Physics 491
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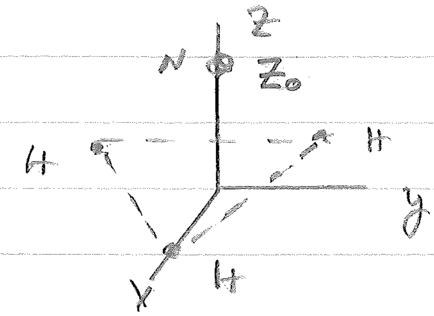
Lecture 14: the Ammonia Molecule

refer to Feynman Vol. III.

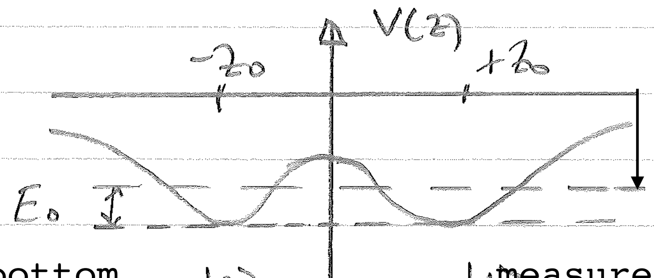
Structure of NH_3: three H-atoms form an equilateral triangle with N along symmetry axis.



$|1\rangle$: N at $+z_0$
$\vec{\mu}_e$ points in $-\hat{z}$ direction

By symmetry there are two stable states at $\pm z_0$. These states are degenerate (same energy)

potential seen by N:



E_b binding Energy

E_0 measured from bottom of potential is positive

measured from energy of states 1

Due to finite barrier, N can tunnel between state $|1\rangle$, $|2\rangle$. This is an example of "two state system".

$$[\hat{H}]_{1,2} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$

A is "exchange energy" due to tunneling amplitude. Diagonalization gives

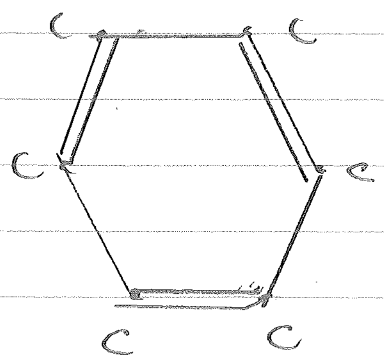
$$E_\pm = E_0 \pm A$$

$$E_- : \ |I\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right) \qquad \text{'uno'}$$
$$E_+ : \ |II\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right) \qquad \text{"duo"}$$

Comments:

① lowest energy state symmetric
② mixing due to tunneling lowers ground state energy. pure QM. effect

Another example: stability of carbon ring:



Benzene molecule
note an H is implied at each vertex
bond length is 109 pm

distance between carbons 139 pm

State w/ rotated double bonds is degenerate. they mix via QM tunneling of electrons around the ring. Carbon ring is unusually stable.

Time dependence

$$(|\mathrm{I}\rangle, |\mathrm{II}\rangle) = (|1\rangle, |2\rangle) \underbrace{\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}}_{[\hat{S}]}$$

$$[\hat{H}]_{\mathrm{I},\mathrm{II}} = [\hat{S}^{\dagger}][\hat{H}]_{12}[\hat{S}]$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} E_0 - A, & E_0 + A \\ E_0 - A, & -E_0 - A \end{pmatrix}$$

$$= \begin{bmatrix} E_0 - A, & 0 \\ 0 & E_0 + A \end{bmatrix}$$ as expected

Components transform as: $\begin{pmatrix} c_{\mathrm{I}} \\ c_{\mathrm{II}} \end{pmatrix} = [S^{\dagger}]\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} c_1 + c_2 \\ c_1 - c_2 \end{pmatrix}$$

take $|\psi(0)\rangle = |1\rangle$. Find $P_{1\to 2}(t) = |\langle 2|\psi(t)\rangle|^2$.

$$|\psi(0)\rangle \xrightarrow[\mathrm{I},\mathrm{II}]{} \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \; ; \; |\psi(t)\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-iE_- t/\hbar} \\ e^{-iE_+ t/\hbar} \end{pmatrix}$$

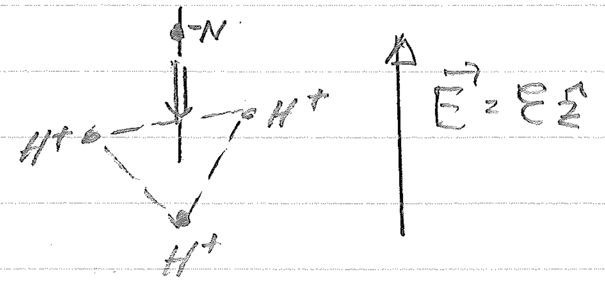
$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-iE_0 t/\hbar}\begin{pmatrix} e^{+iAt/\hbar} \\ e^{-iAt/\hbar} \end{pmatrix}$$

$$\langle 2|\psi(t)\rangle = \left(\frac{1}{\sqrt{2}}\right)^2 e^{-iE_0 t/\hbar}(1, -1)\begin{pmatrix} e^{iAt/\hbar} \\ e^{-iAt/\hbar} \end{pmatrix}$$

$$= i\, e^{-iE_0 t/\hbar} \sin(At/\hbar)$$

$$P_{1\to 2}(t) = \sin^2(At/\hbar)$$

NH_3 in Static Electric Field



additional energy $\hat{H}'$,

$$\hat{H}' = -\vec{\mu}\cdot\vec{E}$$

states 1, 2 have definite $\vec{\mu}_e$: $\left\{ \begin{array}{l} \vec{\mu}_e|1\rangle = -\mu\hat{z}|1\rangle \\ \vec{\mu}_e|2\rangle = +\mu\hat{z}|2\rangle \end{array} \right.$

$$\left[\hat{H}\right]_{1,2} = \begin{pmatrix} E_0 + \mu\mathcal{E} & -A \\ -A & E_0 - \mu\mathcal{E} \end{pmatrix}$$

Diagonalization: $E_\pm = E_0 \pm \sqrt{(\mu\mathcal{E})^2 + A^2} \equiv E_0 \pm \Delta$

$$E_-: |I'\rangle = N_-^{-1/2}\left(A|1\rangle + (\mu\mathcal{E}+\Delta)|2\rangle\right)$$
$$E_+: |II'\rangle = N_+^{-1/2}\left(A|1\rangle + (\mu\mathcal{E}-\Delta)|2\rangle\right)$$

where $N_\mp = A^2 + (\mu\mathcal{E} \pm \Delta)^2$ and $\langle 1|2\rangle \approx 0$

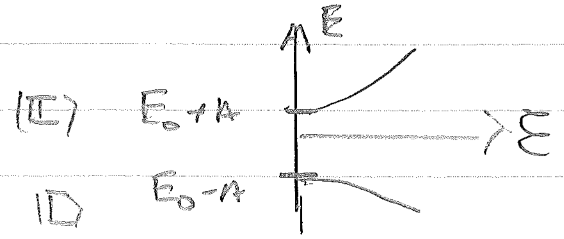
Examine weak and strong field limits separately

Weak field $\mu\mathcal{E} \ll A$

$$\Delta \doteq A\left(1 + \frac{1}{2}\left(\frac{\mu\mathcal{E}}{A}\right)^2\right)$$

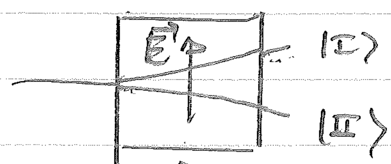
$$\frac{\mu\mathcal{E} \pm \Delta}{A} \doteq \pm 1 + \frac{\mu\mathcal{E}}{A}$$

states are very nearly $|I\rangle$, $|II\rangle$ but with energies that increase quadratically with $\mathcal{E}$.



$\mathcal{E} \ll \frac{A}{\mu}$ weak field

A weak field gradient can separate $|I\rangle$, $|II\rangle$ states



$$\vec{E} = \mathcal{E}\,\hat{z}$$

$$\frac{\partial \mathcal{E}}{\partial z} > 0$$

$$F_z^{\pm} = -\frac{\partial}{\partial z}(\text{energy}) = \mp \frac{\partial}{\partial z}\left(\mathcal{E}^2 \frac{\mu^2}{2A}\right) = \mp \frac{\mu^2}{A}\mathcal{E}\frac{d\mathcal{E}}{dz}$$

Force will be in $+\hat{z}$ direction for lower energy state $|I\rangle$

<u>Induced dipole moment</u>

neglecting overlap $\langle 1|2\rangle = 0$ $\hat{\vec{\mu}}_e$ diagonal in $|1\rangle, |2\rangle$ basis

$$\left[\hat{\vec{\mu}}_e\right]_{1,2} \rightarrow \mu \hat{z} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

Eigenstates are $|I\rangle \rightarrow \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ $|II\rangle \rightarrow \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$$\langle \vec{\mu}_e \rangle_{I,II} = \frac{1}{2}(1, \pm 1)\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} = 0$$

States $|I'\rangle, |II'\rangle$ get <u>induced dipole moments</u>

$$\Delta \overset{2}{=} A + \frac{1}{2}\frac{(\mu\mathcal{E})^2}{A}$$

$$|I'\rangle = \frac{1}{N^{1/2}}\left[A|1\rangle + \left(\mu\mathcal{E} + A + \frac{1}{2}\frac{(\mu\mathcal{E})^2}{A}\right)|2\rangle\right]$$

then to first order in $\mathcal{E}$

$$\langle I'|\vec{\mu}_e|I'\rangle = \frac{\mu\hat{z}}{N}\left(-A^2 + A^2 + 2\mu\mathcal{E}A\right)$$

$$N \overset{2}{=} 2A^2 + \mu\mathcal{E}A \approx 2A^2$$

$$\langle I'|\vec{\mu}_e|I'\rangle = \hat{z}\mu\left(\frac{\mu\mathcal{E}}{A}\right)$$ linear in $\mathcal{E}$

In strong field case, $\langle \vec{\mu}_e \rangle = \pm \mu \hat{z}$ fixed moment

numbers - $2A = 10^{-4}\,eV$ $\mu = 1.42\,D$ ↙ debye

$= 1.42(0.02)\,e\,nm$

$\frac{2A}{\mu\mathcal{E}} = 1$ $\mathcal{E} = \frac{10^{-4}\,eV}{2.84\times10^{-2}\,e\,nm} = 3500\,kV/m$

Strong field $\mu\mathcal{E} >> A$

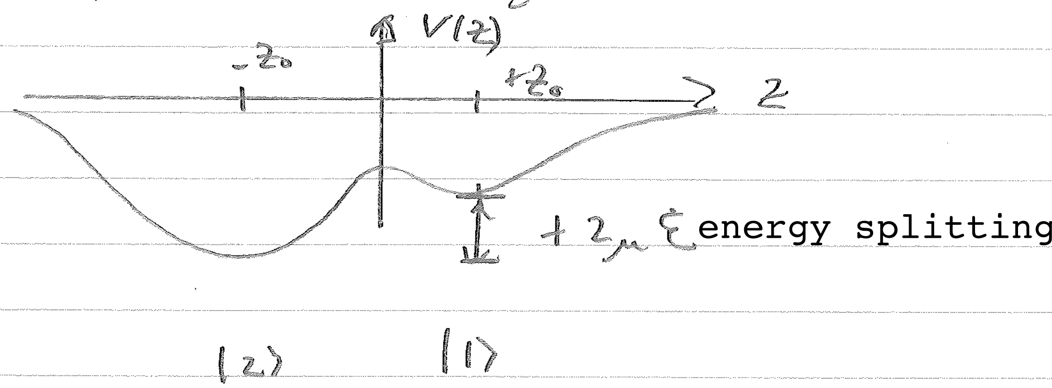
$$\Delta \cong \mu\mathcal{E}\left[1+\frac{1}{2}\left(\frac{A}{\mu\mathcal{E}}\right)^2\right]$$

Energy increases linearly with $\mathcal{E}$

$$\mu\mathcal{E}\pm\Delta = \begin{cases} 2\mu\mathcal{E} & |I'\rangle \Rightarrow |2\rangle \\ 0 & |II'\rangle \Rightarrow |1\rangle \end{cases}$$

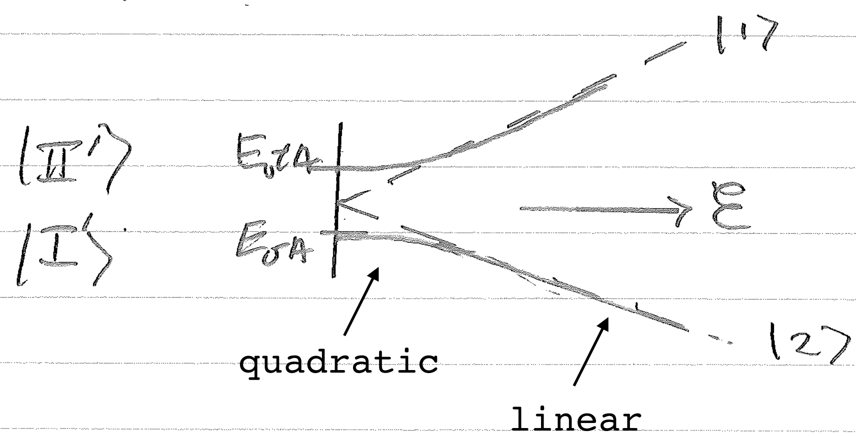
in large field limit
see primed solutions on p.4

large $\mathcal{E}$ prevents tunneling



$$\hat{H}|2\rangle = (E_0 - \mu\mathcal{E})|2\rangle$$
$$\hat{H}|1\rangle = (E_0 + \mu\mathcal{E})|1\rangle$$

Complete solution



the Ammonia Maser

experimentally, $2A = 10^{-4}\,eV$

$$f = \frac{1}{2\pi}\left(\frac{2A}{\hbar}\right) = 24\ GHz$$

$\lambda \approx cm$, microwave

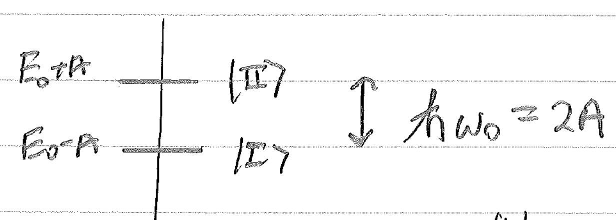
recall $kT @ 300K \cong \left(\frac{1}{40}\right) eV$, so thermal excitation populates both states

$$\frac{N_{II}}{N_{I}} = e^{-2A/k_BT} = e^{-0.004} = 0.996$$

$$\mu \cong ex(1\text{Å}) = \left(\frac{eV}{V}\right) 10^{-10}\,m = \frac{eV}{10^{10}\,V/m}$$

$$\frac{\mu \mathcal{E}}{2A} = 1 \Rightarrow \mathcal{E}_0 = \frac{10^{-4}\,eV}{1eV}\,10^{10}\,V/m = 10^{6}\,V/m$$

An electric field of this size applied at the right frequency will induce resonant transitions and coherent photon emission.



$$f_0 = \frac{\omega_0}{2\pi} = \frac{1}{2\pi}\left(\frac{2A}{\hbar}\right)$$

$$\vec{E}(t) = \hat{z}\,\mathcal{E}_0 \cos(\omega t) \equiv \hat{z}\,\mathcal{E}(t)$$

Rewrite $\hat{H}$ in $|I\rangle, |II\rangle$ basis:

$$(|I\rangle, |II\rangle) = (|1\rangle, |2\rangle)\underbrace{\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}}_{\hat{S}}$$

$$[H]_{I,II} = \hat{S}^{+}[H]_{12}\hat{S} = \hat{S}^{+}\begin{pmatrix} E_0 + \mu\mathcal{E} & -A \\ -A & E_0 - \mu\mathcal{E} \end{pmatrix}\hat{S}$$

$$= \begin{bmatrix} E_0 - A & \mu\mathcal{E}(t) \\ \mu\mathcal{E}(t) & E_0 + A \end{bmatrix}$$

explicitly time dependent H

we can see that field $\mathcal{E}(t)$ couples $|I\rangle, |II\rangle$ states.

Schrödinger equation in this basis:

$$i\hbar \frac{d}{dt}\begin{pmatrix} C_I \\ C_{II} \end{pmatrix} = [H]\begin{pmatrix} C_I \\ C_{II} \end{pmatrix}$$

$$i\hbar \dot{C}_I = (E_0 - A)\,C_I + \mu\mathcal{E}(t)\,C_{II}$$
$$i\hbar \dot{C}_{II} = \mu\mathcal{E}(t)\,C_I + (E_0 + A)\,C_{II}$$

define $E_\pm = E_0 \pm A$

let $C_{I,II} = \gamma_{I,II}\, e^{-i(E_\mp)t/\hbar}$

$$i\hbar\,\dot{\gamma}_{I} = \mu\mathcal{E}(t)\, e^{i(E_+ - E_-)t/\hbar}\,\gamma_{II}$$

$$i\hbar\,\dot{\gamma}_{II} = \mu\mathcal{E}(t)\, e^{-i(E_+ - E_-)t/\hbar}\,\gamma_{I}$$

$$\frac{E_+ - E_-}{\hbar} = \frac{2A}{\hbar} \equiv \omega_0 \quad \text{and} \quad \frac{2\mu\mathcal{E}_0}{\hbar} \equiv \omega_1$$

$$i\,\dot{\gamma}_{I} = \frac{\omega_1}{2}\cos\omega t\, e^{i\omega_0 t}\,\gamma_{II}$$

$$i\,\dot{\gamma}_{II} = \frac{\omega_1}{2}\cos\omega t\, e^{-i\omega_0 t}\,\gamma_{I}$$

expand $\cos\omega t = \frac{1}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)$

define $\Omega = \omega_0 + \omega$

$\Delta = \omega_1 - \omega_0$

$$\dot{\gamma}_{I} = -i\frac{\omega_1}{4}\left(e^{i\Omega t} + e^{-i\Delta t}\right)\gamma_{II}$$

$$\dot{\gamma}_{II} = -i\frac{\omega_1}{4}\left(e^{i\Delta t} + e^{-i\Omega t}\right)\gamma_{I}$$

these equations have no exact analytic solution.
formal solution:

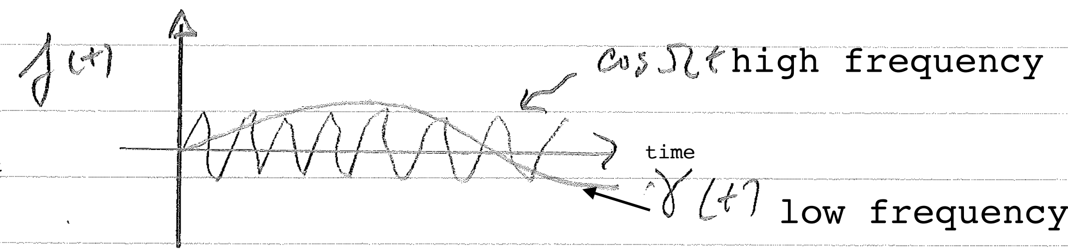
$$\gamma_I(t) = -i\frac{\omega_1}{4}\int_0^t\left(e^{+i\Omega\tau} + e^{-i\Delta\tau}\right)\gamma_{II}(\tau)\,d\tau$$

$$\gamma_{II}(t) = -i\frac{\omega_1}{4}\int_0^t\left(e^{-i\Omega\tau} + e^{i\Delta\tau}\right)\gamma_{I}(\tau)\,d\tau$$

Υ factors vary slowly compared to natural period of oscillator ($2\pi/\omega$_
So they will average to zero in the integral EXCEPT when $\Delta \to 0$,
driving frequency approaches natural frequency.

for $\frac{\omega_1}{\omega_0} = \frac{\mu E_0}{A} \ll 1$ coupling is weak

and $\gamma_{I,II}$ will very slowly compared to ω_0. Ωt terms will average out, but Δt terms will not near $\omega \approx \omega_0$ (resonance)



Ω terms will always average out

$$\int_0^t e^{i\Omega\tau}\gamma_{II}(\tau)\,d\tau \approx 0$$

then
$$\dot{\gamma}_I \cong -i\frac{\omega_1}{4}e^{-i\Delta t}\gamma_{II}$$
$$\dot{\gamma}_{II} \cong -i\frac{\omega_1}{4}e^{+i\Delta t}\gamma_I$$

At resonance $(\Delta = 0)$ these can easily be solved

$$\left.\begin{aligned}\dot{\gamma}_I &= -i\frac{\omega_1}{4}\gamma_{II}\\ \dot{\gamma}_{II} &= -i\frac{\omega_1}{4}\gamma_I\end{aligned}\right\}\quad \begin{aligned}\ddot{\gamma}_I &= \left(\frac{\omega_1}{4}\right)^2\gamma_I\\ \ddot{\gamma}_{II} &= \left(\frac{\omega_1}{4}\right)^2\gamma_{II}\end{aligned}$$

$$\gamma_I(t) = C_I(0)\cos\frac{\omega_1 t}{4} + C_{II}(0)\sin\frac{\omega_1 t}{4}$$

$$\gamma_{II}(t) = -iC_I(0)\sin\left(\frac{\omega_1 t}{4}\right) + iC_{II}(0)\cos\left(\frac{\omega_1 t}{4}\right)$$

$$C_I(t) = e^{-i(E_0 - A)t/\hbar}\left[C_I(0)\cos\frac{\omega_1 t}{4} + C_{II}(0)\sin\frac{\omega_1 t}{4}\right]$$

$$C_{II}(t) = e^{-i(E_0 + A)t/\hbar}\left[-i\, C_I(0)\sin\frac{\omega_1 t}{4} + i\, C_{II}(0)\cos\left(\frac{\omega_1 t}{4}\right)\right]$$

lets take $|\psi(0)\rangle \xrightarrow[I,II]{} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} C_I(0) \\ C_{II}(0) \end{pmatrix}$

probability to measure $E_0 + A$ (state II) at time t !

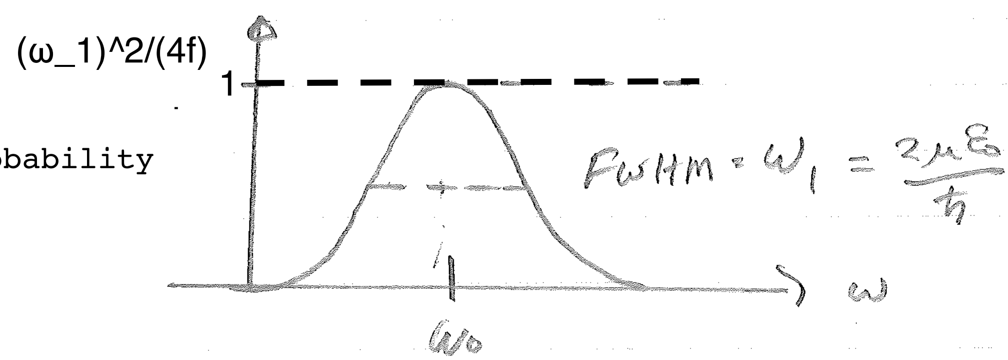
$$P_{I\to II}(t) = \left|\langle II|\psi(t)\rangle\right|^2 = \left|(0,1)\begin{pmatrix} C_I(t) \\ C_{II}(t)\end{pmatrix}\right|^2$$

$$= \left|C_{II}(t)\right|^2 = \sin^2\left(\frac{\omega_1 t}{4}\right)$$

Off resonance, we get Rabi's formula

$$P_{I\to II}(t) = \frac{\omega_1^2}{4f^2}\sin^2\left(\frac{ft}{2}\right)$$

where $f^2 = (\omega_0 - \omega)^2 + \frac{\omega_1^2}{4}$



Transition probability coefficient

Resonance curve

Magnetic Resonance

$$\vec{B} = B_1 \cos\omega t \,\hat{x} + B_0 \hat{z}$$

time varying static

$$\hat{H} = -\vec{\mu}\cdot\vec{B} = \omega_0 \hat{S}_z + \omega_1 \hat{S}_x \cos(\omega t)$$

where $q = -e$ $\omega_i = \frac{eg}{2mc} B_i$ $i = 0, 1$

NOTE: q=-e is Taylor's choice. Then spin |-z> has magnetic moment aligned with field, the lower energy state.

In $|+z\rangle, |-z\rangle$ basis:

$$[\hat{H}] = \frac{\hbar}{2}\begin{bmatrix} \omega_0 & \omega_1 \cos\omega t \\ \omega_1 \cos\omega t & -\omega_0 \end{bmatrix}$$

Math is identical to ammonia maser. For $\omega_1 \ll \omega_0$

$$\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \begin{matrix} c(t)\, e^{-i\omega_0 t/2} \\ d(t)\, e^{+i\omega_0 t/2} \end{matrix}$$

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

expand $\cos\omega t = \frac{1}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)$

define $\Omega = \omega_0 + \omega$

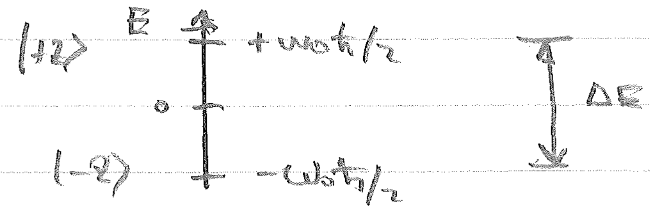
$\Delta = \omega_0 - \omega$

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

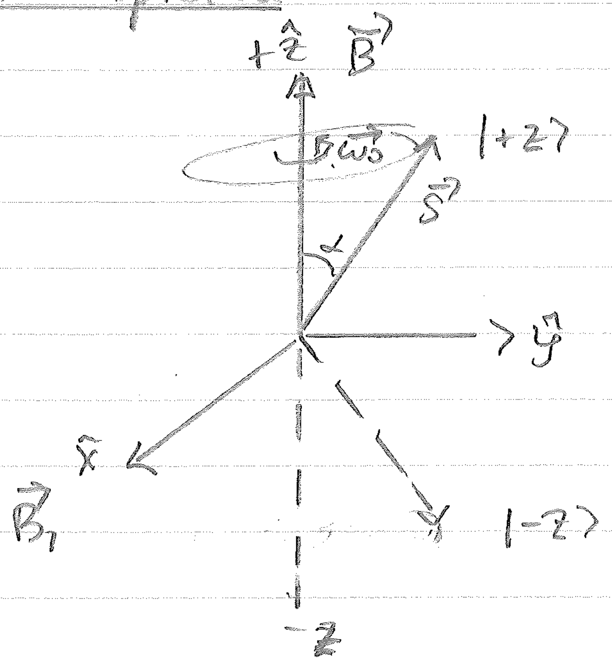
$$\simeq -i\frac{\omega_1}{4}\begin{pmatrix} e^{i\Delta t} \\ e^{-i\Delta t} \end{pmatrix}$$

leading to Rabi's resonance formula.

Resonance condition $\omega = \omega_0 = \Delta E/\hbar$



Classical picture:



$$\cos\alpha = \frac{|\langle \hat{S}_z \rangle|}{\sqrt{\langle \hat{S}^2 \rangle}} = \frac{1}{\sqrt{3}}$$

$\vec{B}_1$ drives transition when $\omega = \omega_0$

For proton $\left.\frac{\omega_0}{2\pi}\right|_{B_0 = 1\text{ Tesla}} = 42.6$ MHz NMR