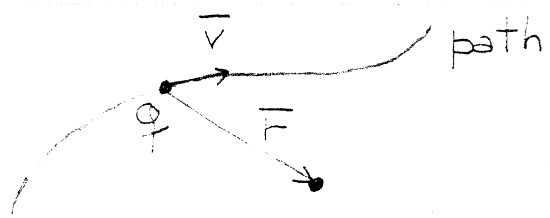
Section I: INTRODUCTION

Bibliography: - Slichter 2.1 to 2.6; 5.4
- Harris: 1.1 to 1.6; 2.1 to 2.4

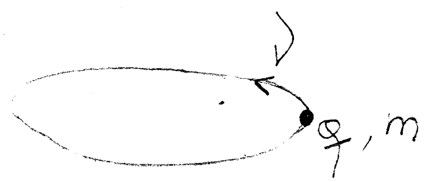
I.1 MOTION OF CHARGED PARTICLES: MAGNETIC MOMENTS

In general, moving charges (currents) will generate magnetic fields:



$$\bar{B} = \underbrace{\frac{\mu_0}{4\pi}}_{10^{-7}} I \int \frac{d\bar{l} \times \bar{r}}{r^3}$$

This equation can be integrated easily in some cases, e.g., for a circular current:



Units: $[\nu]$: $\frac{\text{cycles}}{\text{sec}}$ or $\frac{\text{rev.}}{\text{sec}}$ = Hz

$[\omega]$: $\frac{\text{rad}}{\text{sec}} \Rightarrow \nu = \frac{\omega}{2\pi}$

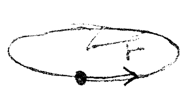
The field **B$_{loop}$** produced at long distances **R = (x,y,z)** is given by

$\bar{R} = (x, y, z)$

$$B_z(R) = \left(\frac{\mu_0}{4\pi}\right) \mu \left(\frac{3z^2 - R^2}{R^5}\right)$$

$$B_x(R) = \left(\frac{\mu_0}{4\pi}\right) \cdot \mu \frac{xz}{R^5}$$

$$B_y(R) = \left(\frac{\mu_0}{4\pi}\right) \cdot \mu \frac{yz}{R^5}$$



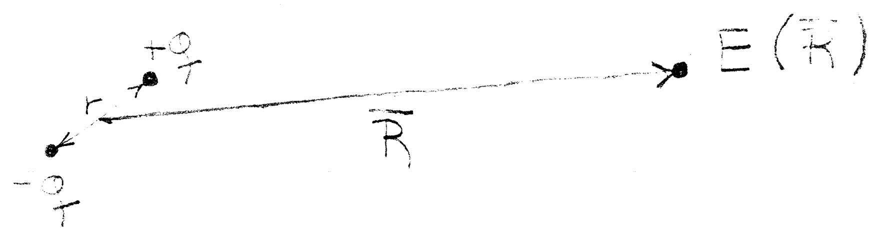
$I = q \cdot \nu$

with:

$\mu = I \cdot (\text{area of loop})$

$= \pi r^2 q \nu$

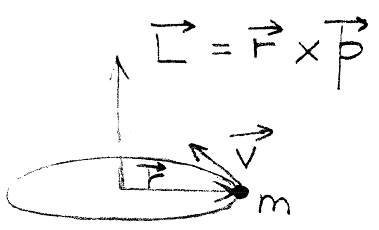
The angular and distance dependence of this magnetic field are analogous to the ones characterizing an electric field produced by an electric dipole



=>A loop of current can be considered as a **magnetic dipole**;

a vector whose
- **magnitude** = $|\bar{\mu}| = I\cdot$(area of loop)
- **orientation**: perpendicular to the loop

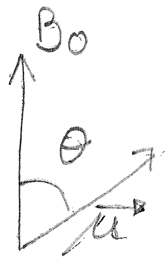
There is another physical quantity used to described circular motions: **angular momentum L**, a constant of motion



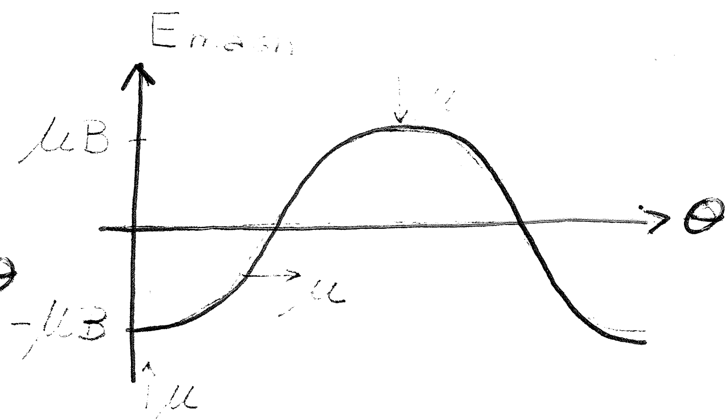
$\vec{L}$
- **magnitude** = $|\bar{L}| = r\cdot m\cdot|v_{\perp}| = 2\pi\nu r^2 m$
- **orientation**:perpendicular to the orbit

=> if the particle is charged, $\vec{L} /\!/ \vec{\mu}$: $\boxed{\vec{\mu} = \left(\frac{q}{2m}\right)\cdot\vec{L}}$

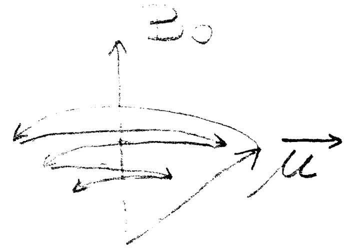
A magnetic moment not only produces a field, it can also interact with ~~one~~ an external field:



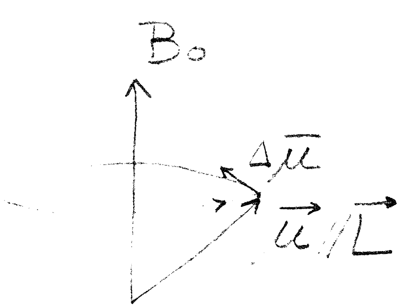
$$E_{magn} = -\vec{\mu}\cdot\vec{B} = -\mu B\cos\theta$$



If there ~~would be~~ were not no angular momentum $\vec{\mu}$ would oscillate



Since there is an $\vec{L} \neq 0$ if $\vec{\mu} \neq 0$ however, we have a motion similar to that of a gyroscope



$$d\vec{L} = \text{torque} = \vec{\mu} \times \vec{B_0}$$

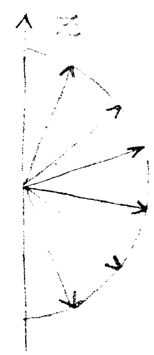
$$\Rightarrow \boxed{\frac{d\vec{\mu}}{dt} = \frac{q}{2m}\,\vec{\mu} \times \vec{B_0}}$$

H.W. Calculate the period of this motion

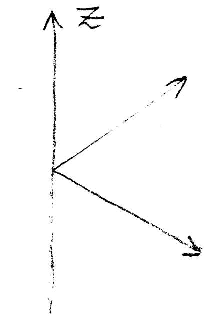
I.2 THE SPIN

Elementary particles (n, p, e) possess a very special angular momentum: **the spin**

classic $\vec{L}$



spin $\vec{S}$



arbitrary number of orientations

only 2 orientations allowed

In the case of nuclei with spin, the number of possible orientations is given by, $\boxed{2 \cdot S+1}$, S = 0, 1/2, 1, 3/2, ...

spin quantum number

The spin of an atomic nucleus depends on:

Z = #protons (atomic number), and **A** = #protons + #neutrons (atomic weight)

If:

Z even, A even (e.g. ^{12}C, ^{16}O) => **no spin**

$$\left.\begin{array}{l}\text{Z even, A odd (e.g. } ^{13}C,\ ^{31}P) \\ \text{Z odd, A even (e.g. } ^{14}N,\ ^{2}H)\end{array}\right\} \Rightarrow \textbf{spin} \geq \textbf{1/2}$$

For a particle of spin S, the total angular momentum of $\vec{S}$

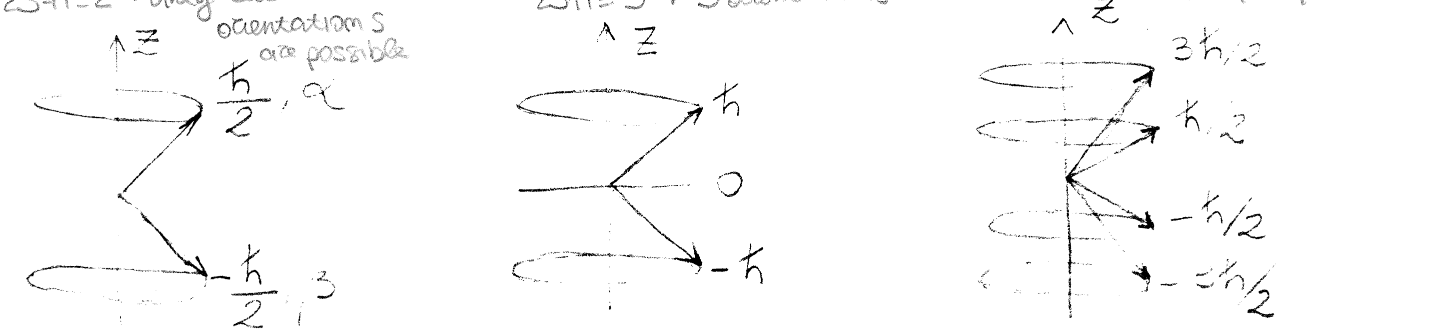
$$|\vec{S}| = \hbar\sqrt{S(S+1)}$$

and the z-component is quantized in units of $\hbar$; it can only be $\hbar m_S$, where $m_S = -S, -S+1, \ldots, S-1, S$

s = 1/2, $|\vec{S}|$ = 0.866 — 2S+1=2 → only two orientations are possible

s = 1, $|\vec{S}|$ = 1.41 — 2S+1=3 → 3 orientations

s = 3/2, $|\vec{S}|$ = 1.93 — 2S+1=4 → 4 orientations



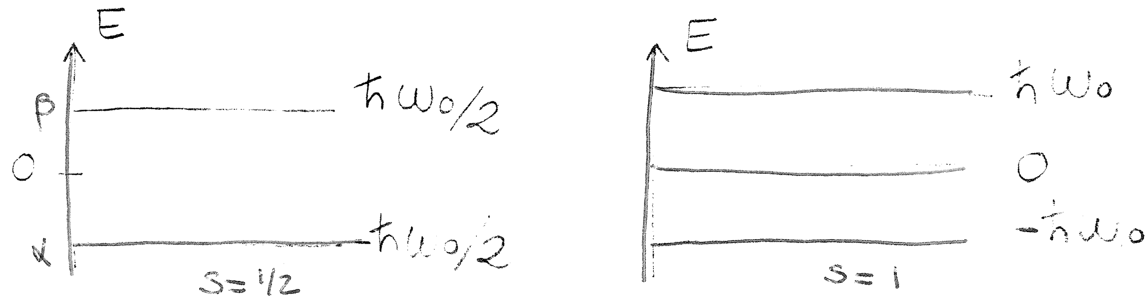
If the particle is charged, it will also have a quantized magnetic moment μ:

$$\boxed{\vec{\mu} = \gamma\hbar\,\vec{S}}$$

The **energy** of a nuclear system in a magnetic field will therefore also be quantized:

$$E = -\vec{\mu}\cdot B_0 = -S_z\hbar\gamma B_0 = -\underbrace{m_S}_{\text{va da } -S \text{ a } +S}\hbar\overbrace{\gamma B_0}^{\omega_0 = \text{LARMOR FREQUENCY}}$$

$$\Rightarrow \boxed{E_{m_S} = -m_S\hbar\omega_0}$$



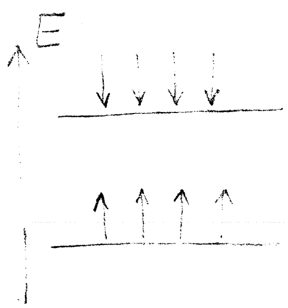
The basic goal of **nuclear magnetic resonance** (NMR) is to determine the value of ω_0

I.3 THE MAGNETIZATION

macroscopic

We have an ensemble of N spins 1/2 in a magnetic field

$$E_{m_s} = -m_s \hbar\omega_0$$



$N_\beta, \; E_\beta \simeq \hbar\omega_0/2$

$N_\alpha, \; E_\alpha \simeq -\hbar\omega_0/2$

$$\frac{N_\beta}{N_\alpha} = \frac{e^{-E_\beta/kT}}{e^{-E_\alpha/kT}} = e^{-\hbar\omega_0/kT} \simeq 1 - \frac{\hbar\omega_0}{kT}$$

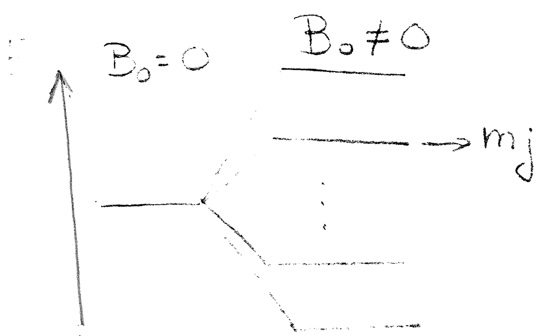
$1-x$

and $N_{TOTAL} = N_\alpha + N_\beta$

$$\left.\begin{aligned} N_\alpha &= \frac{N_{TOTAL}}{2}\left(1 + \frac{\hbar\omega_0}{2kT}\right) \\ N_\beta &= \frac{N_{TOTAL}}{2}\left(1 - \frac{\hbar\omega_0}{2kT}\right) \end{aligned}\right\}$$

At 300 K, 300 MHz = $\nu_0 = \omega_0/2\pi$ $\quad \frac{\hbar\omega_0}{2kT} \approx 10^{-5}$ and $\frac{N_\beta}{N_\alpha} \simeq 1$

In general, for a state j with quantum number m_j ($-S \le m_j \le S$); $\Rightarrow 2S+1$ values



$$\Rightarrow N_j = \frac{N_{TOTAL}}{2S+1}\left(1 + m_j \frac{\hbar\omega_0}{kT}\right)$$

Demonstrates this.

HW what is the population of each level?

we do not have magnetization in x-y plane

The fact that the populations are not the same creates a net **magnetization** $\vec{M_0}$:

$$\vec{M_0} = \sum_j \vec{\mu_j} \cdot N_j$$

Since the only anisotropy occurs along the z axis, for a spin 1/2 system we have a value of M_0 given by:

$$\boxed{\mu = \gamma \hbar m_s}$$

$$M_0 = N_\alpha \cdot (\mu_\alpha)_z + N_\beta (\mu_\beta)_z$$

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

$$N_\alpha = \frac{N_{TOT}}{2}\left(1 + \frac{\hbar\omega_0}{2KT}\right)$$

$$N_\beta = \frac{N_{TOT}}{2}\left(1 - \frac{\hbar\omega_0}{2KT}\right)$$

$$= \frac{N_{TOTAL}}{2} \cdot \frac{\hbar \omega_0}{2kT} \cdot \gamma \hbar$$

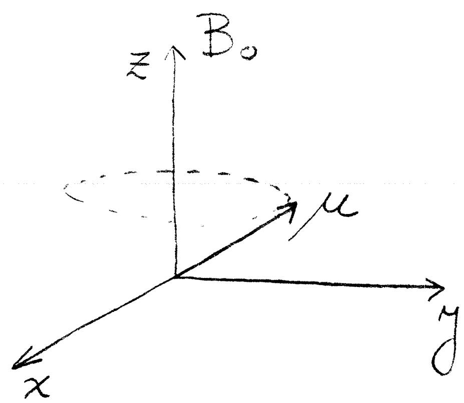
$\omega_0 = \gamma B_0 \Longrightarrow$

$$\boxed{M_0 = \frac{N_{TOT}\gamma^2 \hbar^2 B_0}{4kT}}$$

$\omega = \gamma B_0$

I.4 CLASSICAL MOTION OF A SPIN

Let's assume that spins behave classically; i.e., like little magnets $\vec{\mu}$

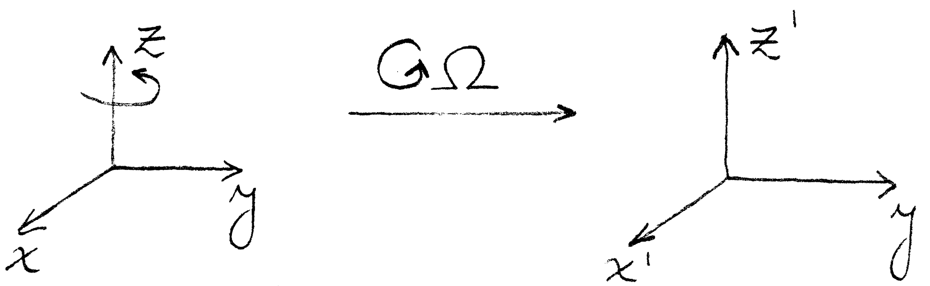


precession

$$(1) \quad \frac{d\vec{\mu}}{dt} = \vec{\mu}(t) \times \gamma B_o$$

the orientation of $\vec{\mu}$ changes according to (1)

To solve this differential equation we go into a frame rotating at a rate Ω around z



$$\frac{d\vec{\mu}}{dt} \longrightarrow \frac{\partial\vec{\mu}}{\partial t} + \vec{\Omega} \times \vec{\mu}$$

$a \times b = -b \times a$

=> In the rotating frame:

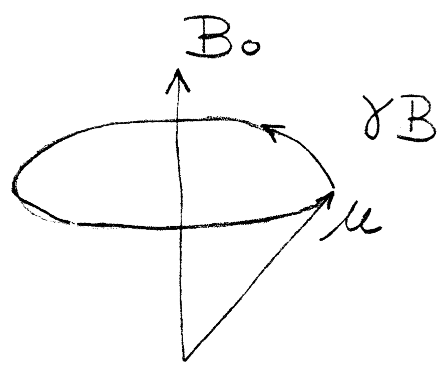
$$\frac{\partial\vec{\mu}}{\partial t} = \mu \times \underbrace{(\gamma B_o - \Omega)}_{B_{eff}}$$

B_{eff} : Effective field in rotating frame

This equation can be solved by assuming

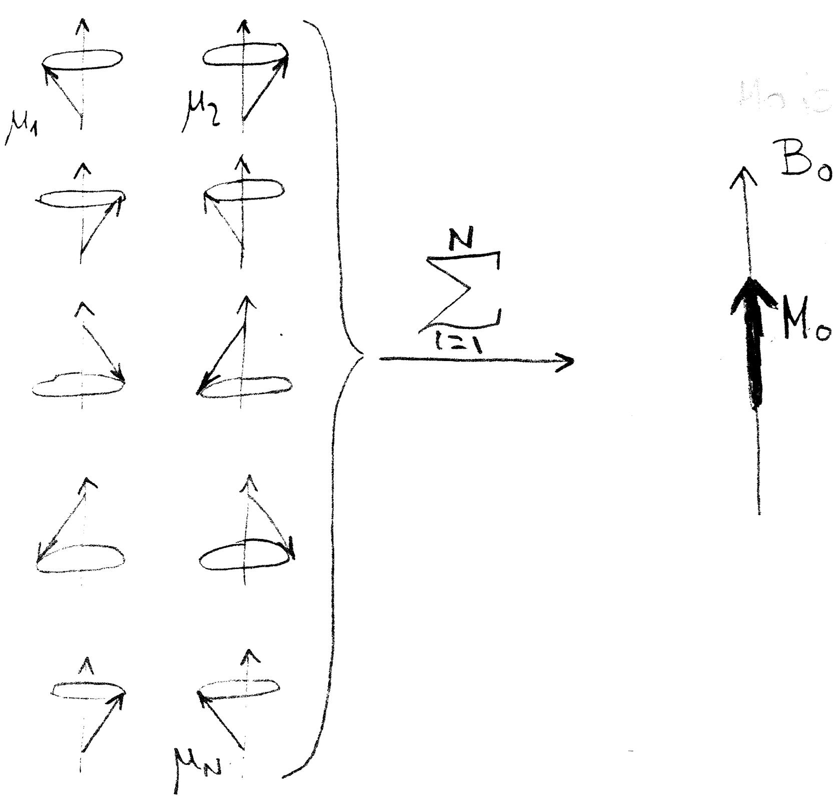
$$\Omega = \gamma B_0$$

Then, since $\frac{\partial \vec{\mu}}{\partial t} = 0$,it follows that $\vec{\mu}$ is constant in the rotating frame or equivalently, that $\vec{\mu}$ precesses at a rate γB_0 in the lab frame: **Larmor precession**



: Precession of an isolated classical spin

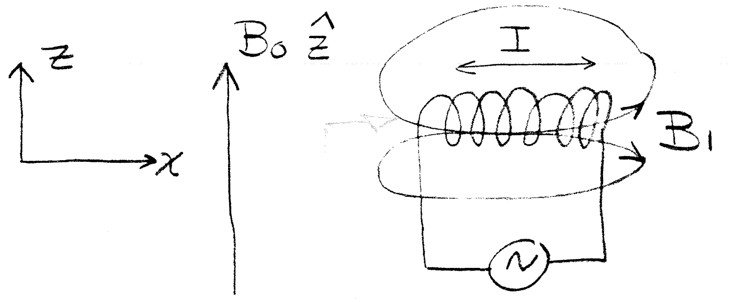
Even though individual spins precess, the net macroscopic magnetization remains static due to the lack of coherence in the x-y plane:



Since the equilibrated magnetization does not evolve in time, we cannot measure the ω_0.

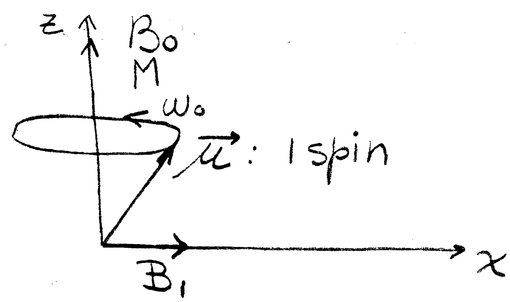
I.5 RF IRRADIATION OF THE SPINS AND THE ROTATING FRAME

Consider a spin 1/2 ensemble in a magnetic field $\mathbf{B_0}$; our goal is to measure $\nu_0 = \omega_0/2\pi$. We do this with the aid of an auxiliary oscillating magnetic field $\mathbf{B_1} \perp \mathbf{B_0}$, generated using an rf coil and an oscillating current source:

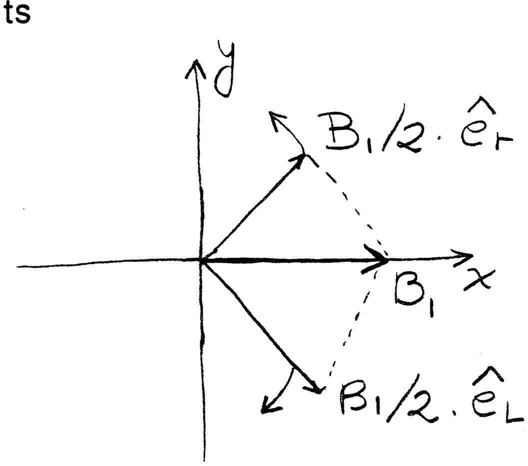


$$I = I_0 \cos(\omega t)$$
$$\Downarrow$$
$$B = B_1 \cos(\omega t + \varphi) \cdot \hat{x}$$
$$|B_1| \approx |10^{-4} B_0| \qquad \varphi \text{ arbitrary set to } 0$$

Classical Description:



A linearly polarized field $\mathbf{B_1}$ // x can be decomposed into 2 counterrotating components



$B_1/2 \cdot \hat{e}_r$ rotates at rate $+\omega$

$B_1/2 \cdot \hat{e}_L$ rotates at rate $-\omega$ (disregard)

The behavior of $\vec{\mu}$:

LAB. FRAME

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{B}$$
$$= \gamma\vec{\mu} \times \left(B_0 \hat{z} + \frac{B_1}{2} \hat{e}_r\right)$$
$$= \gamma\vec{\mu} \times \left[B_0 \hat{z} + \frac{B_1}{2}\left(\cos(\omega t)\cdot\hat{x} + \sin(\omega t)\cdot\hat{y}\right)\right]$$

We go to a reference frame rotating at the rate of $\mathbf{B_1}$ (ω) =>

ROTATING FRAME

$$\frac{\delta\vec{\mu}}{\delta t} = \gamma\vec{\mu} \times \left[\left(B_0 - \frac{\omega}{\gamma}\right)\hat{z} + \frac{B_1}{2}\hat{x}\right]$$

$\omega_1 = \frac{\gamma B_1}{2}$: rate of precession about x

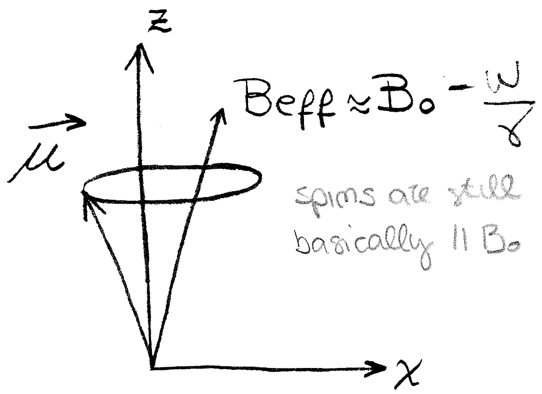
$$= \vec{\mu} \times \left[\underbrace{(\omega_0 - \omega)}_{\Delta\omega \text{ : offset}}\hat{z} + \omega_1 \hat{x}\right]$$

In this rotating frame, there is a precession of $\vec{\mu}$ about

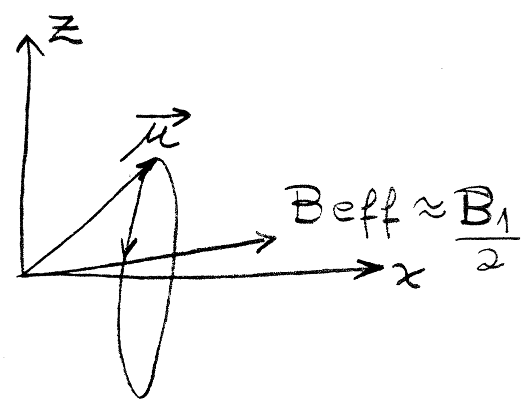
EFFECTIVE FIELD IN THE ROTATING FRAME

$$\boxed{\vec{B}_{eff} = \frac{B_1}{2}\hat{x} + (B_0 - \omega/\gamma)\hat{z}}$$

When $(\mathbf{B_0} - \omega/\gamma) \gg \mathbf{B_1}$ $\qquad$ $(\mathbf{B_0} - \omega/\gamma) \ll \mathbf{B_1}$



off-resonance



<u>on-resonance</u>

$\mathbf{B_1}$ can tilt $\vec{\mu}$ even though it is much smaller than $\mathbf{B_0}$

Cohen-Tannoudji Ch 4

I.6 QUANTUM MECHANICS - REVIEW

(Goldman Ch. 2)

Cohen-Tannoudji Ch 1)

The quantization of the angular momentum cannot be described in classical terms; in order to fully understand its properties one has to resort to quantum mechanics.

In quantum mechanics
- a state is given by a wave function $|\mu>$ (ket)
- events and observables are given by operators $\mathcal{O}$

For instance for a spin 1/2, the measurement of angular momentum can give only 2 results

$\uparrow \; |\alpha>$

$\downarrow \; |\beta>$

The measurement of the spin angular momentum along $\begin{Bmatrix} x \\ y \\ z \end{Bmatrix}$ is represented by three operators $\begin{Bmatrix} S_x \\ S_y \\ S_z \end{Bmatrix}$

Measuring S_z :

$$\underbrace{S_z}_{\text{op.}} \underbrace{|\alpha>}_{\text{func.}} = \underbrace{\frac{\hbar}{2}}_{\text{scalar}} \underbrace{|\alpha>}_{\text{func.}} \Rightarrow$$

$$S_z |\beta> = -\frac{\hbar}{2} |\beta>$$

$|\alpha>$, $|\beta>$ are eigenfunctions of S_z

Let us take a look at what states and operators look like in this new (Hilbert) space

We define vectors (kets) according to their expansions on a basis set:

$$|\Psi\rangle = \sum_i a_i \, |i\rangle$$

This is similar to what we do in $\mathbb{R}^3$-space with vectors, except for a few differences

_The $\{a_i\}$ can be complex numbers
_The dimensionality depends on the system (spin number, coupled spins, etc.)

Important basis sets are those whose components are orthogonal:

$$\text{PRODUCT}\left\{|i\rangle, |j\rangle\right\} = \begin{cases} 1, & \text{if } i=j \\ 0, & \text{OTHERWISE} \end{cases}$$

We describe such products as

$$\underbrace{\langle j|}_{\text{BRA}}\underbrace{\,i\rangle}_{\text{KET}} = \delta_{ij} : \text{Kronecker delta}$$

<u>Dirac Notation</u>

The bra ("<j|") is another type of vector, <u>conjugated</u> to the ket |j>

The product of a bra |i> times a ket <j| (a bracket) is always a complex scalar, even if the states are not orthogonal. This scalar product tells about how much "j" character there is in the "i" state, and viceversa.

It follows that we can expand any state $|\psi\rangle$ as

$$|\psi\rangle = \underbrace{\sum_i \langle i|\psi\rangle |i\rangle = \sum |i\rangle\langle i|\psi\rangle}_{\text{SCALARS COMMUTE WITH STATES \& OPERATORS}} \quad (*)$$

$\langle i|\psi\rangle$: projection of ket state $|\psi\rangle$ into basis element $|i\rangle$

Similarly

$$\langle\psi| = \sum_i \langle\psi|i\rangle\langle i| \qquad (**)$$

(*) and (**) hold for arbitrary ψ's $\Longrightarrow$ it must be truth that

$$\boxed{\sum_i |i\rangle\langle i| = \mathbb{1}}$$

No information is lost by projecting onto a complete orthonormal basis set.

A convenient way of representing bra's & ket's is as vectors

$$|\psi\rangle = \sum_{i=1}^{N} a_i |i\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} ; \quad \langle\psi| = \sum_{i=1}^{N} a_i^* \langle i| = (a_1^*, a_2^*, \ldots, a_N^*)$$

WHERE $\langle i|\psi\rangle = (\langle\psi|i\rangle)^*$

$\Longrightarrow$ $\langle\psi|\varphi\rangle$ can be calculated as a conventional matrix multiplication

$$\Rightarrow \langle\psi|\psi\rangle = \sum_{i=1}^{N} |a_i|^2 . \quad \text{If } \langle\psi|\psi\rangle = 1 \Rightarrow |\psi\rangle \text{ is normalized}$$

If kets are Nx1 vectors, then operators are NxN matrices.

Dem:

Given $|\psi\rangle = \sum a_i |i\rangle$, we compute $|\varphi\rangle = \mathcal{O}|\psi\rangle$

$$|\varphi\rangle = \sum_{i=1}^{N} b_i |i\rangle$$

$$\mathcal{O}|\psi\rangle = 1\cdot\mathcal{O}\cdot 1|\psi\rangle = \left(\sum_i |i\rangle\langle i|\right)\cdot\mathcal{O}\cdot\left(\sum_j |j\rangle\langle j|\right)|\psi\rangle$$

$$= \sum_i \sum_j |i\rangle\langle i|\mathcal{O}|j\rangle\underbrace{\langle j|\psi\rangle}_{a_j}$$

$$= \sum_i \left(\sum_j \langle i|\mathcal{O}|j\rangle a_j\right)|i\rangle$$

$$b_i = \sum_{j=1}^{N} \mathcal{O}_{ij}\, a_j$$: MATRIX MULTIPLICATION OF $\mathcal{O} \times a$

$$\begin{pmatrix} b_1 \\ \vdots \\ b_N \end{pmatrix} = \begin{pmatrix} \mathcal{O}_{11} & \cdots & \mathcal{O}_{1N} \\ & & \\ \mathcal{O}_{N1} & & \mathcal{O}_{NN} \end{pmatrix}\begin{pmatrix} a_1 \\ \vdots \\ a_N \end{pmatrix}$$

In the same manner as we defined conjugate states (bra's), we can define conjugate operators $\mathcal{O}^+$:

$$\boxed{\mathcal{O}|\psi\rangle = |\varphi\rangle \Longleftrightarrow \langle\varphi| = \langle\psi|\mathcal{O}^+}$$

The elements of $\mathcal{O}^+$ can be found from the expression of $\mathcal{O}$

$$\boxed{(\mathcal{O}^+)_{ij} = (\mathcal{O})_{ji}^*}$$

Since operators are matrices, they won't, in general, commute among themselves

$$\mathcal{O}\cdot\mathcal{P} \neq \mathcal{P}\cdot\mathcal{O} \Rightarrow [\mathcal{O},\mathcal{P}] = \mathcal{O}\cdot\mathcal{P} - \mathcal{P}\cdot\mathcal{O} \neq 0$$

They will, however, commute with complex scalars

$$a\cdot\mathcal{O} = \mathcal{O}\cdot a \quad ; \quad a \in \mathbb{C}$$

A very important property of our operators is that they can satisfy an eigenvalue equation:

$$\boxed{\mathcal{O}\underbrace{|\psi\rangle}_{\text{EIGENVECTOR}} = \underbrace{\lambda}_{\text{EIGENVALUE}}\cdot|\psi\rangle}$$

NxN operators can have up to N eigenvectors and N eigenvalues. To find them:

$$|\psi\rangle = \sum_j a_j |j\rangle \Rightarrow$$

$$\Rightarrow \mathcal{O}|\psi\rangle = \lambda|\psi\rangle \Leftrightarrow (\mathcal{O} - \lambda\cdot\mathbb{1})|\psi\rangle = 0 \Leftrightarrow$$

$$\Leftrightarrow \sum_j (\mathcal{O}_{ij} - \lambda\cdot\delta_{ij})\cdot a_j = 0 \quad \text{FOR EACH } i = 1\ldots N$$

This system of simultaneous equations only has non-trivial solutions if

$$\text{DETERMINANT}(\mathcal{O}-\lambda\cdot\mathbb{1}) = \begin{vmatrix} \sigma_{11}-\lambda & \sigma_{12} & \cdots & \sigma_{1N} \\ \vdots & \sigma_{22}-\lambda & & \vdots \\ \vdots & & & \vdots \\ \sigma_{N1} & & & \sigma_{NN}-\lambda \end{vmatrix} = 0$$

This is a polynomial of power λ^N. We solve for its roots $\{\lambda_i\}_{i=1\ldots N}$; for each root we solve the simultaneous equations to find the $\{a_j\}_{j=1\ldots N}$, using the fact that $\sum_j |a_j|^2 = 1$

Here are some important facts about operators.

_To each physical observable O (position, energy, angular momentum) quantum mechanics associates an operator $\mathcal{O}$.

_The only values that we can measure for O are the eigenvalues of the operator $\mathcal{O}$: $\{\sigma_j\}_{j=1...N}$
If this statement is to have physical meaning, then the σ_j's have to be real.
This happens if $\mathcal{O}$ is **hermitian**:

$$\boxed{\mathcal{O} = \mathcal{O}^{+} \Longleftrightarrow \mathcal{O}_{ij} = (\mathcal{O}_{ji})^{*}}$$

_Given a state described by a wavefunction $|\psi\rangle$, we can expand it using $\mathcal{O}$'s eigenstates as a basis set; i.e.

$$\mathcal{O}|j\rangle = \sigma_j |j\rangle \quad ; \; j = 1, \ldots, N$$

$$|\psi\rangle = \sum_{j=1}^{N} c_j |j\rangle$$ (the |j>'s are a complete basis set)

Then the average value of O that we can expect to measure is given by

$$\langle O \rangle = \langle \psi | \mathcal{O} | \psi \rangle$$

$$= \left\{\sum_j c_j^* \langle j|\right\} \mathcal{O} \left\{\sum_i c_i |i\rangle\right\} = \left\{\sum_j c_j^* \langle j|\right\} \left\{\sum_i c_i \underbrace{\mathcal{O}|i\rangle}_{\sigma_i |i\rangle}\right\}$$

$$= \sum_j c_j^* \left\{\sum_i c_i \sigma_i \underbrace{\langle j | i \rangle}_{\delta_{ij}}\right\} =$$

$$\Longrightarrow \boxed{\langle O \rangle = \sum_j c_j^* c_j \sigma_j}$$

$|c_j|^2$: PROBABILITY OF MEASURING σ_j IN AN EXPERIMENT

A fundamental operator is the **Hamiltonian** $\mathcal{H}$: the operator that describes the possible energy levels of the system

$$\boxed{\mathcal{H}|\mu\rangle = E|\mu\rangle}$$

Time-independent Schroedinger equation

In general, $\mathcal{H}$ has several eigenfunctions:

$$\mathcal{H}|\mu_j\rangle = E_j|\mu_j\rangle \quad ; \quad |\mu_j\rangle : \text{stationary states}$$

then, a general state $|\Psi\rangle$ will be given by the linear combination

$$|\Psi\rangle = \sum_j c_j |\mu_j\rangle$$

Where $\{c_j\}$ is a set of complex numbers

$$\sum_j |c_j|^2 = 1$$

and $\{|\mu_j\rangle\}$ is a basis set fulfilling

$$\sum_j |\mu_j\rangle\langle\mu_j| = 1$$

$\mathcal{H}$ also determines the time evolution of a wave function

$$\boxed{-\frac{\hbar}{i}\frac{\partial}{\partial t}|\mu\rangle = \mathcal{H}|\mu\rangle}$$

Time-dependent Schroedinger equation

Then, given

If you know $|\psi(t=0)\rangle$ then you are able to find it at any time "t"

$$|\Psi(t=0)\rangle = \sum_j c_j |u_j\rangle$$

AND $$-\frac{\hbar}{i}\frac{\partial|\Psi\rangle}{\partial t} = \mathcal{H}|\Psi\rangle$$

WE TRY TO CALCULATE $|\Psi(t)\rangle$ FOR ARBITRARY TIMES.

WE KNOW THAT:

$$|\Psi(t)\rangle = \sum_j c_j(t)|u_j\rangle$$

$$> -\frac{\hbar}{i}\frac{\partial|\Psi\rangle}{\partial t} = -\frac{\hbar}{i}\sum_j \frac{dc_j(t)}{dt}|u_j\rangle$$

$$\mathcal{H}|\Psi\rangle = \sum_j c_j(t)\mathcal{H}|u_j\rangle = \sum_j c_j(t)E_j|u_j\rangle$$

MULTIPLYING THESE 2 EXPRESSIONS BY $\langle u_j|$:

$$\frac{dc_j(t)}{dt} = -\left(\frac{i}{\hbar}\right)E_j c_j(t) \Rightarrow \boxed{c_j(t) = c_j^0 e^{-i\underbrace{\frac{E_j}{\hbar}}_{\omega_j}t}}$$

ω_j : BOHR FREQUENCY

I.7 SPIN OPERATORS

The angular momentum of the spin is given by 3 operators

$$\{ S_x, S_y, S_z \}$$

fulfilling $\boxed{[S_i, S_j] = i\,\varepsilon_{ijk} S_k}$

$$\varepsilon_{ijk} = \begin{cases} 1 & i,j,k = x,y,z \text{ or cyclic permutations} \\ -1 & \text{otherwhise} \end{cases}$$

Since $[S_x, S_y] \neq 0$ => an eigenstate of S_z cannot at the same time be eigenstate of S_x, S_y. The eigenstates of S_z:

$$S_z |\alpha\rangle = \frac{\hbar}{2} |\alpha\rangle \qquad \text{or} \qquad S_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle$$

$$S_z |\beta\rangle = -\frac{\hbar}{2} |\beta\rangle \qquad\qquad S_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

We can represent S_z as a 2 x 2 matrix:

$$S_z = \begin{pmatrix} \langle\alpha|S_z|\alpha\rangle & \langle\alpha|S_z|\beta\rangle \\ \langle\beta|S_z|\alpha\rangle & \langle\beta|S_z|\beta\rangle \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

Fulfills the demand that for any observable O: $O_{ij} = O_{ji}^*$

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\beta\rangle \begin{pmatrix} 0 \\ 1 \end{pmatrix} \Rightarrow S_z |\alpha\rangle = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}|\alpha\rangle$$

$$\langle\alpha| = (1\ 0), \quad \langle\beta| (1\ 0)$$

$$S_z |\beta\rangle = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}|\beta\rangle$$

$$S_x |\alpha\rangle = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}|\beta\rangle$$

$$S_x |\beta\rangle = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}|\alpha\rangle$$

S_x, S_y connect states with $\Delta m = \pm 1$ (different z angular momentum)

Raising and lowering operators:

$$S_z \cdot S_x = (\ ) \, i S_y$$
$$S_z \cdot S_\pm = (\ ) \, S_\pm$$

$$S_+ = S_x + i S_y$$
$$S_- = S_x - i S_y$$

$$S_\pm |I, m\rangle = |I, m \pm 1\rangle$$

The total angular momentum $\vec{S}$:

$$S^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Rightarrow [S^2, S_i] = 0 \qquad i = x, y, z$$

If we forget about $\hbar$, $S_i = \frac{1}{2} \sigma_i$; $(\sigma_i)_{i=x,y,z}$ are the Pauli matrices, fulfilling

$$\sigma_i^2 = 1 \quad ; \quad \sigma_i \sigma_j = i \, \varepsilon_{ijk} \sigma_k \, ;$$

Let's go back to a spin 1/2 in a magnetic field. The quantum-mech. Hamiltonian of the system

$$\mathcal{H} = -\vec{\mu} \cdot \vec{B} \qquad : \text{GENERAL}$$

$$\vec{\mu} = \gamma \vec{S} \quad ; \quad \vec{B} = B_0 \cdot \hat{z}$$

$$\mathcal{H} = -\gamma B_0 S_z = -\omega_0 S_z$$

=> The eigenstates of $\mathcal{H} = \{ |\alpha\rangle, |\beta\rangle \}$

$$E_{1/2} = \hbar \omega_0 / 2$$
$$E_{-1/2} = -\hbar \omega_0 / 2$$

We use our new rules to evaluate the evolution of the system

In general my state is a linear combination of $|\alpha\rangle$ and $|\beta\rangle$

Initially, we start with a state $|\Psi\rangle = a^{o}_{1/2}\,|\alpha\rangle + a^{o}_{-1/2}\,|\beta\rangle$

$$a^{o}_{1/2} = a.e^{i\alpha}, \quad a^{o}_{-1/2} = b.e^{i\beta}, \quad a^2+b^2=1$$
$$a, b = \mathbb{R} \geq 0$$

$$\Rightarrow |\Psi(t)\rangle = a\, e^{i(\omega_o t/2 + \alpha)}|\alpha\rangle + b\, e^{i(-\omega_o t/2 + \beta)}|\beta\rangle$$

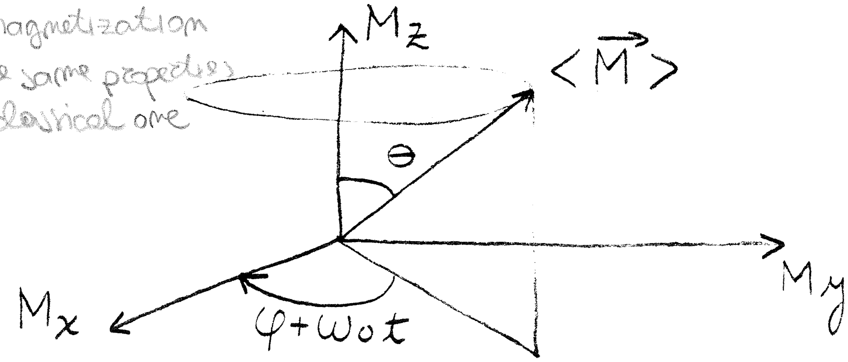
With $|\Psi\rangle$, we evaluate the time dependence of the magnetization

$$\langle \vec{M} \rangle = \gamma\hbar \begin{matrix} \langle S_x \rangle \\ \langle S_y \rangle \\ \langle S_z \rangle \end{matrix} \quad :$$

$$\begin{cases} \langle M_x(t)\rangle = abN\cos(\omega_o t + \varphi)\cdot(\gamma\hbar) & \text{(Eq. 2A)} \\ \langle M_y(t)\rangle = -abN\sin(\omega_o t + \varphi)\cdot(\gamma\hbar) & \text{(Eq. 2B)} \\ \langle M_z(t)\rangle = N(a^2-b^2)(\gamma\hbar/2) & \text{(Eq. 2C)} \end{cases}$$

$N = \#$ of spins

This magnetization have the same properties of the classical one



$$\varphi = \alpha - \beta$$

$$\cos\theta = 2a^2 - 1 = \begin{cases} 1 \longrightarrow a=1,\ b=0 \\ 0 \longrightarrow a=b=1/\sqrt{2} \\ -1 \longrightarrow a=0,\ b=1 \end{cases}$$

$$\langle S_z \rangle = \left(a^* e^{-i\left(\frac{\omega_o t}{2}\right)}\langle\alpha| + b^* e^{+\frac{i\omega_o t}{2}}\langle\beta|\right) S_z \left(a e^{i\left(\frac{\omega_o t}{2}\right)}|\alpha\rangle + b e^{-\frac{i\omega_o t}{2}}|b\rangle\right)$$

$$\Rightarrow |\psi(t)\rangle = \cos\frac{\theta}{2}\, e^{i(\varphi/2+\omega_0 t)} |\alpha\rangle + \operatorname{sen}\frac{\theta}{2}\, e^{-i(\varphi/2+\omega_0 t)} |\beta\rangle$$

{a,b} are related to the probability of finding $|\Psi(t)\rangle$ as $\{|\alpha\rangle \text{ or } |\beta\rangle\}$

$$\text{Prob}(|\alpha\rangle) = \text{rel. pop.}(|\alpha\rangle) = |\langle\alpha|\Psi(t)\rangle|^2 = a^2$$

$$\text{Prob}(|\beta\rangle) = b^2$$

Problem: It is known that upon placing a sample in B_0, there is an induced macroscopic magnetization M_z:

$$M_z = M_0 = \chi \cdot B_0$$

$$M_x = M_y = 0$$

But then, the single-spin equations require $\left\{\begin{matrix} a=0 \\ \text{or} \\ b=0 \end{matrix}\right\}$: complete polarization

There is something **wrong** in this analysis: **One cannot assume that all spins in the sample are described by the same wave-function**

see equations (2A) (2B) (2C)
where we multiplied times (N)

I.8 AN ENSEMBLE OF ISOLATED SPIN-1/2: THE DENSITY MATRIX

The behavior of complete system is given by a sum : average of different wave functions.

—— : Ensemble average

$$\overline{\langle M_x \rangle} = \gamma \hbar \sum_{i=1}^{N} a_i \cdot b_i \cdot \cos(\omega_0 t + \varphi_i)$$

$$\overline{\langle M_y \rangle} = \gamma \hbar \sum_{i=1}^{N} a_i b_i \sin(\omega_0 t + \varphi_i)$$

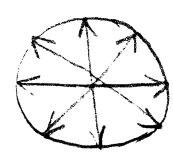
$$\overline{\langle M_z \rangle} = \frac{\gamma \hbar}{2} \sum_{i=1}^{N} \left(|a_i|^2 - |b_i|^2 \right)$$

population = pop

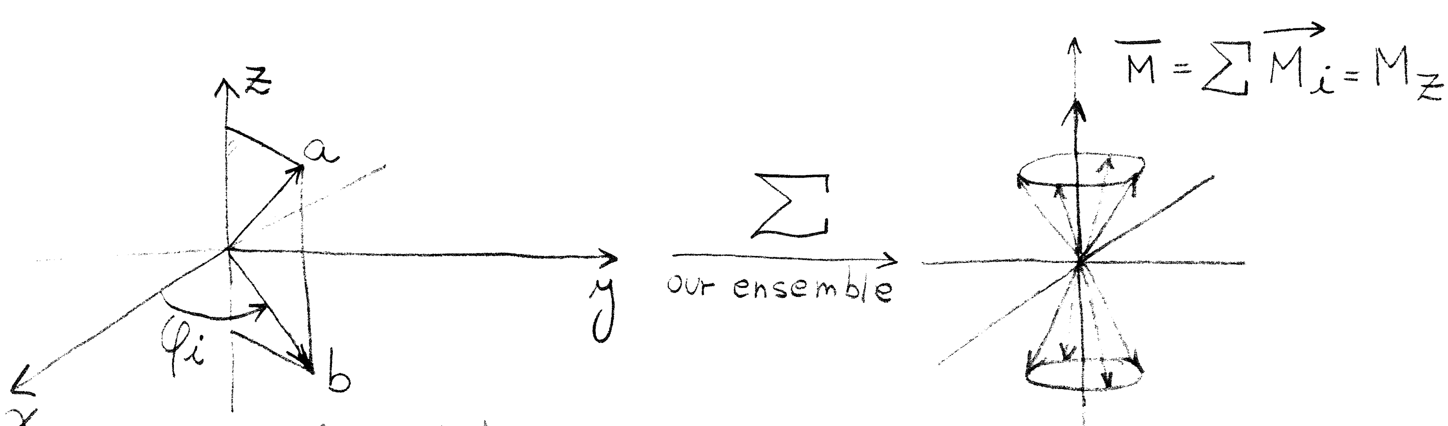
$$\frac{\sum_i |b_i|^2}{\sum_i |a_i|^2} = \frac{\text{pop}\,|\beta\rangle}{\text{pop}\,|\alpha\rangle} = e^{-\hbar\omega_0/kT}$$

$\Rightarrow$ M_z is as in the classical treatment

But all the φ_i are uncorrelated <=> equally distributed:



$$\Rightarrow \overline{\cos(\omega_0 t + \varphi_i)} = \overline{\sin(\omega_0 t + \varphi_i)} = 0$$



a single spin behaves just like a classical $\vec{\mu}$ ($\vec{\mu}$ = magnetic moment)

total system

THE DENSITY MATRIX

The behavior of a macroscopic spin system is not adequately described by a single wave function $|\Psi(t)\rangle$, we look for an alternative formalism.

We know that given the wavefunction of a particle with spin 1/2:

$$|\Psi(t)\rangle = \sum_j c_j |j\rangle \qquad \left\{ |j\rangle = \ldots, |3/2\rangle, |1/2\rangle, |-1/2\rangle, |-3/2\rangle, \ldots \right\}$$

The expectation value that we measure for the macroscopic magnetization is:

$$\overline{\langle M_i \rangle} = \overline{\langle \Psi | M_i | \Psi \rangle} = \overline{\left(\sum_k c_k^* \langle k|\right) M_i \left(\sum_j c_j |j\rangle\right)}$$

it's an element of my operator

$$= \sum_{j,k} \overline{c_k^* c_j} \underbrace{\langle k | M | j \rangle}$$

$\langle k | M | j \rangle = k, j$ – element of a matrix representing operator M

the average $\overline{c_k^* c_j}$ consider a STATISTICAL AVERAGE

$\overline{c_k^* c_j} = j, k$ – element of a matrix representing operator ρ : the density matrix

$$\langle M \rangle = \sum_{j,k} \rho_{jk} \cdot M_{kj} = \sum_j \left(\langle j | \rho\right) \underbrace{\left(\sum_k |k\rangle\langle k|\right)}_{1} \left(M |j\rangle\right)$$

$$= \sum_j \langle j | \rho . M | j \rangle$$

$$\Longleftrightarrow \boxed{\langle M \rangle = Tr(\rho . M)}$$

NB Tr( ) = sum of diagonal elements

ρ has all the information that has to be known about our system. $(N \times N)$ dimension

The system is now described by operators : LIOUVILLE SPACE

Now states are matrices

Hilbert space = it's the space where bra and ket live.

I.9 TIME EVOLUTION OF THE DENSITY MATRIX

Starting from the time-dependent Schroedinger equation

$$i\hbar \frac{\partial|\Psi\rangle}{\partial t} = \mathcal{H}|\Psi\rangle$$

and expanding $|\Psi\rangle = \sum_j c_j\,|j\rangle$ on an arbitrary basis {|j>}, it follows that

$$* \langle k| \qquad i\hbar\left(\sum_j \dot{c}_j\,|j\rangle\right) = \sum_j c_j\,\mathcal{H}|j\rangle$$

$$\langle k|j\rangle = \delta_{kj} \qquad i\hbar\,\dot{c}_k = \sum_j c_j \langle k|\mathcal{H}|j\rangle$$

$$\Rightarrow \dot{\rho}_{nm} = \frac{\partial}{\partial t}\left(\overline{c_n c_m^*}\right) = \overline{\underbrace{\dot{c}_n}_{\frac{1}{i\hbar}\left(\sum_j c_j\langle n|\mathcal{H}|j\rangle\right)} c_m^*} + \overline{c_n \underbrace{\dot{c}_m^*}_{\left(\frac{-1}{i\hbar}\right)\left(\sum_j c_j^*\langle j|\mathcal{H}|m\rangle\right)}}$$

$$= \frac{1}{i\hbar}\left[\left(\sum_j \underbrace{\overline{c_j c_m^*}}_{\langle j|\rho|m\rangle}\langle n|\mathcal{H}|j\rangle\right) - \left(\sum_j \underbrace{\overline{c_n c_j^*}}_{\langle n|\rho|j\rangle}\langle j|\mathcal{H}|m\rangle\right)\right]$$

$$= \frac{1}{i\hbar}\left[\sum_j \langle n|\mathcal{H}\underbrace{|j\rangle\langle j|}_{1}\rho|m\rangle - \sum_j \langle n|\rho\underbrace{|j\rangle\langle j|}_{1}\mathcal{H}|m\rangle\right]$$

$$= \frac{1}{i\hbar}\left[\langle n|\mathcal{H}\rho - \rho\mathcal{H}|m\rangle\right]$$

$$\Longleftrightarrow \boxed{i\hbar\,\dot{\rho} = [\mathcal{H},\rho]}$$

The Sch. eq for ρ
Liouville-von Neumann Eq

$\rho(t) = U(t)\rho(0)U^{+}(t)$

$\dot\rho(t) = \dot U \rho_0 U^{+} + U \rho_0 \dot U^{+}$ where $\dot U = -\frac{i\mathcal{H}}{\hbar} U$

There is a formal solution to this equation if $\mathcal{H}$ is time independent:

$$\boxed{\rho(t) = \underbrace{e^{-i\mathcal{H}t/\hbar}}_{\mathcal{U}(t)\text{: Time evolution operator}} \cdot \rho(0)\, e^{i\mathcal{H}t/\hbar}}$$

$U(t)$: Unitary operator fulfilling $U \cdot U^{+} = \mathbb{1} \Leftrightarrow U^{+} = U^{-1}$

Unitary operator doesn't change the norm of a state

What is $\mathcal{U}(t)$? We had that $e^{x} = 1 + x + \frac{x^2}{2} + \ldots$

$$e^{-i\mathcal{H}t/\hbar} = 1 - \frac{it}{\hbar}\mathcal{H} - \frac{t^2}{2\hbar^2}\mathcal{H}^2 + \cdots$$

Remember that $e^{A} \cdot e^{B} \neq e^{B} \cdot e^{A} \neq e^{A+B}$, unless $[A,B] = 0$!

Let's assume a spin ensemble in the presence of B_0; we look for the **density matrix** in **thermal equilibrium**:

The Hamiltonian $\mathcal{H} = \omega_0 S_z$ has eigenstates

$$|n\rangle : \quad \mathcal{H}|n\rangle = E_n |n\rangle$$

with relative populations

$$pop(|n\rangle) = \rho_{nn} = \frac{e^{-E_n/kT}}{\sum_j e^{-E_j/kT}} = \frac{e^{-E_n/kT}}{Z}$$

The off-diagonal elements of ρ :

$$\rho_{mn} = \overline{c_m c_n} = 0$$

Since it is easy to proof that

$$e^{-\mathcal{H}/kT} |n\rangle = e^{-E_n/kT} |n\rangle$$

$$\Rightarrow \boxed{\rho_{eq} = \frac{e^{-\mathcal{H}/kT}}{Z}}$$

Moreover, since in most cases E_n << kT (high-temperature approximation)

$$\boxed{\rho_{eq} = \frac{1 - \mathcal{H}/kT}{Z}}$$

For a spin 1/2 $\mathcal{H} = -\omega_0 S_z$

here $Z = 1 = \frac{1}{2} + \frac{1}{2}$

$$\Rightarrow \quad \rho_{eq} = \begin{pmatrix} \frac{1}{2} + \hbar\omega_0/2kT & 0 \\ 0 & \frac{1}{2} - \hbar\omega_0/2kT \end{pmatrix}$$

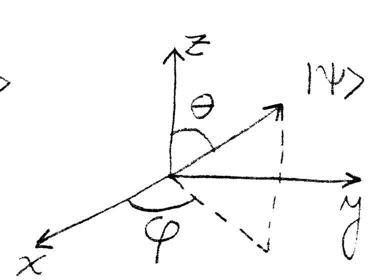
Total populations: $\rho_{11} + \rho_{22} = 1$

Off-diagonal elements (coherences) = 0

A more specific calculation for spin-1/2. We saw that in Hilbert space

$$|\psi\rangle = \cos\frac{\theta}{2}\, e^{i\varphi/2}|\alpha\rangle + \sin\frac{\theta}{2}\, e^{-i\varphi/2}|\beta\rangle$$

$$= a|\alpha\rangle + b|\beta\rangle$$



where $|a|^2 = \text{prob}\,|\alpha\rangle$, $|b|^2 = \text{prob}\,|\beta\rangle$

NB The elements off-diagonal are $\neq 0$ when the states $|\alpha\rangle$ and $|\beta\rangle$ can someway talk to eachother

The corresponding density matrix

$$\rho = \begin{pmatrix} \overline{\cos^2\frac{\theta}{2}} & \overline{\cos\frac{\theta}{2}\sin\frac{\theta}{2}\, e^{-i\varphi}} \\ \overline{\cos\frac{\theta}{2}\sin\frac{\theta}{2}\, e^{i\varphi}} & \overline{\sin^2\frac{\theta}{2}} \end{pmatrix} \underset{\substack{\downarrow \\ \varphi \text{ UNCORRELATED} \\ \text{OVER ENSEMBLE}}}{=} \begin{pmatrix} \cos^2\frac{\theta}{2} & 0 \\ 0 & \sin^2\frac{\theta}{2} \end{pmatrix}$$

If the sample is unpolarized; $\text{prob}\,|\alpha\rangle = \text{prob}\,|\beta\rangle \Leftrightarrow$

$$\rho_{\text{UNPOLARIZED}} = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} = \frac{1}{2}\cdot \mathbb{1}$$

In a magnetic field, $\text{prob}\,|\beta\rangle = e^{-\hbar\omega_0/kT} \cdot \text{prob}\,|\alpha\rangle \Leftrightarrow$

$$\rho_{\text{POLARIZED}} = \begin{pmatrix} e^{\hbar\omega_0/2kT} & 0 \\ 0 & e^{-\hbar\omega_0/2kT} \end{pmatrix}$$

I.10 ISOLATED SPIN 1/2 ENSEMBLES: EQUIVALENCE BETWEEN CLASSICAL AND QUANTUM-MECHANICAL DESCRIPTIONS

In general, the ρ of a spin 1/2 system can be written as

$$\rho_0 = \underbrace{a_0}_{\text{irrelevant}} \mathbb{1} + \underbrace{a_x \sigma_x + a_y \sigma_y + a_z \sigma_z}_{\text{components of angular momentum}} \qquad \{\mathbb{1}, \underbrace{\sigma_x, \sigma_y, \sigma_z}_{\text{Pauli matrices}}\} \text{ basis set}$$

$$\sigma_i = \frac{2}{\hbar} S_i \quad \begin{cases} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} : z \\ \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} : y \\ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} : x \end{cases}$$

Let's assume $\mathcal{H} = -\omega_0 S_z$

$$\Rightarrow \boxed{\rho(t)} = e^{+i\omega_0 S_z t/\hbar} \rho_0 \, e^{-i\omega_0 S_z t/\hbar} = ?$$

$$\text{anything} \cdot \mathbb{1} \cdot \text{anything}^{-1} = \mathbb{1} \quad : \text{trivial}$$

$$e^{i\omega_0 S_z t/\hbar} \cdot S_z \cdot e^{-i\omega_0 S_z t/\hbar} = S_z \quad : \text{trivial}$$

$$e^{i\omega_0 t S_z/\hbar} = e^{i(\omega_0 t/2)\sigma_z} = e^{i\alpha\sigma_z} = \mathbb{1} + i\alpha\sigma_z + \underbrace{(i)^2}_{-1}\frac{\alpha^2}{2}\underbrace{\sigma_z^2}_{1} +$$

$$+ (-1)i\frac{\alpha^3}{3!}\sigma_z + \frac{\alpha^4}{4!}\overbrace{\sigma_z^2}^{\mathbb{1}} = \mathbb{1}\left\{1 - \frac{\alpha^2}{2} + \frac{\alpha^4}{4!} - \dots\right\} + $$

$$+ i\sigma_z\left\{\alpha - \frac{\alpha^3}{3!} + \frac{\alpha^5}{5!} - \dots\right\}$$

$$= \boxed{\mathbb{1}\cos(\alpha) + i\sigma_z \sin(\alpha)}$$

$$\Rightarrow e^{i\omega_0 S_z t} S_x \, e^{-i\omega_0 S_z t} = \left[\mathbb{1}\cos(\alpha) + i\sigma_z \sin(\alpha)\right]\left(\frac{\hbar}{2}\sigma_x\right)\left[\mathbb{1}\cos(\alpha) - i\sigma_z \sin(\alpha)\right]$$

$$= S_x\cos^2\alpha + i\frac{\hbar}{2}\overbrace{\sigma_z\sigma_x}^{i\sigma_y}\cos(\alpha)\sin(\alpha) - i\frac{\hbar}{2}\cos(\alpha)\sin(\alpha)\underbrace{\sigma_x\sigma_z}_{-i\sigma_y}$$

$$+\frac{\hbar}{2}\sin(\alpha)\sin(\alpha)\underbrace{\sigma_z\underbrace{\sigma_x\sigma_z}_{-\cancel{i}\sigma_y = -i\sigma_y}}_{-\sigma_x} = S_x[\cos^2\alpha - \text{sen}^2\alpha] + S_y[-2\,\text{sen}\alpha\cos\alpha] = S_x\cos(\omega_0 t) - S_y\sin(\omega_0 t)$$

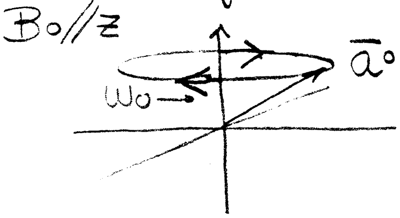
$$\Rightarrow e^{i\omega_0 S_z t} S_x e^{-i\omega_0 S_z t} = S_x\cos(\omega_0 t) - S_y\sin(\omega_0 t)$$

Similarly: $e^{-i\mathcal{H}t} S_y e^{i\mathcal{H}t} = S_y\cos(\omega_0 t) + S_x\sin(\omega_0 t)$

(*)

$$\Rightarrow \rho(t) = a_0\mathbb{1} + a_z(t)\sigma_z + a_y(t)\sigma_y + a_x(t)\sigma_x$$

with
$$a_z(t) = a_z^0$$
$$a_x(t) = a_x^0\cos(\omega_0 t) + a_y^0\sin(\omega_0 t)$$
$$a_y(t) = a_y^0\cos(\omega_0 t) - a_x^0\,\cancel{\cos}\,\sin(\omega_0 t)$$



$\overline{a}$ precesses around z at a rate ω_0

Since $\vec{M} = \gamma\hbar N\cdot\vec{S} \Rightarrow$ $\langle S_i\rangle = \mathrm{Tr}(\rho\cdot S_i)$

$$\langle M_i\rangle = \gamma\hbar N.\langle S_i\rangle = \gamma\hbar N.\mathrm{Tr}(\rho . S_i),$$

and Pauli matrices are orthogonal $(\mathrm{Tr}\,\sigma_i\sigma_j = \delta_{ij})$,

$$\Rightarrow \boxed{\langle M_i(t)\rangle = \gamma\hbar N . a_i(t)}$$

It is only valid for ISOLATED SPIN 1/2

Corresponds exactly with the classical magnetizations

In the classical picture the trick was the ROTATING FRAME
we'll use the quantum correspondence

Now we investigate what quantum mechanics predicts upon **irradiating** the spin ensemble
In the lab frame:

$$i\hbar\dot{\rho} = [\mathcal{H}, \rho]$$

$$\mathcal{H} = -\vec{\mu}\cdot\vec{B} = -\gamma\hbar\left\{B_0 S_z + B_1\cos(\omega t)S_x\right\}$$

Again, we separate B_1 into rotating components:

(*) We saw this before, it is $e^{-i\omega S_z t} S_x e^{i\omega S_z t}$

$$(B_1/2)\left[\underbrace{S_x\cos(\omega t) + S_y\sin(\omega t)}_{(*)}\right] \quad \text{left-handed}$$

and counterrotating components:

we discard this because it is far from Larmor freq

$$(B_1/2)\left[S_x\cos(-\omega t) + S_y\sin(-\omega t)\right] \quad \text{right-handed}$$

$$\text{Then,} \quad \mathcal{H} = -\hbar\omega_0 S_z - \hbar\omega_1\left[\underbrace{S_x\cos(\omega t) + S_y\sin(\omega t)}_{e^{-i\omega t S_z}\cdot S_x\cdot e^{i\omega t S_z}}\right]$$

ρ's time evolution in lab frame

$$\Rightarrow i\hbar\dot{\rho} = \mathcal{H}\rho - \rho\mathcal{H}$$

$$= e^{-i\omega t S_z}\hbar\left[-\omega_0 S_z - \omega_1 S_x\right]e^{i\omega t S_z}\cdot\rho - \rho\, e^{-i\omega t S_z}\hbar\left[-\omega_0 S_z - \omega_1 S_x\right]e^{i\omega t\cdot S_z} \quad (*)$$

We replace now ρ by $\rho_r = \underbrace{e^{i\omega t S_z}}_{\text{rotation about z axis at a rate } \omega t\text{: rotating frame transformation}}\rho\, e^{-i\omega t S_z} = f(t)\cdot g(t)\cdot h(t)$

ρ's evolution in the rotating frame

$$\Rightarrow \dot{\rho}_r = i\omega S_z\cdot\rho_r + e^{i\omega t S_z}\cdot\dot{\rho}\cdot e^{-i\omega t S_z} - i\omega\rho_r\cdot S_z$$

$$\Leftrightarrow e^{i\omega t S_z}\cdot\dot{\rho}\cdot e^{-i\omega t S_z} = \dot{\rho}_r + i\omega\left[\rho_r S_z - S_z\rho_r\right]$$

substituting $\dot{\rho}$ with (*) we get rid of the time dependence

Multiplying $(*)$ by: $e^{i\omega t S_z}\ (*)\ e^{-i\omega t S_z}$

$$\Rightarrow i\hbar\dot{\rho}_r - \hbar\omega[\rho_r S_z - S_z\rho_r] =$$

$$= \hbar(\omega_0 S_z - \omega_1 S_x)\, e^{i\omega t S_z}\cdot\rho\cdot e^{-i\omega t S_z} -$$

$$- e^{i\omega t S_z}\cdot\rho\cdot e^{-i\omega t S_z}\,\hbar(-\omega_0 S_z - \omega_1 S_x)$$

$$= -\hbar\omega_0 S_z\rho_r - \hbar\omega_1 S_x\rho_r + \hbar\omega_0\rho_r S_z + \hbar\omega_1\rho_r S_x$$

$$\Leftrightarrow \boxed{i\hbar\dot{\rho}_r = [\mathcal{H}_r, \rho_r]}$$

, where the new $\mathcal{H}_r$

$$\mathcal{H}_r = -\hbar\underbrace{(\omega_0-\omega)}_{\text{offset }\Delta\omega}S_z - \hbar\omega_1 S_x$$

The field B_0 was reduced by ω/γ, B_1 went static

It is TIME INDEPENDENT

The frequency along z is $(\omega_0-\omega)$, therefore when we use an irradiating field with $\omega=\omega_0$ (resonance) the magnetic field is only rotating along X

With these transformations it can be shown that the coefficient of the Pauli matrices behave as the classical magnetization vector:

$$\boxed{\begin{aligned}\dot{a}_x &= -\Delta\omega\, a_y\\ \dot{a}_y &= \Delta\omega\, a_x + \omega_1 a_z\\ \dot{a}_z &= -\omega_1 a_y\end{aligned}}$$

HW Demonstrate

I.12 PROBLEMS

1) Calculate the difference in population between the spin states of
   i) ^{13}C at 7 T, 300 K
   ii) ^{25}Mg at 7 T, 300 K.

2) Considering that the natural abundance of ^{25}Mg is 10 times larger than that of ^{13}C, at what temperature should a MgO sample be placed to make the $-1/2 \longrightarrow +1/2$ transition of the ^{25}Mg as populated as the $-1/2 \longrightarrow +1/2$ transition of CO at 298 K?

3) Find the expression of the net magnetization M_0 as a function of B_0 and the temperature for an arbitrary spin.

4) i) Using the fact that $\langle\psi|\varphi\rangle = (\langle\varphi|\psi\rangle)^*$, show that the operator corresponding to a physical observable $\mathcal{O}$ is Hermitian; i.e. fulfills

$$\langle\psi|\mathcal{O}|\varphi\rangle = (\langle\varphi|\mathcal{O}|\psi\rangle)^*$$

In a matrix representation show that this is equivalent to the requirement $\mathcal{O}_{ij} = \mathcal{O}_{ji}^*$
   ii) Which of the following is not an observable operator:
$$I^2,\ I_z,\ I_x,\ I_+$$

5) Calculate: $[I^2, I_+]$, $[I^2, I_x]$, $[I^2, I_z]$, $[I_z, I_+]$

6) Show that $I^2 = I_z^2 + 1/2\,(I_+I_- + I_-I_+)$

7) Demonstrate that if 2 Hermitian operators A, B fulfill [A, B] = 0, then they possess a common basis of eigenstates.

8) Demonstrate that the eigenvalues of a hermitian operator are real, and that the eigenstates associated with different eigenvalues are orthogonal.

9) Using the matrix representation of the spin 1/2 operators, fill up this table (and keep a copy you will need it!)
(assume h = 1)
pàma

aup

	I_x	I_y	I_z	I^2	I_+	I_-
I_x	$I^2/3$	$i/2\ I_z$	$-i/2\ I_y$	$3/4\ I_x$	$(I_+I_-)/2$	$(I_-I_+)/2$
I_y	$4iI_-I_+$	$I^2/3$	$-iI_x$	$I_y/3$	$(I_+I_-)/2i$	$\frac{i}{2}I_-I_+$
I_z	iI_y	iI_x	$I^2/3$	$I_z/3$	$-I_+$	I_-
I^2	$3I_x$	$3I_y$	$3I_z$	$I^2/3$	$I_+/3$	$I_-/3$
I_+	$(I_-I_+)\frac{1}{2}$	$(I_-I_+)/2i$	I_+	$I_+/3$	$=$	$\frac{4}{3}I^2-(I_+I_-)$
I_-	$(I_+\cdot I_-)\frac{1}{2}$	$i(I_+I_-)/2$	$-I_-$	$I_-/3$	$\frac{4}{3}I^2-(I_-I_+)$	$-$

10) Calculate the eigenstates and eigenvalues of I_x, I_y, I_z, in terms of $|\alpha\rangle, |\beta\rangle$

11) The I_z eigenstates for a spin 1: $I_z|+1\rangle=\hbar|+1\rangle$; $I_z|0\rangle=0$; $I_z|-1\rangle=-\hbar|-1\rangle$

Using the fact that the raising and lowering operators have the following effects:

$$I_+|+1\rangle=0\ ; \quad I_+|0\rangle=\sqrt{2}\,|+1\rangle\ ; \quad I_+|-1\rangle=\sqrt{2}\,|0\rangle$$

$$I_-|+1\rangle=\sqrt{2}\,|0\rangle\ ; \quad I_-|0\rangle=\sqrt{2}\,|-1\rangle\ ; \quad I_-|-1\rangle=0$$

Calculate the matrix form of I_x, I_y, I_z and I^2.

12) Generalize the expressions (2A) - (2C) for the case of a spin 1. (see page 22)

13) i) Find the matrix expressions for the evolution operators

$$\mathcal{U}_z(\phi_z)=e^{i\phi_z I_z}\ ; \quad \mathcal{U}_x(\phi_x)=e^{i\phi_x I_x}\ ; \quad \mathcal{U}_y(\phi_y)=e^{i\phi_y I_y}$$

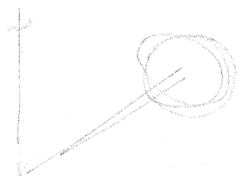
ϕ_i rotation about z, x or y.

ii) Demonstrate that unitary operators do not change the norm of a state. Unitary operations can therefore be thought of as generalized "rotations" or "translations" of vectors.

~~14~~) Using the explicit matrix representation for the spin operators and the operators of the previous problem, fill out the following table (and keep a copy of it, you will need it!).

$\phi_y I_x = I_x \cos\phi_y - I_z \,\mathrm{sen}\,\phi_y$

$\phi_z I_x = I_x \cos\phi_x + I_y \,\mathrm{sen}\,\phi_x$



$$I_x \xrightarrow{\mathcal{U}_x(\phi_x)} I_x$$
$$I_x \xrightarrow{\mathcal{U}_y(\phi_y)} I_x \cos\phi_y - I_z \sin\phi_y$$
$$I_x \xrightarrow{\mathcal{U}_z(\phi_z)} \boxed{I_x \cos\phi_z + I_y \sin\phi_y}$$

$U_x^{-1} I_x U_x$

$\phi_x I_y = I_y \cos\phi_x + I_z \,\mathrm{sen}\,\phi_x$

$\phi_z I_y = I_y \cos\phi_z - I_x \,\mathrm{sen}\,\phi_z$

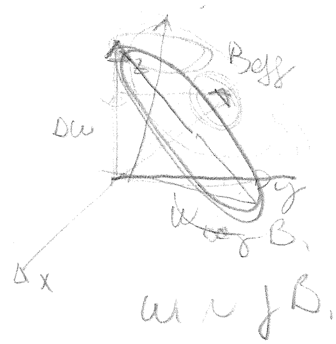
$$I_y \xrightarrow{u(\phi_x)} I_y \cos\phi_x + I_z \,\mathrm{sen}\,\phi_x$$
$$I_y \longrightarrow$$
$$I_y \longrightarrow I_y \cos\phi_z - I_x \,\mathrm{sen}\,\phi_z$$

$\Delta\omega = \omega_0 - \omega_x$
$= \gamma B_0 - \omega$

$\phi_x I_z = I_z \cos\phi_x - I_y \,\mathrm{sen}\,\phi_x$

$\phi_y I_z = I_z \cos\phi_y + I_x \,\mathrm{sen}\,\phi_y$

$$I_z \xrightarrow{u(\phi_x)} I_z \cos\phi_x - I_y \,\mathrm{sen}\,\phi_x$$
$$I_z \xrightarrow{u(\phi_y)} I_z \cos\phi_y + I_x \,\mathrm{sen}\,\phi_y$$
$$I_z \xrightarrow{u(\phi_z)}$$



Find a graphical representation for these rotations.

15) In the presence of a B_1 rf field oscillating at a rate ω, the macroscopic magnetization in the rotating frame precesses around a $\vec{B}_{eff}$ according to

$$\vec{B}_{eff} = \frac{1}{\gamma}\left(\overset{\omega_0-\omega}{\Delta\omega}\,\hat{z} + \omega_1 \hat{x}\right)$$

$\omega_0 = \gamma B_0$

$\omega_1 = \gamma B_1$

$(\Delta\omega)^2 + (\omega_1)^2$

i) Calculate the precession rate of the magnetization.

ii) Calculate the trajectory followed by M if M(t=0) = (0, 0, M_0).

iii) What range of ω_1 (as a function of $\Delta\omega$) are required to bring the

$M(t)$ ...

magnetization from the z-axis into the x-y plane?

iv) Describe the phase that a magnetization originally // to z makes with respect to the y-axis as a function of $\Delta\omega$ for a fixed value of ω_1

16) What are the eigenstates and eigenvalues of the Hamiltonian

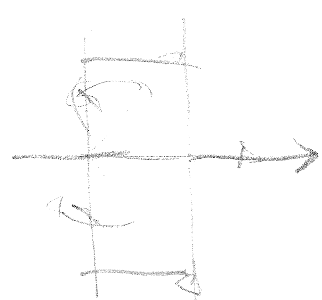
$$\mathcal{H} = -\Delta\omega\, I_z - \omega_1 I_x$$

OK

17) Show that in the rotating frame, the counter-rotating component of B_1 rotates at a rate 2ω

$$-\Delta\omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} - \omega_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\begin{pmatrix} +\Delta\omega & -\omega_1 \\ \omega_1 & -\Delta\omega \end{pmatrix}$$



$$H = -\omega_0 I_z + \left(I_x \cos\omega t + I_y \operatorname{sen}(\omega t)\right) + (\quad - \quad)$$

$$e^{-i\phi I_z}\, H\, e^{+i\phi I_z}$$