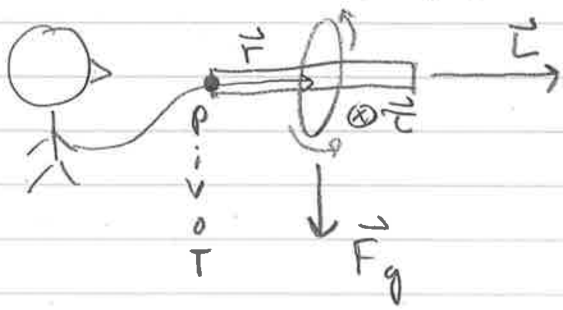
NMR Notes

- The wheel analogy

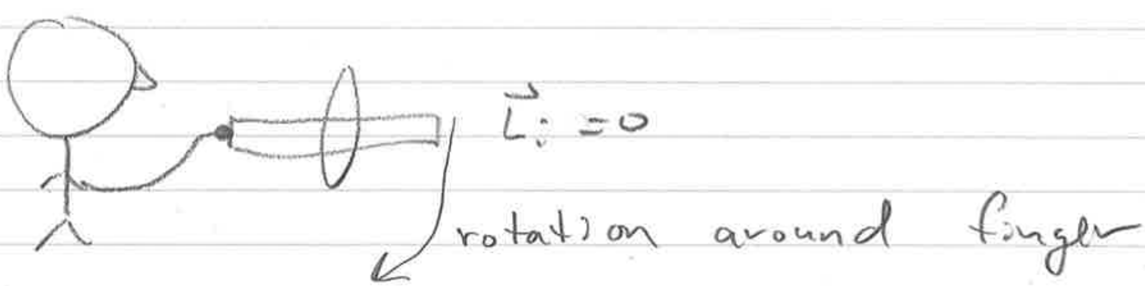



$$\vec{\tau} = \frac{d\vec{L}}{dt} = \vec{r} \times \vec{F}_g$$

The change in angular momentum must always be in the direction of the torque.

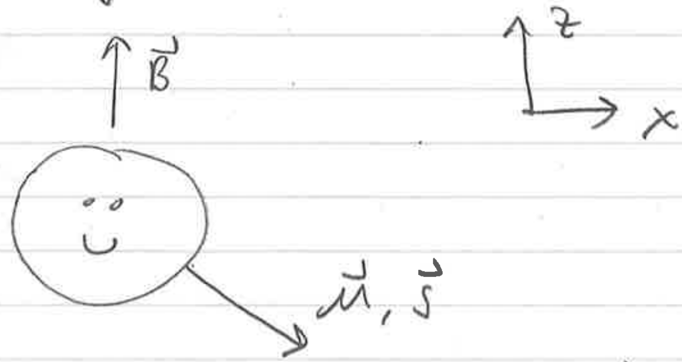
Hence when the wheel is rotating as above the axis of $\vec{L}$ swings into the page.

Q1: If the wheel were released as above from rest, it would rotate down as follows.




How can you understand this based on the torque / angular momentum eqn?

- A classical magnetic moment in a $\vec{B}$ field




$\tau = \vec{\mu} \times \vec{B}$ $\qquad\qquad$ $H = -\vec{\mu} \cdot \vec{B} = -\mu B \cos\theta$

Q2 How does $\vec{\mu}$ change over time?

Q3 why does $\vec{\mu}$ not swing up into $\vec{B}$? That's the lowest energy state. What would be needed for the spin to change orientation in this way?

- The QM version of above $\vec{B} = B_0 \hat{k}$

$\hat{H} = -\hat{\mu} \cdot \vec{B} = \omega_0 \hat{S}_z$

To handle all of the cases in 1 shot consider an arbitrary state in the $S_z$ basis.
(v. initial)

$$|\psi(0)\rangle = a|+z\rangle + b|-z\rangle \rightarrow \begin{pmatrix} a \\ b \end{pmatrix}$$

Since the $\hat{H}$ I have at this stage is time independent

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle$$
$$\rightarrow \begin{pmatrix} a\, e^{-i\omega_0 t/2} \\ b\, e^{i\omega_0 t/2} \end{pmatrix}$$

Q4 What happens to the probability to find the particle in the state $|+z\rangle$?

Q5 What about the probability to find the particle in the state $|+x\rangle$? I'll do a little algebra here for you. To keep things simple, I'll limit attention to real $a + b$.

$$|\langle +x|\psi(t)\rangle|^2 = \left| \left(\tfrac{1}{\sqrt{2}}, \tfrac{1}{\sqrt{2}}\right) \begin{pmatrix} a\, e^{-i\omega_0 t/2} \\ b\, e^{i\omega_0 t/2} \end{pmatrix} \right|^2$$

$$= \frac{a^2}{2} + \frac{b^2}{2} + \frac{ab}{2}\left(e^{-i\omega_0 t} + e^{i\omega_0 t}\right)$$

$$= \frac{a^2}{2} + \frac{b^2}{2} + ab\cos\omega_0 t$$

To make sense of this, consider some examples.

- Suppose the particle was in the initial state $|+z\rangle$, what happens?
- Suppose $|\psi(0)\rangle = |+x\rangle$ what happens?
- What if $a = \sqrt{\frac{9}{10}}$, $b = \sqrt{\frac{1}{10}}$?

Q6 Are your answers to Q5 somewhat consistent with your classical picture?

## – The perturbing field!

Lets turn on the rest of the Hamiltonian, ie add a field that will change the z component of the spin.

$$\hat{H} = \omega_0 \hat{S}_x + \omega_1 \cos \omega t \, \hat{S}_x$$

Since $\hat{H}$ is time dependent, we'll use the Schrödinger directly

1) $$\hat{H} \, |\psi(t)\rangle = i \frac{d}{dt} |\psi(t)\rangle$$

$$\hat{H} \xrightarrow[\text{z basis}]{} \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 \cos \omega t \\ \omega_1 \cos \omega t & -\omega_0 \end{pmatrix}$$

Again taking $|\psi(t)\rangle \xrightarrow[S_z \text{ basis}]{} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}$

So in the z basis 1) becomes

$$\frac{1}{2} \begin{pmatrix} \omega_0 & \omega_1 \cos \omega t \\ \omega_1 \cos \omega t & -\omega_0 \end{pmatrix} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = i \begin{pmatrix} \dot{a}(t) \\ \dot{b}(t) \end{pmatrix}$$

So if you do out the matrix multiplication you get 2 coupled ODEs to solve.
<u>Choose your own adventure</u>: I'll now start solving these odes to get the Rabi formula for the evolution of the states in the NMR field, Townsend only does an approximate version. If you'd rather skip the gory details and just interpret the result, go to page 8.

## Journey to the Rabi formula



We'll start with the same move as Townsend, assume a sol'n of the form $\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \begin{pmatrix} c(t)\, e^{-i\omega_0 t/2} \\ d(t)\, e^{i\omega_0 t/2} \end{pmatrix}$ in other words, it's some extra stuff times what the sol'n would have been w/o the $\omega_1$ term in H.

If we plug in the trial sol'n we get

$$i \begin{pmatrix} \dot{c}(t) \\ \dot{d}(t) \end{pmatrix} = \frac{\omega_1}{4} \begin{pmatrix} \left(e^{i(\omega_0+\omega)t} + e^{i(\omega_0-\omega)t}\right) d \\ \left(e^{i(\omega-\omega_0)t} + e^{-i(\omega_0+\omega)t}\right) c \end{pmatrix}$$

It takes a few lines of algebra to show this. It might be fun in your next class. I'll attach mine at the end, page A1.

If we were going to integrate to find c(t), the integral would involve the terms

$$\int e^{i(\omega_0+\omega)t}\, d(t)\, dt + \int e^{i(\omega_0-\omega)}\, d(t)\, dt$$

Townsend says that the first term is zero because the exponential is "rapidly oscillating" and d(t) evolves more slowly.

Q7 Make a sketch to support the argument that the 1st integral is 0 as long as the integral is taken over a time that is much longer than the period $2\pi/\omega_0+\omega$

Q8 Why do we expect d(t) to evolve more slowly, ie at a lower frequency than $\omega_0+\omega$?

With the "rapidly osillating" term dead, we have

2) $\dot{c} = -i\frac{\omega_1}{4} e^{i(\omega_0-\omega)t} d$

Take a time derivative of this and use it, along with the other eqn

$\dot{d} = -i\frac{\omega_1}{4} e^{-i(\omega_0-\omega)t} c$

to eliminate all of the $d$ and $\dot{d}$. I find

$$\ddot{c} - i(\omega_0-\omega)\dot{c} + \left(\frac{\omega_1}{4}\right)^2 c = 0$$

Q9 If you have time, show this

Linear ODEs have exponential solutions, so you could try $c(t) = c(0)e^{i\lambda t}$, solve for $\lambda$ and construct the sol'n.

Plugging in, we get

$$-\lambda^2 + (\omega_0-\omega)\lambda + \left(\frac{\omega_1}{4}\right)^2 = 0$$

So there are 2 sol'ns for $\lambda$

$$\lambda_\pm = \frac{(\omega_0-\omega) \pm \sqrt{(\omega_0-\omega)^2 + \omega_1^2/4}}{2}$$

So the general sol'n for $c(t)$ is

$$c = c_+ e^{i\lambda_+ t} + c_- e^{i\lambda_- t}$$

Plugging this into eqn 2 and solving for $d$ yields

$$d(t) = \frac{-\gamma}{\omega_1} e^{-i(\omega_0 - \omega)t}\left(\lambda_+ c_+ e^{i\lambda_+ t} + \lambda_- c_- e^{i\lambda_- t}\right)$$

If we assume we're in the $|+z\rangle$ state at $t=0$ then $c(0) = 1$ and $d(0) = 0$

$$\Downarrow \qquad\qquad\qquad \Downarrow$$

$$c_+ + c_- = 1 \qquad\qquad \lambda_+ c_+ + \lambda_- c_- = 0$$

$$\Rightarrow \quad c_+ = \frac{\lambda_-}{\lambda_- - \lambda_+} \qquad\qquad c_- = -\frac{\lambda_+}{\lambda_- - \lambda_+}$$

Now the probability that we flip is

$$|\langle -z|\psi\rangle|^2 = |b(t)|^2 = |d(t)|^2$$

$$= \left(\frac{\gamma}{\omega_1}\right)^2 \left| \frac{\lambda_+\lambda_-}{\lambda_- - \lambda_+}\left(e^{i\lambda_+ t} - e^{i\lambda_- t}\right)\right|^2$$

$$= \left(\frac{\gamma}{\omega_1}\right)^2 \left(\frac{\lambda_+\lambda_-}{\lambda_- - \lambda_+}\right)^2 \left(2 - e^{i(\lambda_+ - \lambda_-)t} - e^{-i(\lambda_+ - \lambda_-)t}\right)$$

$$= \left(\frac{\gamma}{\omega_1}\right)^2 \left(\frac{\cancel{(\omega_0-\omega)^2} - \cancel{(\omega_0-\omega)^2} - \omega_1^2/4}{\cancel{4}\sqrt{(\omega_0-\omega)^2 + \omega_1^2/4}}\right)^2 \left(2 - 2\cos(\lambda_+ - \lambda_-)t\right)$$

$$\downarrow\ 1 - \cos\theta = 2\sin^2\frac{\theta}{2}$$

$$= \frac{\omega_1^2}{16\left((\omega_0-\omega)^2 + \omega_1^2/4\right)} 4\sin^2\left[\frac{\sqrt{(\omega_0-\omega)^2 + \omega_1^2/4}\ t}{2}\right]$$

3) $$= \frac{\omega_1^2/4}{(\omega_0-\omega)^2 + \omega_1^2/4} \sin^2\left[\frac{\sqrt{(\omega_0-\omega)^2 + \omega_1^2/4}\ t}{2}\right]$$

So that's the Rabi formula for the probability of a spin flip in a static magnetic field in the $\hat{k}$ direction plus an oscillating magnetic field in the $\hat{\imath}$ direction! Woo hoo!

## Interpretation

Q 10 Check that eqn 3 reduces to the expected result when $\omega_1 = 0$

Q 11 At what $\vec{B}_x$ oscillation frequency is the probability to flip maximized?

Q 12 If we drive off resonance, does it take more or less time to reach max probability of a spin flip relative to driving on resonance?

Q 13 What happens if we make the $\vec{B}_x$ field stronger, ie the amplitude of the $B_x$ oscillations is larger?

If we have a population of particles in the static $\hat{k}$ B-field at some temperature, we expect to find more of them in the low energy state, but we'll find some in the high energy state. When we turn on the driving $B_x$ field, we disturb this thermal equalibrium. Watching how long it takes for this equalibrium to re-establish provides information about the material.

$$i\begin{pmatrix}\dot a\\ \dot b\end{pmatrix} = i\begin{pmatrix}\dot c\, e^{-i\omega_0 t/2} \cancel{- i\frac{\omega_0}{2} c\, e^{-i\omega_0 t/2}} \\ \dot d\, e^{i\omega_0 t/2} \cancel{+ i\frac{\omega_0}{2} d\, e^{i\omega_0 t/2}}\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}\cancel{\omega_0 c\, e^{-i\omega_0 t/2}} + \omega_1 \cos\omega t\, d\, e^{i\omega_0 t/2} \\ \omega_1 \cos\omega t\, c\, e^{-i\omega_0 t/2} \cancel{- \omega_0 d\, e^{i\omega_0 t/2}}\end{pmatrix}$$

$$i\begin{pmatrix}\dot c\\ \dot d\end{pmatrix} = \frac{\omega_1}{2}\cos\omega t\begin{pmatrix} d\, e^{i\omega_0 t} \\ c\, e^{-i\omega_0 t}\end{pmatrix}$$

$$= \frac{\omega_1}{4}\left(e^{i\omega t} + e^{-i\omega t}\right)\begin{pmatrix} d\, e^{i\omega_0 t} \\ c\, e^{-i\omega_0 t}\end{pmatrix}$$

$$= \frac{\omega_1}{4}\begin{pmatrix}\left(e^{i(\omega_0+\omega)t} + e^{i(\omega_0-\omega)t}\right) d \\ \left(e^{-i(\omega_0+\omega)t} + e^{-i(\omega_0-\omega)t}\right) c\end{pmatrix}$$