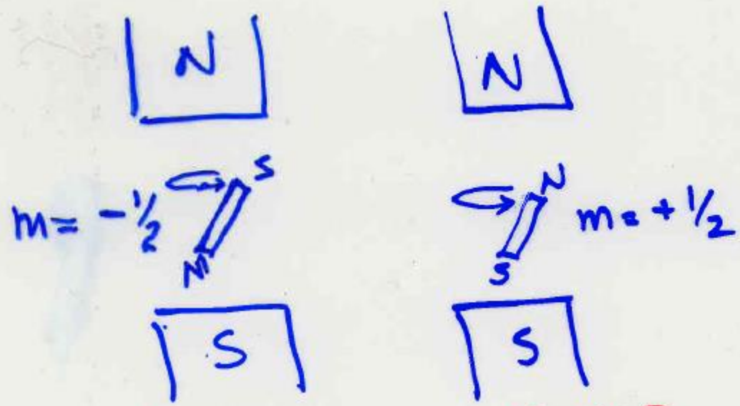
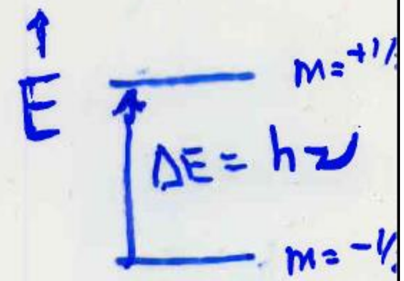


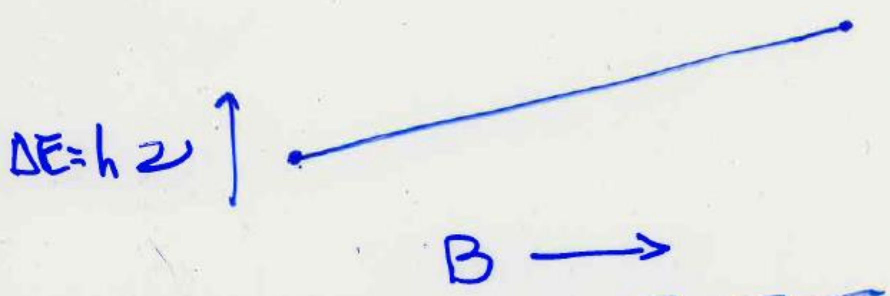


$$\Delta E = -\mu B_0 = h\nu$$

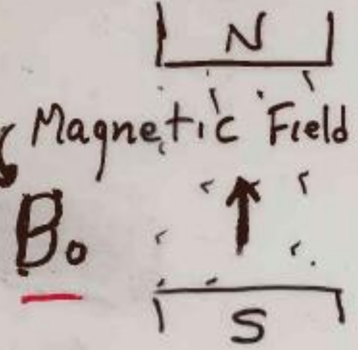
magnetic dipole moment

Field Strength.

So RESONANT FREQ ν, proportional to Field.



NMR & MRI



N ↑ ——— $m = +1/2$

$\Delta E = h\nu = 2\mu_m B_o$

magnetic dipole (μ_m)

← Magnetic field strength (B_o)

↓ N ——— $m = -1/2$

For a proton in 12 Tesla Field $\nu = 600$ MHz

Recall $\Delta E = h\dfrac{c}{\lambda}$ so $\dfrac{\Delta E}{hc} = \dfrac{1}{\lambda} = \boxed{\text{wavenumbe}}$ *

(c ← speed of light)

$$\frac{600 \times 10^{6}\ s^{-1}}{3 \times 10^{10}\ cm\ s^{-1}} = 200 \times 10^{-4}\ cm^{-1} = \boxed{0.02\ cm^{-1}}$$

Boltmann Constant in $\frac{cm^{-1}}{K} = \frac{K_B}{hc} = \frac{1.38\times10^{-23}\,J/K}{6.62\times10^{-34}\,Js\;3\times10^{10}\,cm}$

$$= \boxed{0.697\,\frac{cm^{-1}}{K}}$$

Ratio of spin up to spin down:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}} = e^{-\frac{\Delta E/hc}{\frac{k_B}{hc}T}} = e^{-\frac{0.02\,cm^{-1}}{0.697\frac{cm^{-1}}{K}\,300}}$$

$$= e^{-\frac{0.02}{207}} = e^{-0.0001} = 0.9999$$

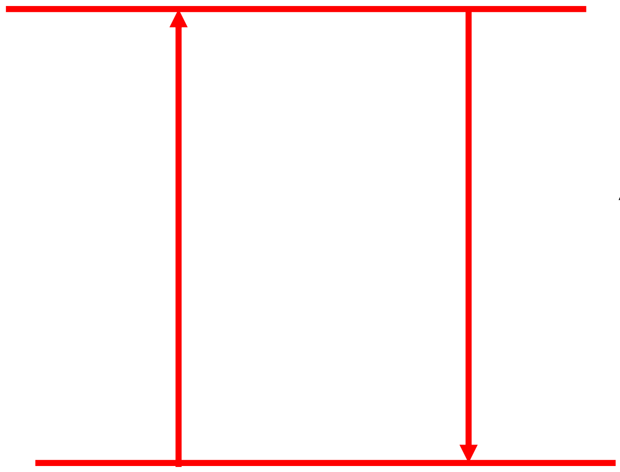
$k_B T$ at $300K = 207\,cm^{-1}$

3. Equilibrium Density Matrix

At equilibrium, the distribution of energies of the independent systems of an ensemble will be such that

$$\frac{C_m C_m^*}{C_n C_n^*} = e^{-\frac{(E_m - E_n)}{k_B T}} = \frac{\langle \rho_{mm} \rangle}{\langle \rho_{nn} \rangle}$$

i.e., the Boltzmann distribution.



$\Delta E = 0.02\ cm^{-1}$

Absorption and stimulated emission virtually same

You have shown that there is NO fluorescence

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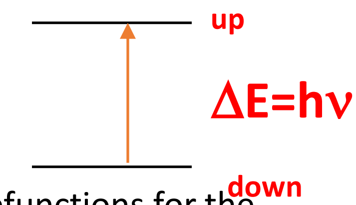
Thur, 21nov13

Although the there are two quantum ***"energy levels":***
spin up and spin down, there is a continuous mixture.
The spins are all in ***superposition*** states.



$$\Psi_{total} = c_{up}\Psi_{up} + c_{down}\Psi_{down}$$

Ψ_{up} and Ψ_{down} are "orbitals" i.e., wavefunctions for the nuclear spin.

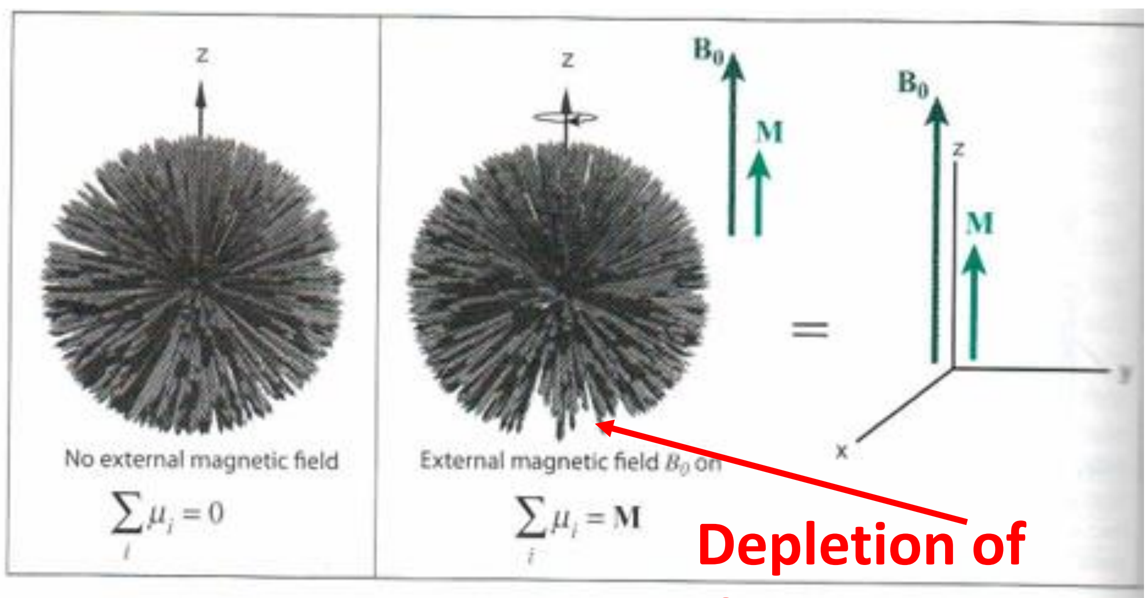
The ***square*** of the coefficients gives probability to observe in the ***up*** state

$$c^2_{up} + c^2_{down} = 1$$

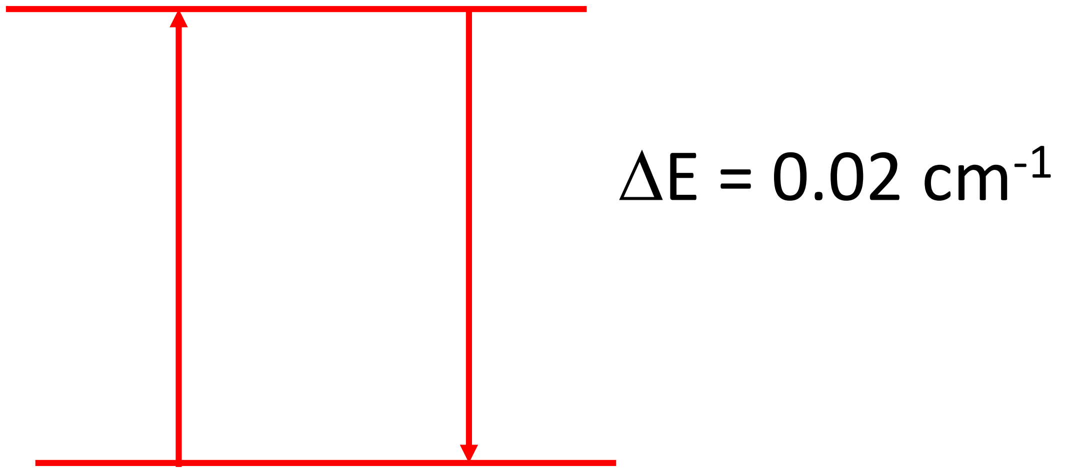
The lines pointing in all directions give an idea of the proportion of spin up and spin down for each of the spins.

An earlier slide shows there is only 0.01% less probability to be in the high energy state because $\Delta E << kT$.

FIGURE 14.3 Visualizing a large number of nuclear magnetic moments of a bulk sample in a bundle. In the absence of any external field (left panel) all nuclear moments μ_i are randomly distributed. In a strong external field along the z-axis (B_0, right panel), the individual moments are very weakly biased towards the z-axis (the bias is exaggerated 100 fold in the right panel). A vector sum of all of the individual moments reveals the bulk magnetization **M** parallel to $\mathbf{B_0}$. As we discuss shortly, the individual nuclear moments rotate around B_0, a motion termed 'precession.'



Depletion of those pointing down

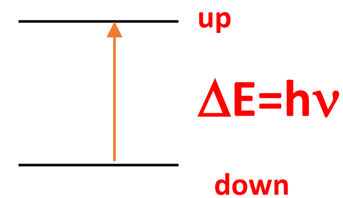


Absorption and stimulated emission virtually same

You have shown that there is NO fluorescence

Pulse of radiofrequency COHERENTLY excites just those molecules whose transition moments are parallel to magnetic field.

Although the there are two quantum ***"energy levels":***
spin up and spin down, there is a continuous mixture.
The spins are all in ***superposition*** states.



$$\Psi_{total} = c_{up}\Psi_{up} + c_{down}\Psi_{down}$$

Ψ_{up} and Ψ_{down} are "orbitals" i.e., wavefunctions for the nuclear spin.

The ***square*** of the coefficients gives probability to observe in the ***up*** state

$$c^2_{up} + c^2_{down} = 1$$

The lines pointing in all directions give an idea of the proportion of spin up and spin down for each of the spins.

An earlier slide shows there is only 0.01% less probability to be in the high energy state because $\Delta E << kT$.

Coherently excited excess NET population in ground is turned sideways by a $\pi/2$ pulse, creating a radiating oscillating magnetic moment

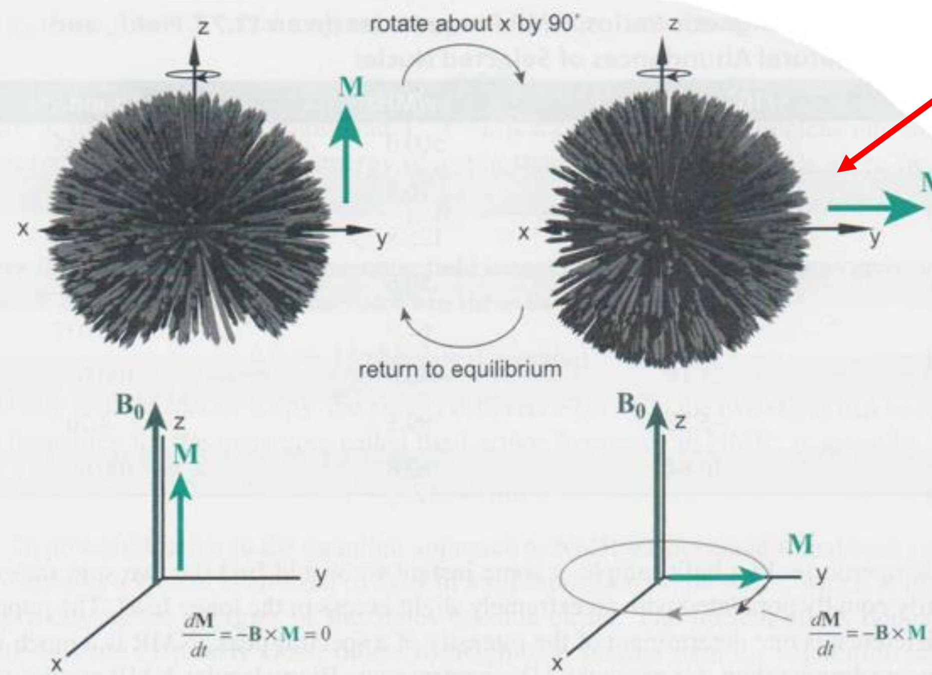
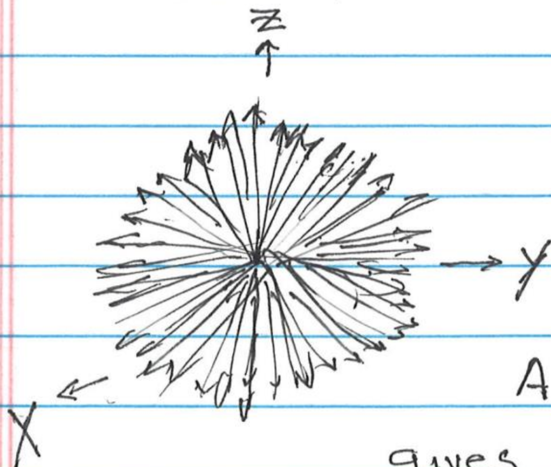


FIGURE 14.4 Schematic of the behavior of both individual and bulk magnetic moments that are parallel (left) or perpendicular (right) to the B_0 field. At equilibrium (left) the individual moments precess but M does not. If the nuclei have been perturbed, then both the individual and bulk moments precess (right panel). The dynamics of the bulk magnetization M are always due to the average behavior of a large number of nuclear spins.

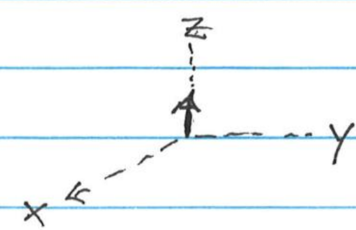
Pictorially, if we draw an arrow for the value of $\vec{\rho}$ for each member of the ensemble for a case where

$H_{22}-H_{11} \ll k_B T$, i.e., $\langle \rho_{22}\rangle \cong \langle \rho_{11}\rangle$



The density of arrows is nearly the same for every direction in ρ space.

Addition of all the arrows gives



Spin echo, Photon Echo Link

https://en.wikipedia.org/wiki/Spin_echo

5↑

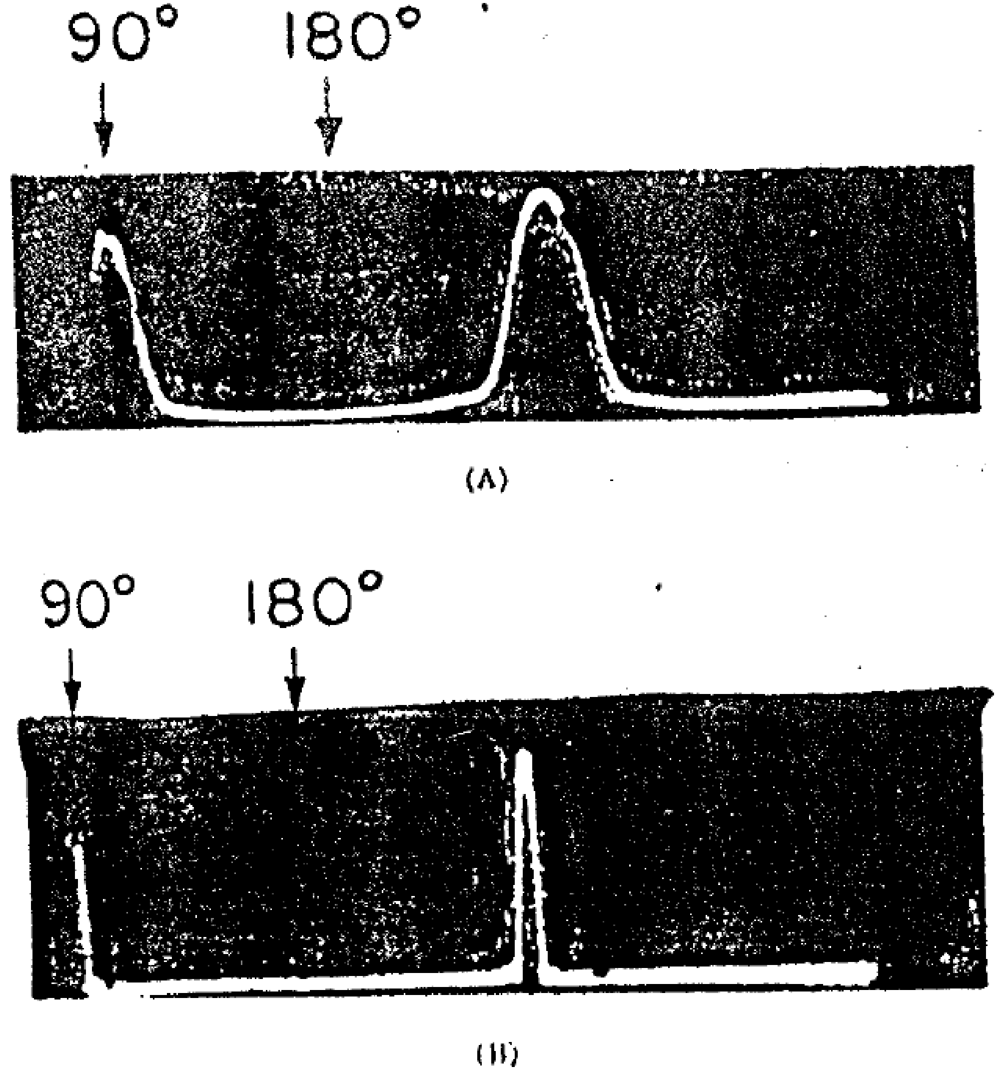


FIG. 4. Effect of the homogeneity of the field on the widths of tails and echoes. The tails and echoes associated with a sample (A) in a very homogeneous field are wide compared to those associated with a sample (B) in a less homogeneous field.

Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

From the reading for Lec. 30-31: Time in Quantum Mechanics

Let $|\Theta\rangle = c_1(t_1)\,|1\rangle + c_2(t_2)\,|2\rangle$, where $|1\rangle$ and $|2\rangle$ depend on space only. Then,

$$\frac{\partial \Psi}{\partial t} = \frac{\partial c_1(t)}{\partial t}|1\rangle + \frac{\partial c_2(t)}{\partial t}|2\rangle = -i\widehat{H}|1\rangle c_1(t) - i\widehat{H}|2\rangle c_2(t)$$

Get two equations by multiplying on the left by $\langle 1|$ and by $\langle 2|$.

$$\boxed{\begin{aligned} \frac{\partial c_1(t)}{\partial t} &= -i\frac{H_{11}}{\hbar}c_1(t) - i\frac{H_{12}}{\hbar}c_2(t) \\ \frac{\partial c_2(t)}{\partial t} &= -i\frac{H_{21}}{\hbar}c_1(t) - i\frac{H_{22}}{\hbar}c_2(t) \end{aligned}}$$

This is the ***exact*** two-state form of the Schroedinger equation.

Evolution if $c_1(0) = 1$ and $c_2(0) = 0$

c_1: $1 \rightarrow 0 \rightarrow$ **-1** $\rightarrow 0 \rightarrow 1$

c_2: $0 \rightarrow$ **-i** $\rightarrow 0 \rightarrow i \rightarrow 0$

We see that the result is a periodic return to the initial state--the characteristic of ***resonance.***
In terms of the state function (vector):

$$|1\rangle \rightarrow \frac{|1\rangle - i|2\rangle}{\sqrt{2}} \rightarrow -i|2\rangle \rightarrow \frac{-|1\rangle - i|2\rangle}{\sqrt{2}} \rightarrow -|1\rangle \rightarrow \frac{-|1\rangle + i|2\rangle}{\sqrt{2}} \rightarrow i|2\rangle \rightarrow \frac{|1\rangle + i|2\rangle}{\sqrt{2}} \rightarrow |1\rangle$$

$$\boxed{-i = e^{-\frac{i\pi}{2}} = \cos(90) - i\sin(90) = -i}$$

Precisely the SAME information can be expressed with the more useful products of the coefficients, i.e., the **density matrix.**

$$|\Psi\rangle\langle\Psi| = (c_1|1\rangle + c_2|2\rangle)(c_1^*\langle 1| + c_2^*\langle 2|)$$

$$= c_1c_1^*|1\rangle\langle 1| + c_1c_2^*|1\rangle\langle 2| +$$

$$c_2c_1^*|2\rangle\langle 1| + c_2c_2^*|2\rangle\langle 2| \text{ , which defines the density matrix,}$$

$$\rho(t) = \begin{pmatrix} c_1c_1^* & c_1c_2^* \\ c_2c_1^* & c_2c_2^* \end{pmatrix} = \begin{pmatrix} \cos^2(\omega t) & i\cos(\omega t)\sin(\omega t) \\ -i\cos(\omega t)\sin(\omega t) & \sin^2(\omega t) \end{pmatrix}$$

Time Evolution of the Density:

The **Feynman-Vernon-Hellwarth** Equations

This starts with the Liouville Equation, which Follows easily from the Schroedinger Equation

$$|\dot{\psi}\rangle = -i\mathcal{H}|\psi\rangle$$

$$\langle\dot{\psi}| = i\langle\psi|\mathcal{H}^\dagger \qquad \text{Hermitian Conjugate}$$

$$\dot{\rho} = \frac{d\,|\psi\rangle\langle\psi|}{dt} = |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}|$$

A. Getting to Know F.V.H Equations

1. The 3 Cases from NOTES

Case 1 $\quad H_{11} = H_{22}$, $\quad H_{12} = H_{21}$ = real & positive

(Resonance) $\quad$, $\psi(0) = |1\rangle$, $\rho_{11}(0) = 1$

Ω_x = Positive $\qquad \rho_{22}(0) = 0$

$\Omega_y = 0 \qquad \rho_{12}(0) = \rho_{21}(0) = 0$

$\Omega_z = H_{11} - H_{22} = 0$

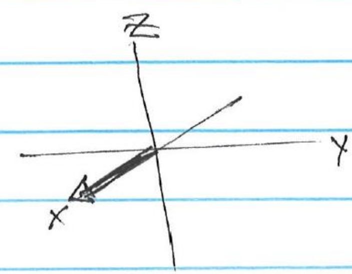
$$\rho_x = \rho_{12} + \rho_{21} = 0$$

$$\rho_y = -i(\rho_{12} - \rho_{21}) = 0$$

$$\rho_z = \rho_{11} - \rho_{22} = 1$$

$$\rho(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$\vec{\Omega} =$



Cross product rules

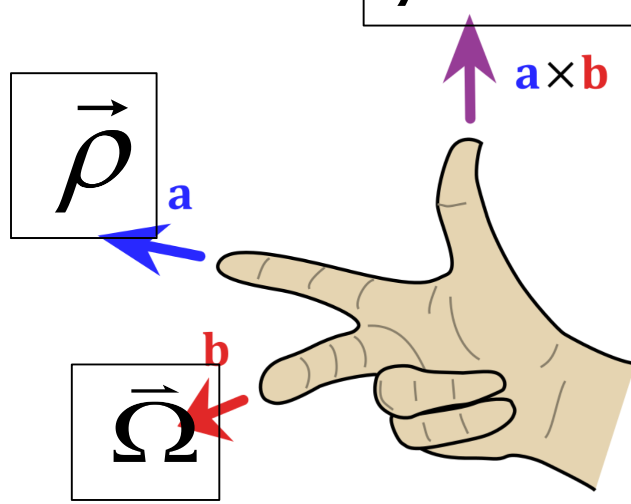
i, j, k = unit vectors pointing in x, y z directions

i x j = k   j x k = i,   k x i = j

j x i =-k   k x j = -i,   i x k = -j

Right hand rule

$$\boxed{\vec{\rho}\times\vec{\Omega}=\dot{\vec{\rho}}}$$



$$\dot{\vec{\rho}} = \vec{\rho}\times\vec{\Omega}$$

$$\dot{\rho}_x = \rho_y\Omega_z - \rho_z\Omega_x$$

$$\dot{\rho}_y = \rho_z\Omega_x - \rho_x\Omega_z$$

$$\dot{\rho}_z = \rho_x\Omega_y - \rho_y\Omega_{zx}$$

from NOTES 8, p. 4

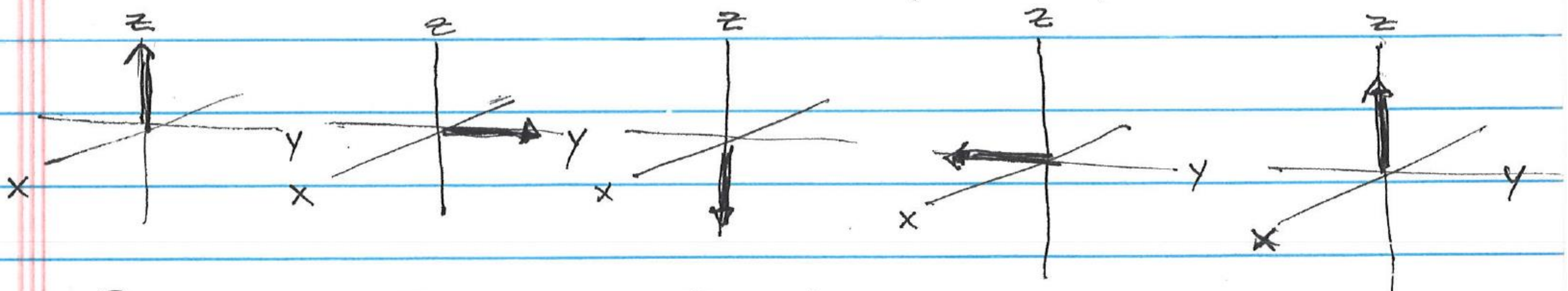
Case 1

$\psi = c_1 |1\rangle + c_2 |2\rangle \qquad c_1 = \cos\omega t \qquad -i\sin\omega t$

$$\omega = \frac{H_{12}}{\hbar}$$

ωt:	0	$\pi/4$	$\frac{\pi}{2}$	$\frac{3\pi}{4}$	π
$\psi =$	$\|1\rangle$	$\frac{\|1\rangle - i\|2\rangle}{\sqrt{2}}$	$-i\|2\rangle$	$\frac{-\|1\rangle - i\|2\rangle}{\sqrt{2}}$	$-\|1\rangle$
$\underset{\approx}{\rho}$	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1/2 & +i/2 \\ -i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -i/2 \\ i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$

$\vec{e}$



	$e_z = 1$	$e_y = 1$	$e_z = -1$	$e_y = -1$	$e_z = 1$
$2\omega t$	0	$\pi/2$	π	$\frac{3\pi}{2}$	2π

Notes: • Density is periodic with frequency = $2\omega t$

Rabi frequency $= 2\omega = \frac{2H_{12}}{\hbar} = \omega_1$

• a "$\frac{\pi}{2}$ pulse" equalizes population

• a "π pulse" inverts population

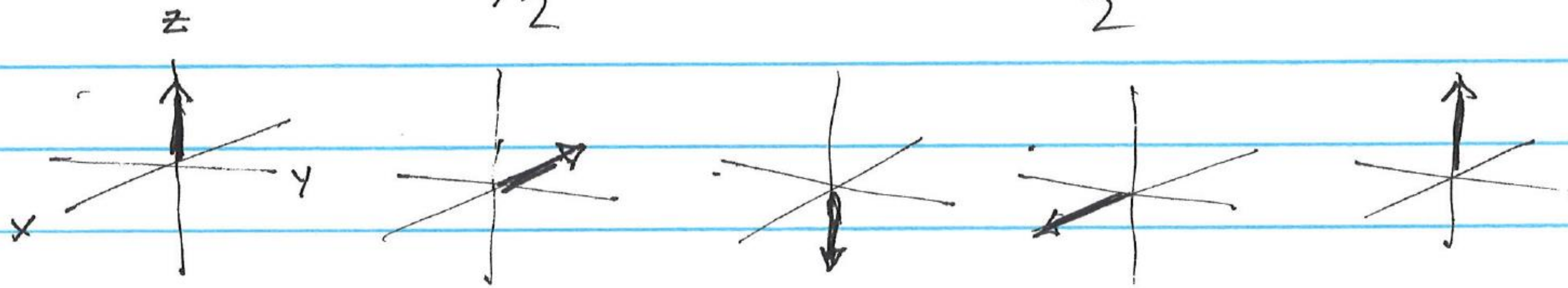
Where ρ_{11} & ρ_{22} = population of states 1 & 2

Case 2 : $H_{11} = H_{22}$ H_{12} = pure imaginary.

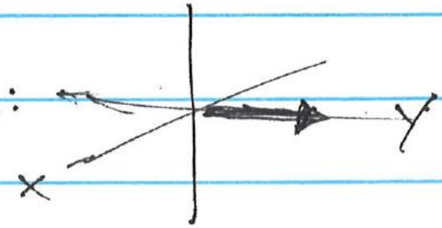
Ω_y = positive $\Omega_x = \Omega_z = 0$

$\psi(0) = |1\rangle$

$2\omega t$	0	$\pi/2$	π	$\frac{3\pi}{2}$	2π



$\vec{\Omega}$:



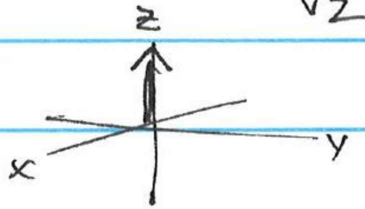
Case 1 & 2 = pure nutation

Case 3 $H_{11} - H_{22} > 0$ $H_{12} = 0$

Ω_z = positive $\Omega_x = \Omega_y = 0$

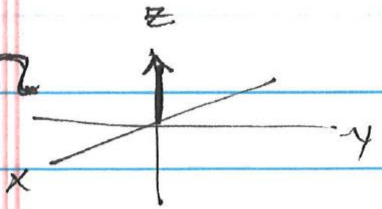
$\psi(0) = \frac{|1\rangle + |2\rangle}{\sqrt{2}}$ $\rho_x = 1$ $\rho_z = \rho_y = 0$

Ω



$$\rho_{12} = C_1^{(0)} C_2^{*(0)} e^{-i(E_1 - E_2)t/\hbar} = \frac{1}{2} e^{-i\omega t}$$

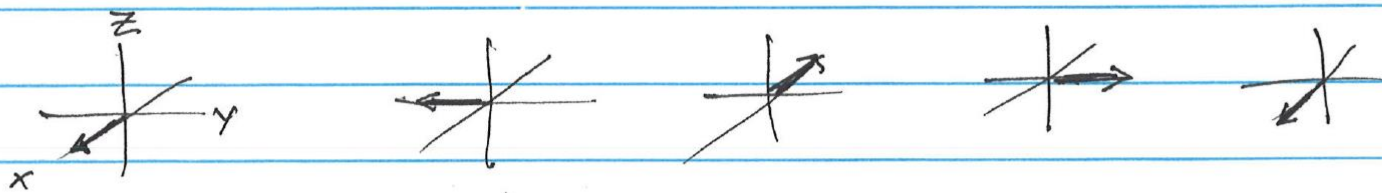
ω = Larmor Frequency

Ω 

$H_{12} = H_{21} = 0 \quad \Omega_x = \Omega_y = 0$

Free Precession

ωt	0	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$	2π
$\underset{\sim}{\rho}$	$\begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -i/2 \\ i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & i/2 \\ -i/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$
ρ_x	1	0	-1	0	1
ρ_y	0	-1	0	1	0
ρ_z	0	0	0	0	0

$\vec{\rho}$ 

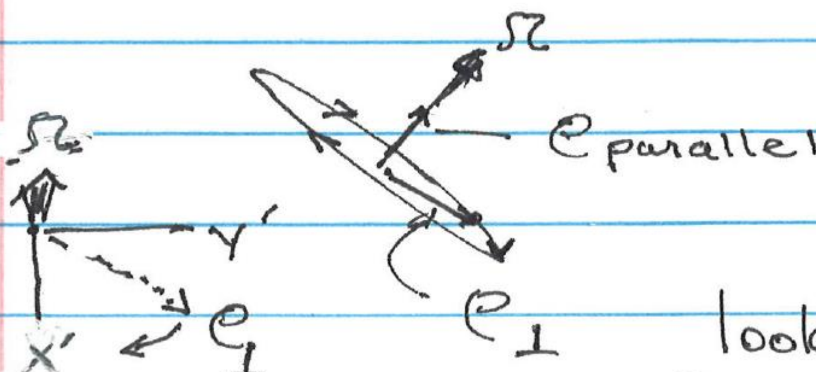
General Case.

$H_{11} \neq H_{22}$

$H_{12} = a + ib$

$$\vec{\Omega} = 2a\,\vec{i} + 2b\,\vec{j} + (H_{11} - H_{22})\,\vec{k}$$

$\vec{e}$ has a component $\perp$ to $\vec{\Omega}$ and a component parallel to $\vec{\Omega}$



precession of $e_\perp$ is by <u>LEFT HAND RULE</u> (in most books), i.e., looking in $-\vec{\Omega}$ direction the $e_\perp$ moves <u>clockwise</u>