \hat{H}_{\text{eff}} = -(\omega_0 - \omega) \hat{I}_z - \omega_1 \hat{I}_x \]

  Time independent \hspace{2cm} \text{Effective field in the rotating frame just like the classical case}
RF Excitation

• Assuming RF pulse is on resonance (i.e. ω=ω₀), \( |\psi'(\tau)\rangle \) at the end of a constant pulse of length \( \tau \) is:

\[
|\psi'(\tau)\rangle = e^{-i\tau \hat{H}_{\text{eff}}} |\psi'(0)\rangle = c_\alpha e^{-i\phi_\alpha} \left[ \cos\left(\frac{1}{2} \omega_1 \tau\right)|\alpha\rangle + i \sin\left(\frac{1}{2} \omega_1 \tau\right)|\beta\rangle \right] \\
+ c_\beta e^{-i\phi_\beta} \left[ \cos\left(\frac{1}{2} \omega_1 \tau\right)|\beta\rangle + i \sin\left(\frac{1}{2} \omega_1 \tau\right)|\alpha\rangle \right]
\]

• Case 1: \( \omega_1 \tau = 180^\circ \)

\[
|\psi'(\tau_{180})\rangle = i \left( c_\alpha e^{-i\phi_\alpha} |\beta\rangle + c_\beta e^{-i\phi_\beta} |\alpha\rangle \right) \quad \Rightarrow \quad \langle \hat{\mu}_z \rangle = \frac{\hbar \gamma}{2} \left( c_\beta^2 - c_\alpha^2 \right)
\]
RF Excitation

- General case:
  \[ |\psi'(\tau)\rangle = e^{-i\hat{H}_{\text{eff}}\tau} |\psi'(0)\rangle = c_{\alpha} e^{-i\phi_{\alpha}} \left[ \cos\left(\frac{1}{2} \omega_{1}\tau\right) |\alpha\rangle + i \sin\left(\frac{1}{2} \omega_{1}\tau\right) |\beta\rangle \right] \\
  + c_{\beta} e^{-i\phi_{\beta}} \left[ \cos\left(\frac{1}{2} \omega_{1}\tau\right) |\beta\rangle + i \sin\left(\frac{1}{2} \omega_{1}\tau\right) |\alpha\rangle \right] \]

- Case 2: \( \gamma_{1}B_{1}\tau = 90^\circ \) (about x axis)
  \[ |\psi'(\tau_{90})\rangle = \frac{\sqrt{2}}{2} \left[ \left( c_{\alpha} e^{-i\phi_{\alpha}} + ic_{\beta} e^{-i\phi_{\beta}} \right) |\alpha\rangle + \left( c_{\beta} e^{-i\phi_{\beta}} + ic_{\alpha} e^{-i\phi_{\alpha}} \right) |\beta\rangle \right] \]

Single Spin

\[
\langle \hat{\mu}_{x} \rangle = \hbar \gamma c_{\alpha} c_{\beta} \cos \Delta \phi \\
\langle \hat{\mu}_{y} \rangle = -\frac{1}{2} \hbar \gamma \left( c_{\alpha}^{2} - c_{\beta}^{2} \right) \\
\langle \hat{\mu}_{z} \rangle = \hbar \gamma c_{\alpha} c_{\beta} \sin \Delta \phi
\]

 Ensemble average

\[
\langle \hat{\mu}_{x} \rangle = 0 \\
\langle \hat{\mu}_{y} \rangle = -\frac{1}{2} \hbar \gamma \left( c_{\alpha}^{2} - c_{\beta}^{2} \right) \\
\langle \hat{\mu}_{z} \rangle = 0
\]
as expected
RF Excitation

- In summary $90^\circ_x$ RF pulse causes:
  1) equalization of probabilities of $\{|\alpha\rangle,|\beta\rangle\}$ states $\Rightarrow M_z = 0$.
  2) a phase coherence between $\{|\alpha\rangle,|\beta\rangle\}$ states generating $M_y$.

There is something subtle, yet fundamentally wrong, about the above diagrams. What is it?
Linear Superposition of States

Consider the following two examples:

- **System 1**: \( N_\alpha \) and \( N_\beta \) spins with \( |\psi_\alpha\rangle = |\alpha\rangle \) and \( |\psi_\beta\rangle = |\beta\rangle \) respectively such that \( N = N_\alpha + N_\beta \), \( N_\alpha / N = c_\alpha^2 \), and \( N_\beta / N = c_\beta^2 \).

→ Implies that a given spin has probabilities \( c_\alpha^2 \) and \( c_\beta^2 \) of being in state \( |\alpha\rangle \) and \( |\beta\rangle \) respectively.

However, System 1 virtually **never** occurs in practice! It is wrong to claim that all spins are either “spin up” or “spin down”.

![Diagram](509x143 to 649x281)
Linear Superposition of States

• **System 2**: $N$ spins each with wavefunction $|\psi\rangle = c_\alpha e^{-i\phi_\alpha} |\alpha\rangle + c_\beta e^{-i\phi_\beta} |\beta\rangle$.

→ **Does NOT** imply that a given spin has probabilities $c_\alpha^2$ and $c_\beta^2$ of being in state $|\alpha\rangle$ and $|\beta\rangle$ respectively.

“**Cones**”: picture doesn’t work

“**Polarization**”: works better, but still not very realistic

Here, spins are almost fully polarized in $z$
Linear Superposition of States

• System 2 spins are described by a **linear superposition of states** as opposed to the **statistical mixture** of states in System 1.

**Example:** If we insist that each spin is always either “spin up” or “spin down” (System 1), then for all spins: \( \{c_\alpha, c_\beta\} = \{1, 0\} \) or \( \{c_\alpha, c_\beta\} = \{0, 1\} \). Hence this system could *never* generate any transverse magnetization.

\[
\begin{align*}
\langle \hat{\mu}_x \rangle &= \hbar \gamma c_\alpha c_\beta \cos(\omega_0 t + \Delta \phi) \\
\langle \hat{\mu}_y \rangle &= -\hbar \gamma c_\alpha c_\beta \sin(\omega_0 t + \Delta \phi)
\end{align*}
\]

\[\Rightarrow \quad \langle \hat{\mu}_x \rangle = \langle \hat{\mu}_x \rangle = 0 \quad \text{independent of any phase coherences}\]

For System 2, all spins have perfect phase coherence.
Actual MR Experiments

• In a real NMR experiment, we actually deal with a statistical mixture of spins each of which is described by a linear superposition of states (topic for next lecture).

• **System 3**: \( N \) spins with wavefunctions \( |\psi_i\rangle = c_{\alpha i} e^{-i\phi_{\alpha i}} |\alpha\rangle + c_{\beta i} e^{-i\phi_{\beta i}} |\beta\rangle \)
  where \( i=1,..N, c_{\alpha i}, c_{\beta i}, \phi_{\alpha i}, \) and \( \phi_{\beta i} \) real constants for which \( c_{\alpha i}^2 + c_{\beta i}^2 = 1 \).

At typical magnetic fields and temperatures, spins are polarized almost isotropically in space, with the term “almost” referring to a slight preference for the +z component (~10ppm for \(^1\text{H}, B_0 = 3\) Tesla, \( T = 37^\circ\text{C} \))

We’ll make use of this alternative energy diagram when studying relaxation.
Summary

• Quantum mechanical derivations show that $\langle \hat{\mu}_x \rangle$, $\langle \hat{\mu}_y \rangle$, and $\langle \hat{\mu}_z \rangle$ faithfully reproduce the classically-derived behavior of $M_x$, $M_y$, and $M_z$ (e.g. Larmor precession, RF excitation, etc).

• Rigorous but with limited intuition.

• Subsequent lectures will show that Liouville Space description of NMR and, in particular, the Product Operator Formalism is….
  — Mathematically easier.
  — Retains intuition associated with classical vector formulation.
  — Readily extended to the case of interacting spins (coupling).
Next Lecture: NMR in Liouville Space