Chapter 16.

Magnetic Effect

dynamic magnetic effect

NMR : nuclear magnetic resonance
NQR : nuclear quadrupole resonance
EPR : electron paramagnetic resonance
FMR : ferromagnetic resonance
SWR : spin wave resonance
AFMR : antiferromagnetic resonance
CESR : conducting electron spin resonance

- ○ Defect에 의한 electronic structure
- ○ Spin이 움직임으로 주위의 변화
- ○ Spin에 의한 Internal magnetic field 변화, chemical shift, knight shift
- ○ Collective spin excitation

NMR : complex molecule의 structure determination identification
extremly high resolution attainable in diamagnetic liquid.

Nuclear Magnetic Resonance $\vec{\mu} = \gamma\hbar I$

Energy interaction with the applied magnetic field.

$\vec{B_a} = B_0\hat{z}$ $\quad U = -\vec{\mu}\cdot\vec{B_a}$ $\quad U = -\mu_z B_0 = -\gamma\hbar B_0 I_z$

allowded values of I_z $\quad m_I = I, I-1, I-2, \cdots, -I$

$u = -m_I\gamma\hbar B_0$

$\hbar\omega_0 =$ energy difference between the two levels

$= \gamma\hbar B_0 \qquad (\omega_0 = \gamma B_0)$

proton $\quad \gamma = 2.675\times10^4 \ s^{-1}\cdot gauss^{-1}$
$\quad = 2.675\times10^8 \ s^{-1}\cdot tesla^{-1}$

$\nu\,(MHz) = 4.258 \cdot B_0(kilogauss) \quad = 42.58 \cdot B_0(tesla)$

electron spin 인 경우

$\nu\,(GHz) = 2.80 \cdot B_0(kilogauss) \quad = 28.0 \cdot B_0(tesla)$

Equation of Motion

the rate of change of angular monentum = torque

$\hbar\frac{d\vec{\mu}}{dt} = \vec{\mu}\times\vec{B_a} \qquad \vec{\mu} = \gamma\hbar\vec{I}$

$\therefore \quad \frac{d\vec{\mu}}{dt} = \gamma\vec{\mu}\times\vec{B_a}$ nuclear magnetization $\vec{M} = \sum \vec{\mu_i}$ (/volume)

$$\frac{d\vec{M}}{dt} = \gamma\vec{M}\times\vec{B_a}$$

Let $\vec{B_a} = B_0\hat{z}$ 이고,

equilibrium에서 $\vec{M} = M\hat{z} = \chi_0 B = \frac{cB_0}{T}$ 이면 where $c = \frac{N\mu^2}{3k_B}$

Magnetization of a system $I = \frac{1}{2}$

population difference $N_1 - N_2$

$$M_z = (N_1 - N_2)\mu$$

$$\left(\frac{N_2}{N_1}\right)_0 = \exp\left(-\frac{2\mu B_0}{k_B T}\right)$$

equal magnetization $M = N_\mu \tanh\left(\frac{\mu_B}{k_B T}\right)$

만약, thermal equilibrium이 아니면 $\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$

T_1 : longitudinal relaxation time or spin lattice relaxation time

$T = 0$ 에서 unmagnetized specimen을 $B_0\hat{z}$ 에 넣었다.

$$\int_0^M \frac{dM_z}{M_0 - M_z} = \int_0^t \frac{dt}{T_1}$$

$$\log\frac{M_0 - M_z}{M_0} = -\frac{t}{T_1}$$

$$\therefore \quad M_0 - M_z(t) = M_0 e^{-\frac{t}{T_1}}$$

$$\therefore \quad M_z(t) = M_0\left(1 - e^{-\frac{t}{T_1}}\right)$$

3가지 process : 1. direct (phonon을 주고 받음)
2. Raman (phonon의 scattering)
3. Orbach (Intervention of a third state)

Magnetic energy $-\vec{M}\cdot\vec{B_a}$ decreases as M_z approaches its new equilibrium value

B field를 가했다. M_z 가 어떻게 변화하나

$$\frac{dM_z}{dt} = \gamma(\vec{M}\times\vec{B_a})_z + \frac{M_0 - M_z}{T}$$

M will relax to the equilibrium value M_0

transverse magnetization은 zero로 decay하는데,

equilibrium으로 가는 relaxation time은같지 않다. Transverse relaxation time

$$\frac{dM_x}{dt} = \gamma(\overrightarrow{M} \times \overrightarrow{B_a})_x - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma(\overrightarrow{M} \times \overrightarrow{B_a})_y - \frac{M_y}{T_2} \qquad \textit{Bloch equation}$$

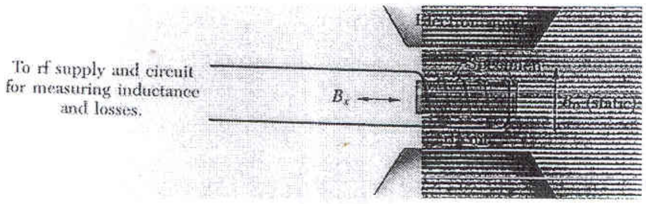
T_2 is called transverse relaxation time

결국, M_x , M_y는 random한 상태로 변할 것이다.

처음엔 M_x , M_y가 in phase 였다가 random하게 된다.

T_2는 얼마나 빨리 random한 상태로 되는지를 결정.

실험 : rf Magnetic field를 $\hat{x}$, $\hat{y}$ 축으로 가한다.



$B_a = B_0 \hat{z}$, $M_z = M_0$ 이면

$$\frac{dM_x}{dt} = \gamma B_0 M_y - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma B_0 M_x - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = 0$$

We look for damped oscillatory solutions

$$M_x = m\exp\left(-\frac{t}{T'}\right)\cos(\omega t) \qquad M_y = m\exp\left(-\frac{t}{T'}\right)\sin(\omega t)$$

$$-\frac{1}{T'}\exp\left(-\frac{t}{T'}\right)\cos(\omega t) - \omega m\exp\left(-\frac{t}{T'}\right)\sin(\omega t)$$

$$= -\gamma B_0 m\exp\left(-\frac{t}{T'}\right)\sin(\omega t) - \frac{1}{T_2} m\exp\left(-\frac{t}{T'}\right)\cos(\omega t)$$

$$\begin{pmatrix} T' = T_2 \\ \omega = \gamma B_0 \end{pmatrix}$$

만약 x방향, y방향으로 rotating magnetic field를 걸어주면

$B_x = B_1\cos(\omega t)$: $B_y = -B_1\sin(\omega t)$

resonance는 driving field가 near $\omega_0 = \gamma B_0$ 일 때 일어난다.

$$\Delta\omega \cong \frac{1}{T_2}$$

After calculation.

power absorption $P(\omega) = \dfrac{\omega\gamma M_z T_2}{1+(\omega_0-\omega)^2 T_2^2}$

half-width $\frac{1}{2} P(\omega) = P(\omega_0)$

$$\therefore \frac{1}{2}\omega_0 = \frac{\omega}{1+(\omega_0-\omega)^2 T_2^2}$$

$$\therefore [1+(\omega_0-\omega)^2 T_2^2]\omega_0 = 2\omega$$

$$1+(\omega_0-\omega)^2 T_2^2 \cong 2$$

$$(\omega_0-\omega)^2 T_2^2 = 1 \quad \left(\Delta\omega = \frac{1}{T_2}\right)$$

Line width

Magnetic dipole moment에 의한 line broadening

$$\Delta B = \frac{3(\overrightarrow{\mu_2}\cdot\overrightarrow{r_{12}})\overrightarrow{r_{12}} - \overrightarrow{\mu_2}\, r_{12}^2}{r_{12}^5}$$: μ_2 에 의한 μ_1 에서의 B field

$$B_i \simeq \frac{\mu}{r^3}$$

가장 가까운 항 r=a 가 기여

$$B_i \approx \frac{1.4\times10^{-23}\ G\cdot cm^3}{8\times10^{-24}\ cm^3} \approx 2\ gauss = 2\times10^{-4}\ tesla$$

Motional Narrowing

서로 움직이면 line width가 매우 많이 감소한다.

액체에서 proton resonance의 line width는 10^{-5} of the width of ice

T_2 : dephasing 하는 시간 (local perturbation in the magnetic field intensity)

$(\Delta\omega)_0 \approx \gamma B_i$ local frequency deviation due to a perturbation B_i

μ_1 μ_2

μ_2 가 fluctuation 한다.

$\therefore$ 1번에의 phase angle $\delta\phi = \pm\gamma B_i \tau$

n번 계속한다.

$$\langle\phi^2\rangle = n(\delta\phi)^2 = n\gamma^2 B_i^2 \tau^2$$

dephase 하는데 걸리는 step n

$$\therefore T_2 = n\tau = \frac{1}{\gamma^2 B_i^2 \tau} \ : [dephasing\ time]$$

처음 유도식 $T_2 \cong \dfrac{1}{\gamma B_i}$ 와 매우 다르다.

$\Delta\omega = \frac{1}{T_2} = (\gamma B_i)^2 \tau$ rigid lattice line width 이다.

τ 가 작으면 $\Delta\omega$ 가 작다 motional narrowing 이라 한다.

물분자의 rotational relaxation Time : 10^{-10} sec

$(\Delta\omega)_0 \approx 10^5\ s^{-1}$

$(\Delta\omega)_0 \cdot \tau \approx 10^{-5}$

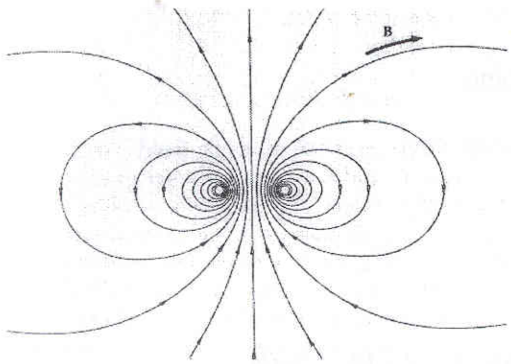
$\Delta\omega = (\Delta\omega)_0^2 \cdot \tau \approx 1\ \text{sec}^{-1}$

∴ motional narrowing은 10^{-5} 정도이다.

Hyperfine Splitting

=> 핵의 magnetic moment와 electron의 magnetic moment 사이 interaction

: electron의 magnetic moment의 움직임에 따라 핵에 B field가 생겨난다.



⇒ orbital angular moment가 없어도 spin 만 있으면 B field가 나타난다.

Dirac equation의 결과

$\mu_B = \frac{e\hbar}{2mc}$ [Bohr Magneton ; electron의 magnetic moment]

electric current associated with the circulation

$I \sim e \times \frac{c}{\lambda_e}$ $I = \frac{e}{T} = \frac{e}{(\lambda_e/c)}$

$\lambda_e = \frac{\hbar}{mc} \sim 10^{11}\ cm$ 전자의 orbit는 (대강) compton wavelength 정도이다.

Magnetic field produced by the current

$B \sim \frac{I}{\lambda_e c} \sim e\frac{c}{\lambda_e}\frac{1}{\lambda_e c} \sim \frac{e}{\lambda_e^2}$

핵에서 느끼는 B field

$\overline{B} \cong \frac{e}{\lambda_e^2} \cdot |\Phi(0)|^2 \lambda_e^3$

$\cong e|\Phi(0)|^2 \lambda_e$ $\mu_B = e\hbar/2mc = \frac{1}{2} e\lambda_e$

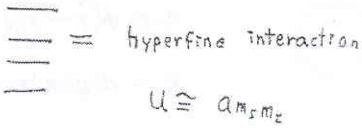
Hyperfine interaction energy

$$U = -\overrightarrow{\mu_1} \cdot \overrightarrow{B} = -\overrightarrow{\mu_1} \cdot \overrightarrow{\mu_B} |\Phi(0)|^2$$

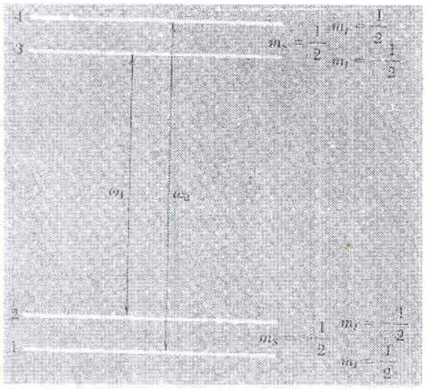
$$\sim \gamma \hbar \mu_B |\Phi(0)|^2 \overrightarrow{I} \cdot \overrightarrow{S}$$

$$U = a\overrightarrow{I} \cdot \overrightarrow{S}$$

Zeeman energy splitting



two electronic transition



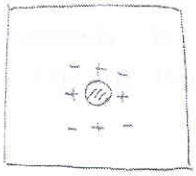
hydrogen에서

ground energy splitting 1420 MHz

Radio frequency line of interstellar atomic hydrogen

Paramagnetic Point defect

alkalihalide donor atoms in Silicon



F - center

one electron bound at the vacancy

Cl^-이 없어짐

6개 Alkali atom n.nbd

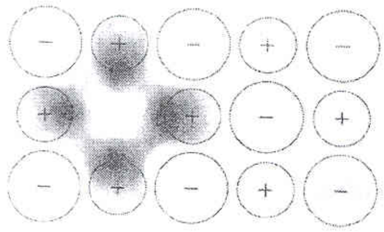
12개 Cl^- N.NNbd

Alkali ion의 valence electron의 wave function $\phi(\overrightarrow{r})$

LCAO approximation

$$\Psi = c\sum_p \phi(\overrightarrow{r} - \overrightarrow{r_p})$$

Spin resonance line of an F center

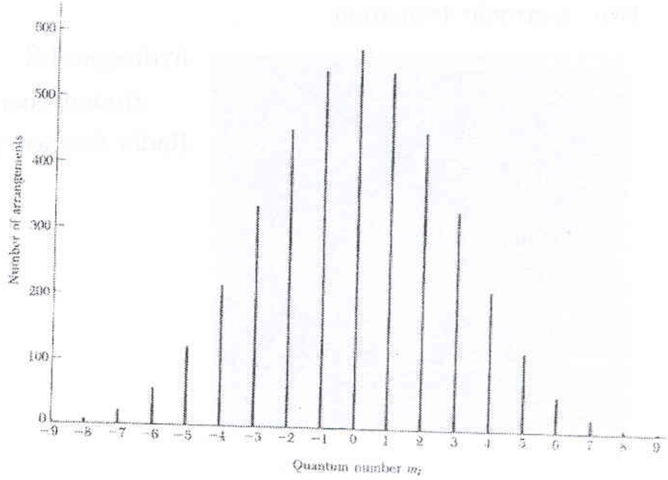


전자와 ⊕ nuclear 사이의 interation으로 electron의 상태를 알 수 있다.

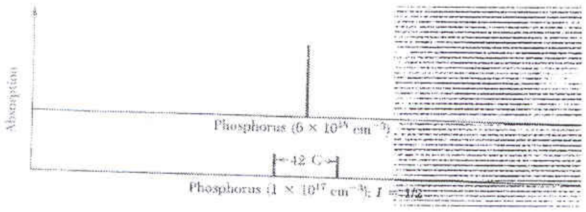
$$\phi = c_1\phi(\vec{r}-\vec{r_1}) + c_2\phi(\vec{r}-\vec{r_2}) + c_3\phi(\vec{r}-\vec{r_3}) + c_4\phi(\vec{r}-\vec{r_4})$$

n_i= *degeneracy number*

Degenaracy is separated!
:[오른쪽그림]



Donor atoms in silicon



Donor가 많아지면 rapidly hopping of electron에 의해 motional narrowing이 일어난다.

Knight shift

핵의 spin resonance가 diamagnetic solid 일 때보다 metal 일 때 shift 된다.

conduction electron의 효과

Interaction energy of nucleus of spin I and magnetogyric ratio

$$U = (-\gamma_I \hbar B_0 + a\langle S_z\rangle)I_z$$

외부B field hyperfine structure due to conduction electron.

$$M_z = gN\mu_B\langle S_z\rangle = \chi_s B_0$$:Pauli spin susceptibility χ_s

$$= \left(-\gamma_I\hbar + \frac{a\chi_s}{gN\mu_B}\right)B_0 I_z$$

$$= -\gamma_I\hbar B_0\left(1+\frac{\Delta B}{B_0}\right)I_z$$

Knight shift $k = -\frac{\Delta B}{B_0} = \frac{a\chi_s}{gN\mu_B\gamma_I\hbar}$ where $a = \gamma\hbar\mu_B|\Psi(0)|^2$

$= \frac{\gamma\hbar\mu_B|\Psi(0)|^2\chi_s}{gN\mu_B\gamma_I\hbar}$ $\gamma = \gamma_I$

$= \frac{\chi_s|\Psi(0)|^2}{gN}$ $g = 2$

$= \frac{\chi_s|\Psi(0)|^2}{2N}$

magnetic gyroratio의 fractional change 이다.

knight shift $k \cong \frac{\chi_s|\Psi(0)|^2}{N}$

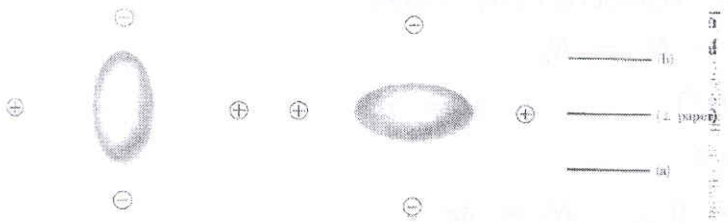
Metal 과 free atom인 경우의 knight shift가 같지 않다.

∵ $\Psi(r)$ 이 약간 다르기 때문이다.

예: Li $|\Psi(0)|^2 \rightarrow 0.44$ *metal*
$\rightarrow 0.49$ *free atom*

Nuclear Quadrupole Resonance

$$eQ = \frac{1}{2}\int(3z^2 - r^2)\rho(\vec{r})d^3x$$



: 핵의 모양

Nuclear in its enviroment

Quadrupole moment ⇒ energy splitting

3개로만 나누어지는가? $(2I+1)$ state로 나누어 진다.

Nuclear Quadrupole resonance

: in the absence of static magnetic field에서 일어난다.

Cl_2, Br_2, I_2 : splitting $10^7 \sim 10^8$ Hz

Ferromagnetic Resonance

Spin resonance at microwave frequency in ferromagnetic.

Nuclear spin resonance

핵의 spin에 의해 핵의 magnetic moment가 생긴다.

∴ 외부의 B field 에 의해 splitting 된다.

외부에서 rf transverse field를 가하면 precessional frequency와 같을 때 에너지를 흡수한다.

Magnetic selection rule $\Delta m_s = \pm 1$

◦ χ', χ'' 가 크다.

magnetization이 electron, nuclear paramagnet 보다 매우 커 splitting이 크다.

◦ Speciman의 shape가 매우 중요하다.

◦ Strong exchange coupling resonance line width 가 매우 작다.

Shape Effect in FMR

$$B_x^{\,i} = B_x^{\,0} - N_x M_x\ ,\quad B_y^{\,i} = B_y^{\,0} - N_y M_y\ ,\quad B_z^{\,i} = B_z^{\,0} - N_z M_z$$

$$\frac{dM_x}{dt} = \gamma(M_y\ B_z^{\,i} - M_z\ B_y^{\,i}) = \gamma\ [M_y(\ B_z^{\,0} - N_z M_z) - M_z(\ B_y^{\,0} - N_y M_y)]$$

$$= \gamma\ [B_0 + (N_y - N_z)]M_y$$

$$\frac{dM_y}{dt} = \gamma\ [M(-N_x M_x) - M_x(B_0 - N_z M_z)]$$

$$= -\gamma\ [B_0 + (N_x - N_z)M]M_x$$

$$\begin{vmatrix} i\omega & \gamma\ [B_0 + (N_y - N_z)M] \\ -\gamma\ [B_0 + (N_x - N_z)M] & i\omega \end{vmatrix} = 0$$

$$\omega^2 = \gamma^2[B_0 + (N_y - N_z)M][B_0 + (N_x - N_z)M]$$

만약 Sphere이면 $N_x = N_y = N_z$

$$\omega^2 = \gamma^2[\ B_0^{\,2}] \qquad \therefore\ \omega = \gamma B_0$$

만약 sharp하면 $B_0 \perp$ 축

$$N_x = N_y = 0\ ,\qquad N_z = 4\pi$$

$$\omega^2 = \gamma^2[B_0 - 4\pi M][B_0 - 4\pi M]$$

$$\therefore\quad \omega = \gamma(B_0 - 4\pi M)$$

$B_0 \parallel plate$

$$N_x = N_z = 0\ ,\ N_y = 4\pi$$

$$\omega_0 = \gamma\ [B_0(B_0 + 4\pi M)]^{\frac{1}{2}}$$

Spin wave resonance

uniform rf magnetic field

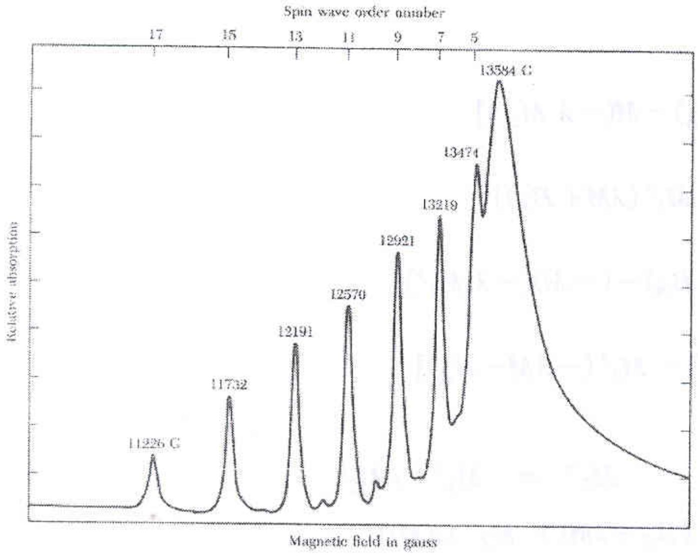
: longwavelength spin wave를 excite시킨다.

spin wave resonance

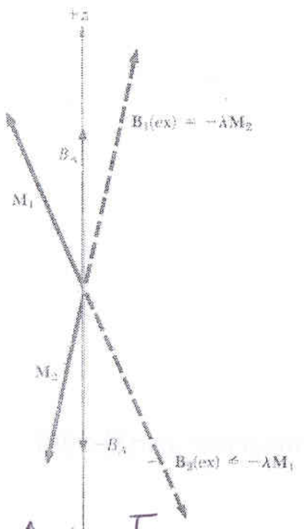
$$\omega_0 = \gamma\ (B_0 - 4\pi M) + Dk^2$$

예 : [그림은 다음 페이지에...]

$$= \gamma\ (B_0 - 4\pi M) + D\left(\frac{n}{\pi L}\right)^2$$



Anti-ferromagnetic Resonance



$$U_k(\theta_1) \;=\; k\ \sin^2\theta_1$$

Anti-Ferromagnetic Resonance

Exchange interaction between $\overrightarrow{M_1}$, $\overrightarrow{M_2}$ is treated in the mean field approximation.

exchange field

$$\overrightarrow{B_1}(ex) \;=\; -\lambda\overrightarrow{M_2} \qquad\qquad \overrightarrow{B_2}(ex) \;=\; -\lambda\overrightarrow{M_1}$$

$$\overrightarrow{B_1} \;= -\lambda\overrightarrow{M_2} + B_A\hat{z} \qquad\qquad \overrightarrow{B_2} \;= -\lambda\overrightarrow{M_1} + B_A\hat{z}$$

$$\frac{dM_x}{dt} \;=\; \gamma\,(\overrightarrow{M}\times\overrightarrow{B_a})_x - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} \;=\; \gamma\,(\overrightarrow{M}\times\overrightarrow{B_a})_y - \frac{M_y}{T_2}$$

let $M_1^{\,z} \;=\; M\ ,\quad M_2^{\,z} \;=\; -M$

linearized equation of motion

$$\frac{dM_1^x}{dt} = \gamma [M_1^y(\lambda M+B_A)-M(-\lambda M_2^y)]$$

$$\frac{dM_1^y}{dt} = \gamma [M(-\lambda M_{2x})- M_1^x(\lambda M+B_A)]$$

$$\frac{dM_2^x}{dt} = \gamma [M_2^y(-\lambda M-B_A)-(-M)(-\lambda M_1^y)]$$

$$\frac{dM_2^y}{dt} = \gamma [-M(-\lambda M_1^x)- M_2^x(-\lambda M-B_A)]$$

$$M_1^+ = M_1^x+i M_1^y \qquad M_2^+ = M_2^x+i M_2^y$$

$$\therefore \quad -i\omega M_1^+ = -i\gamma [M_1^+(B_A+\lambda M)+ M_2^+(\lambda M)]$$

$$-i\omega M_2^+ = i\gamma [M_2^+(B_A+\lambda M)+ M_1^+(\lambda M)]$$

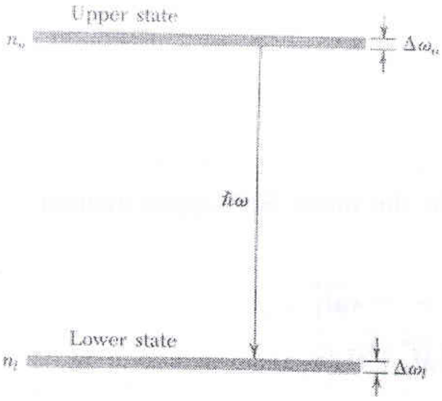
these equation have a solution if $B_E \equiv \lambda M$

$$\begin{vmatrix} \gamma (B_A+B_E)-\omega & \gamma B_E \\ \gamma B_E & \gamma (B_A+B_E)+\omega \end{vmatrix} = 0$$

Antiferromagnetic resonance frequency

$$\omega_0^2=\gamma^2(B_A+2B_E)$$

Principle of Maser Action



electromagnetic wave의 magnetic part만 생각

$$P=\left(\frac{\mu B_{rf}}{\hbar}\right)^2 \cdot \frac{1}{\Delta\omega}$$

$$\Delta\omega=\Delta\omega_u+\Delta\omega_l$$

Fermi Golden rule의 결과이다.

$$P=\left(\frac{\mu B_{rf}}{\hbar}\right)^2 \cdot \frac{1}{\Delta\omega} \hbar\omega \cdot (n_u-n_l)$$

$n_u < n_l$ thermal equilibrium. laser가 나오지 않는다.

$n_u > n_l$ emission

B_{rf}가 크면 emission이 더 나온다.

$n_u = n_l$ 이 될 때까지 emission이 나온다.

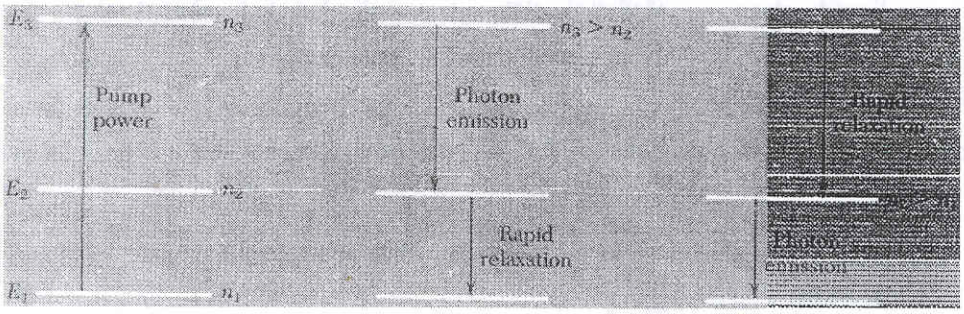
Cavity안에 넣어 계속 반사시키며 maser 유도

Cavity에 의해 흡수된다.

$$P_L = \frac{B_{rf}^2 V}{8\pi} \frac{\omega}{Q}$$ [Q: factor of cavity]

maser가 작동하기 위해서는 emitted power P가 power loss P_L보다 더 커야 한다.

Three level laser



three level Maser

$$\frac{dn^2}{dt} = - n_2 P(2\rightarrow 1) - n_2 P(2\rightarrow 3) + n_3 P(3\rightarrow 2) + n_1 P(1\rightarrow 2)$$

steady state 에서는 $\frac{dn_2}{dt} = 0$

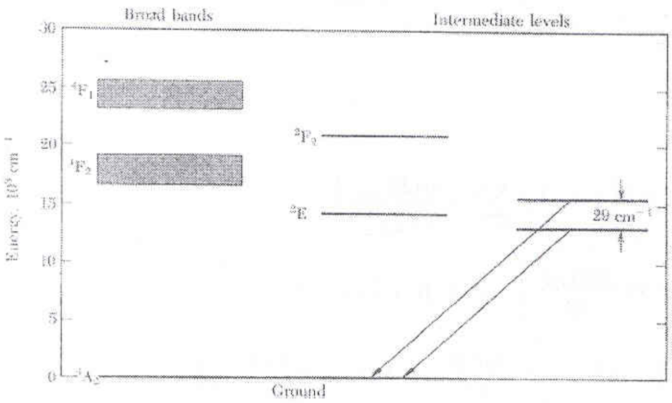
Saturation이 되면 $n_1 = n_3$

$$\therefore n_2 [P(2\rightarrow 1) + P(2\rightarrow 3)] = n_1 [P(3\rightarrow 2) + P(1\rightarrow 2)]$$

$$\therefore \quad \frac{n_2}{n_1} = \frac{P(3\rightarrow 2) + P(1\rightarrow 2)}{P(2\rightarrow 1) + P(2\rightarrow 3)}$$

Ruby laser는 three level maser이다.

★Ruby laser



[매우 빠르게(10^{-7}sec)decay phonon이 에너지를 잡아먹는다.]

(이 level 에 오래 머무른다.

∵ 5×10^{-3}sec 정도이다.

∴갑자기 나온다.

input energy의 1%정도가 Laser로 나온다.)