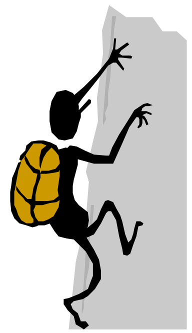
Lecture #6
NMR in Hilbert Space



- 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.
  - F. Bloch, W. Hansen, and M. Packard, Nuclear Induction. *Phys. Rev.*, 69: 127, 1946
  - E. M. Purcell, H. C. Torrey and and R. V. Pound. Resonance absorption by nuclear magnetic moments in a solid. *Phys. Rev.*, 69: 37, 1946.
  - 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.

$$\hat{\mu}_p = \gamma \hat{L}_p = \gamma \hbar \hat{I}_p, \qquad p = \{x, y, z\}$$

magnetic moment — angular momentum — spin

eigenkets of $\hat{I}_z$

- 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:

$$\underline{I}_{x,} = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \underline{I}_{y,} = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \underline{I}_{z,} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Spin Operators

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

$$\left[\hat{I}_x,\hat{I}_y\right]=i\hat{I}_z \qquad \left[\hat{I}_y,\hat{I}_z\right]=i\hat{I}_x \qquad \left[\hat{I}_z,\hat{I}_x\right]=i\hat{I}_y$$

from which it follows that $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$ commute <u>cyclically</u>:

$$\left(\hat{\hat{I}}_p\right)^n \hat{I}_q = \begin{cases} \left[\hat{I}_p,\hat{I}_q\right], & n \text{ odd} \\ \hat{I}_q, & n \text{ even} \end{cases} \qquad p,q = x,y,z;\ \ p \neq q$$

superoperation notation

- 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

$$\left[\hat{I}^2,\hat{I}_x\right]=\left[\hat{I}^2,\hat{I}_y\right]=\left[\hat{I}^2,\hat{I}_z\right]=0$$

Spin Operators

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

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

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

⇨ I is known as the spin quantum number.

⇨ 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 $I = ½$: $|\alpha\rangle = |\tfrac{1}{2}, +\tfrac{1}{2}\rangle \equiv |+\rangle$ and $|\beta\rangle = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \equiv |-\rangle$.

shorthand notation

Space quantization

- In a magnetic field $\vec{B} = B_0\hat{z}$, magnetic moment is quantized in z (remember Stern-Gerlach experiment).
- Pictorial drawings for spin 1/2 nuclei ($e.g.$ ^{1}H, ^{31}P, ^{13}C)

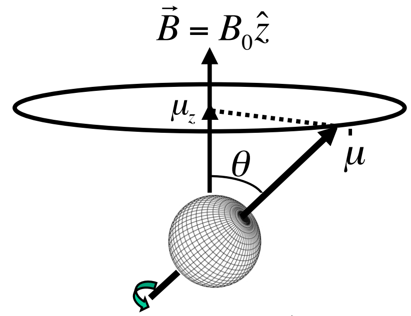
Picture 1: "cones" (used by de Graaf)

angle between spin and magnetic field

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

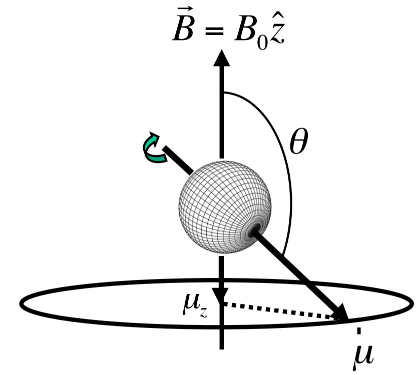
discrete!

"spin up, parallel"



$$\theta = 54.7^\circ,\ I = \tfrac{1}{2},\ m = \tfrac{1}{2}$$
$$\mu_z = \tfrac{1}{2}\gamma\hbar,\ |\vec{\mu}| = \tfrac{\sqrt{3}}{2}\gamma\hbar$$

"spin down, anti-parallel"

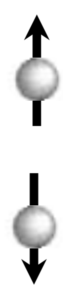


$$\theta = 125.3^\circ,\ I = \tfrac{1}{2},\ m = -\tfrac{1}{2}$$
$$\mu_z = -\tfrac{1}{2}\gamma\hbar,\ |\vec{\mu}| = \tfrac{\sqrt{3}}{2}\gamma\hbar$$

Picture 2: "polarization" (used by Levitt)

Single spin

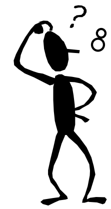
Arrow depicts the direction for which magnetic moment is well defined, i.e. $= \frac{1}{2}\gamma\hbar$ with probability 1.0



$= |\alpha\rangle$

$= |\beta\rangle$

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 $\hat{H}(t)$.

  $\mathcal{E} = \hbar\left\langle \hat{H} \right\rangle = \hbar\langle\psi|\hat{H}|\psi\rangle$ (remember, we defined $\hat{H}$ as energy/$\hbar$)

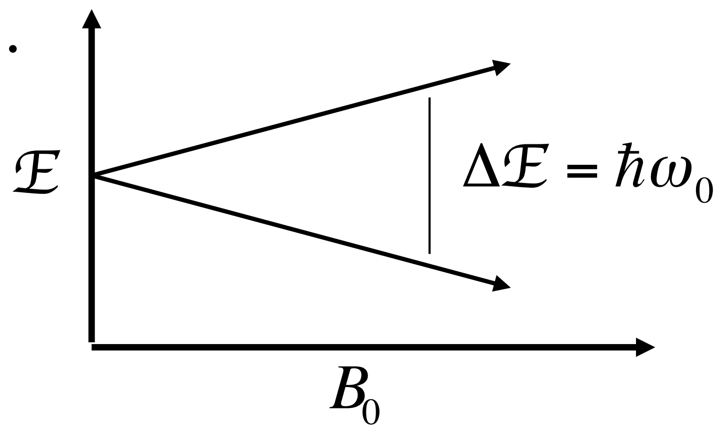
- Classically, the potential energy of a dipole in a magnetic field is:

  $\mathcal{E} = -\vec{\mu} \cdot \vec{B} = -\mu_z B_0$ (assumes field is in z direction)

- Substituting the operator corresponding to μ_z, yields the quantum mechanical Hamiltonian operator.

$$\hat{H} = -\gamma B_o \hat{I}_z = -\omega_0 \hat{I}_z$$

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



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:

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

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

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

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

c_α, c_β, ϕ_α, and ϕ_β real constants where $c_\alpha^2 + c_\beta^2 = 1$.

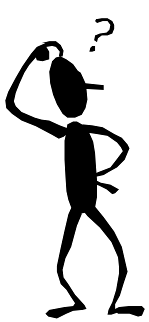
Longitudinal Magnetization

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

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

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

$$= \frac{\hbar\gamma}{2}\left(P_\alpha - P_\beta\right)$$ 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_α and P_β?

Boltzman 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

Boltzmann constant

partition function (normalization factor)

$$P_n = \frac{1}{Z} e^{-E_n/kT} \quad \text{where} \quad Z = \sum_i e^{-E_i/kT}.$$

absolute temperature

sum over all possible energies

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

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

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

factor of two from Z term

(compare Lecture 2, slide 14)

Transverse Magnetization

- Some useful equations:

$$\hat{I}_x|\alpha\rangle = \tfrac{1}{2}|\beta\rangle \qquad \hat{I}_y|\alpha\rangle = \tfrac{i}{2}|\beta\rangle$$

$$\hat{I}_x|\beta\rangle = \tfrac{1}{2}|\alpha\rangle \qquad \hat{I}_y|\beta\rangle = -\tfrac{i}{2}|\alpha\rangle$$

- Letting $\Delta\phi = \phi_\beta - \phi_\alpha$, yields (after some algebra)

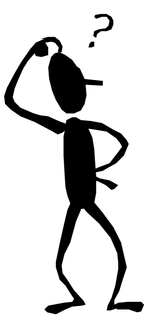
$$\langle \hat{\mu}_x \rangle = \hbar\gamma \langle \psi | \hat{I}_x | \psi \rangle = \frac{\hbar\gamma}{2}\left(c_\alpha c_\beta e^{-i(\omega_0 t + \Delta\phi)} + c_\beta c_\alpha e^{+i(\omega_0 t + \Delta\phi)} \right)$$

$$= \hbar\gamma c_\alpha c_\beta \cos(\omega_0 t + \Delta\phi)$$

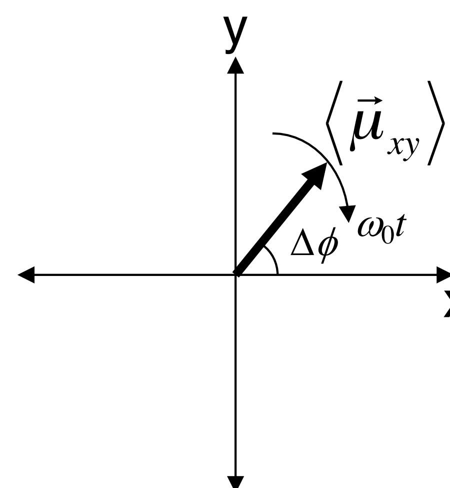
Larmor precession!

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 ϕ_α and ϕ_β arbitrary?



free precession

Ensemble of Identical Spins

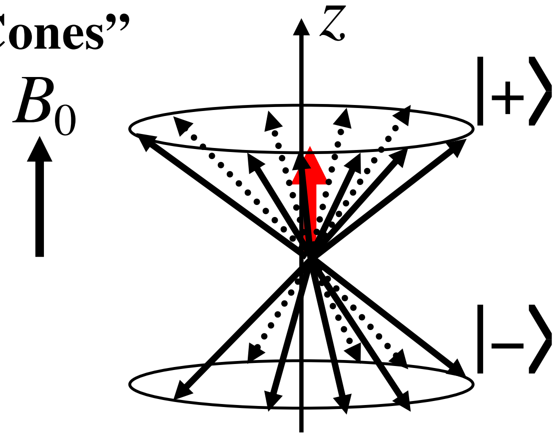
- Consider an ensemble of N independent spins with ϕ_α and ϕ_β (and by extension $\Delta\phi$) randomly distributed.

average over ensemble

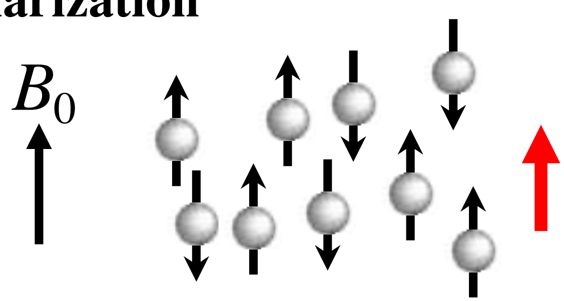
$$\overline{\langle \hat{\mu}_x \rangle} = \overline{\langle \hat{\mu}_y \rangle} = 0$$

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

"Cones"



"Polarization"



$$\overline{\langle \hat{\mu}_z \rangle} = N \frac{\hbar^2 \gamma^2 B_0}{4kT}$$

$$M_z = \frac{N}{V} \frac{\hbar^2 \gamma^2 B_0}{4kT} = \rho \frac{\hbar^2 \gamma^2 B_0}{4kT}$$

spins/volume

RF Excitation

- In order to get transverse magnetization, we need to establish some phase relationship (<u>coherence</u>) among spins.

$\Rightarrow$ RF excitation

- In the presence of a rotating magnetic field, the Hamiltonian is:

$$\hat{H}(t) = -\omega_0 \hat{I}_z - \omega_1 \left(\hat{I}_x \cos \omega t - \hat{I}_y \sin \omega t \right) \text{ where } \omega_1 = \gamma B_1 .$$

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

$$\left| \psi' \right\rangle = e^{-i\omega t \hat{I}_z} \left| \psi \right\rangle \text{ and } \hat{H}' = e^{-i\omega t \hat{I}_z} \hat{H} e^{i\omega t \hat{I}_z} = e^{-i\omega t \hat{\hat{I}}_z} \hat{H}$$

(Change of basis)

- Using Schrödinger's equation and the chain rule for differentiation:

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

Time independent

Effective field in the rotating frame just like the classical case

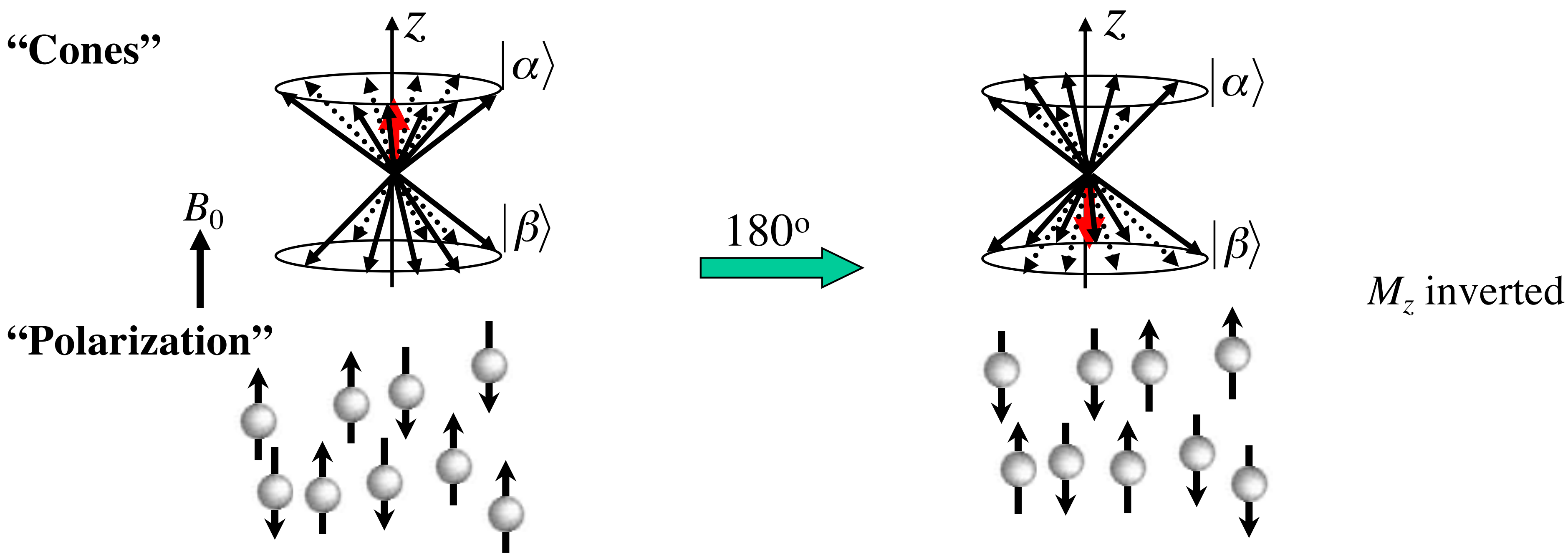
RF Excitation

- Assuming RF pulse is on resonance ($i.e.$ $\omega=\omega_0$), $|\psi'(\tau)\rangle$ at the end of a constant pulse of length τ is:

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

- Case 1: $\omega_1\tau=180^{\circ}$

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



RF Excitation

- General case:

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

- Case 2: $\gamma_1 B_1 \tau = 90^o$ (about x axis)

$$\left|\psi'(\tau_{90})\right\rangle = \tfrac{\sqrt{2}}{2}\left[\left(c_\alpha e^{-i\phi_\alpha} + ic_\beta e^{-i\phi_\beta}\right)\left|\alpha\right\rangle + \left(c_\beta e^{-i\phi_\beta} + ic_\alpha e^{-i\phi_\alpha}\right)\left|\beta\right\rangle\right]$$

<u>Single Spin</u>

$$\left\langle\hat{\mu}_x\right\rangle = \hbar\gamma c_\alpha c_\beta \cos\Delta\phi$$
$$\left\langle\hat{\mu}_y\right\rangle = -\tfrac{1}{2}\hbar\gamma\left(c_\alpha^2 - c_\beta^2\right)$$
$$\left\langle\hat{\mu}_z\right\rangle = \hbar\gamma c_\alpha c_\beta \sin\Delta\phi$$

$\Rightarrow$

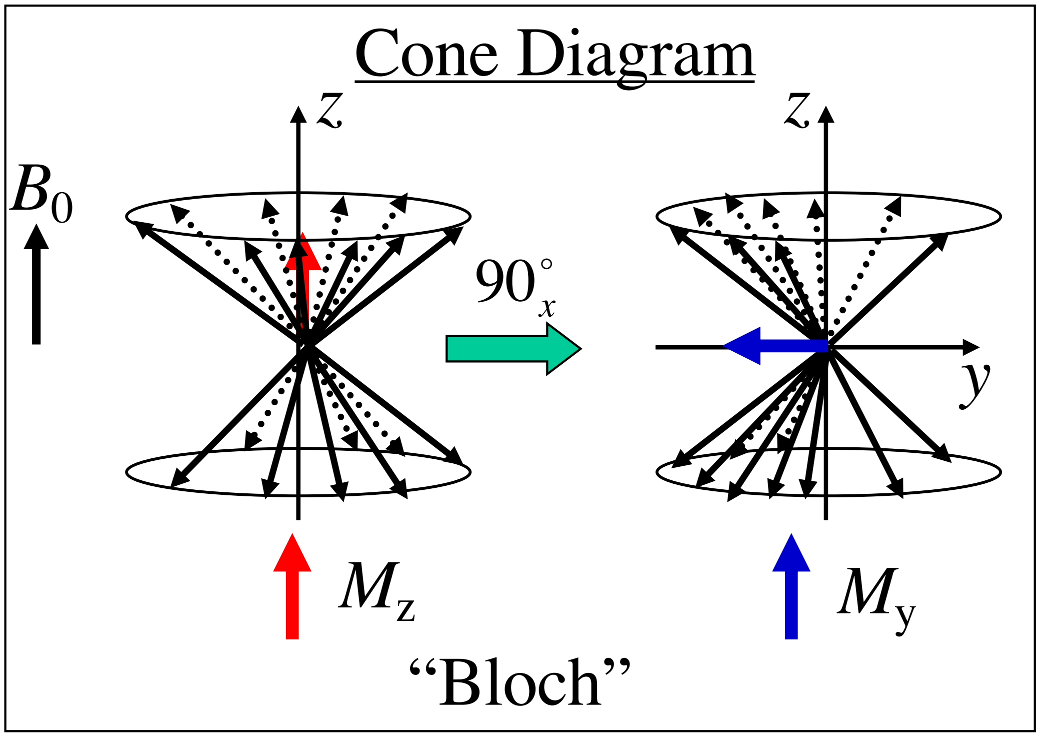
<u>Ensemble average</u>

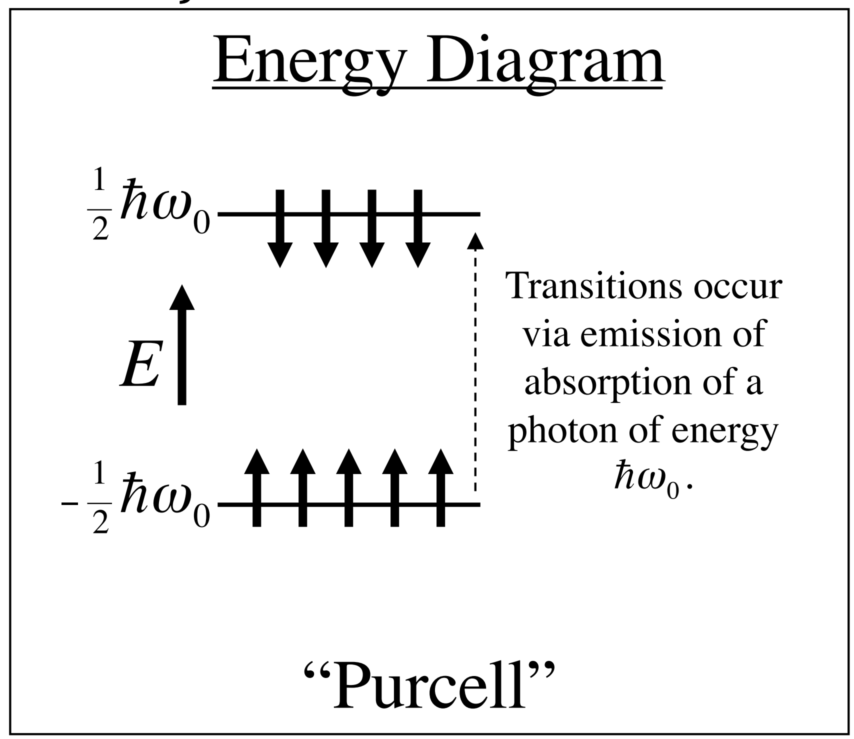
$$\overline{\left\langle\hat{\mu}_x\right\rangle} = 0$$
$$\overline{\left\langle\hat{\mu}_y\right\rangle} = -\tfrac{1}{2}\hbar\gamma\left(c_\alpha^2 - c_\beta^2\right)$$
$$\overline{\left\langle\hat{\mu}_z\right\rangle} = 0$$

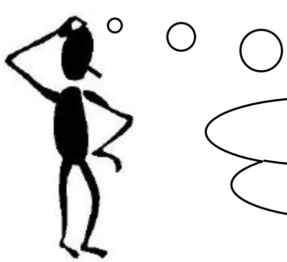
as expected

RF Excitation

- In summary 90°_{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.







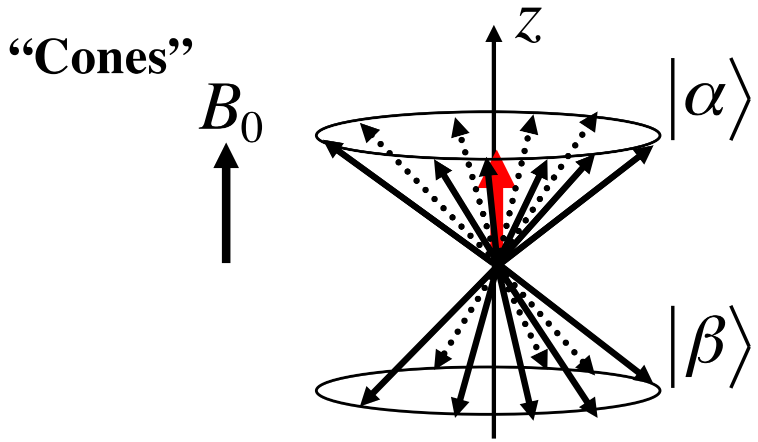
There is something subtle, yet fundamentally wrong, about the above diagrams. What is it?

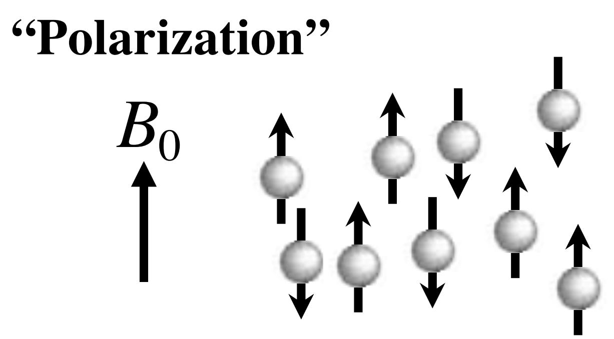
Linear Superposition of States

Consider the following two examples:

- System 1: N_α and N_β 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_α^2 and c_β^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" of "spin down".

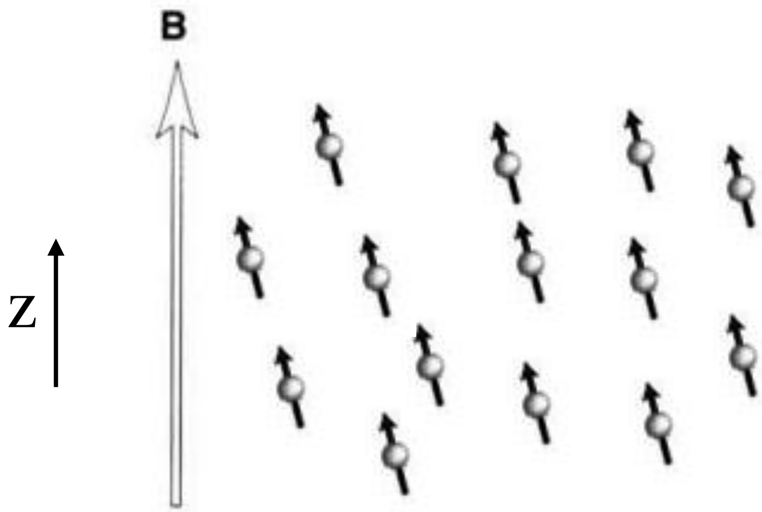
Linear Superposition of States

- 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_α^2 and c_β^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 <u>linear</u> <u>superposition</u> <u>of</u> <u>states</u> as opposed to the <u>statistical</u> <u>mixture</u> of states in System 1.

<u>Example</u>: 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.

$$\langle \hat{\mu}_x \rangle = \hbar\gamma c_\alpha c_\beta \cos(\omega_0 t + \Delta\phi)$$

product always = 0

$$\langle \hat{\mu}_y \rangle = -\hbar\gamma c_\alpha c_\beta \sin(\omega_0 t + \Delta\phi)$$

$$\Rightarrow \quad \overline{\langle \hat{\mu}_x \rangle} = \overline{\langle \hat{\mu}_x \rangle} = 0 \longleftarrow$$

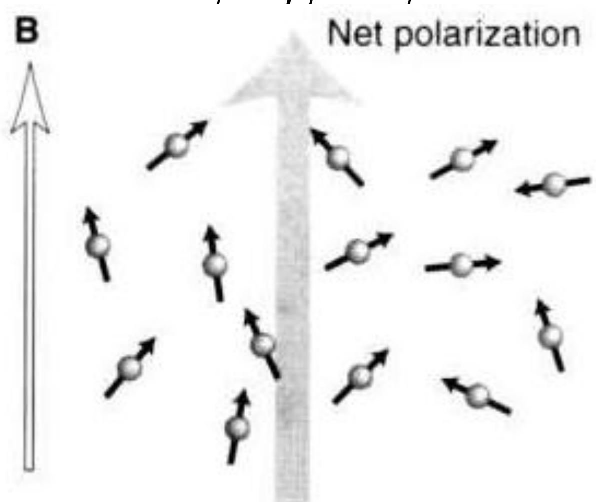
independent of any phase coherences

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 ϕ_{β_i} real constants for which $c_{\alpha_i}^2 + c_{\beta_i}^2 = 1$.

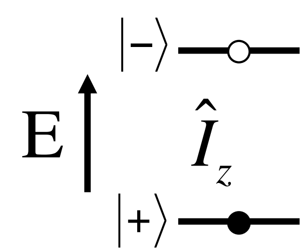
Polarization diagram



$\hat{I}_z$

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]H, B_0 = 3 Tesla, T = 37°C)

Energy diagram



○ = population deficit
● = population excess

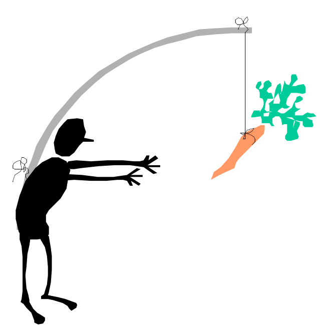
We'll make use of this alternative energy diagram when studying relaxation.

Summary

- Quantum mechanical derivations show that $\overline{\langle \hat{\mu}_x \rangle}$, $\overline{\langle \hat{\mu}_y \rangle}$, and $\overline{\langle \hat{\mu}_z \rangle}$ 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 <u>Product</u> <u>Operator</u> <u>Formalism</u> 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