Chapter 7 Four-Wave Mixing phenomena

We will discus in this chapter the general nonlinear optical processes with four interacting electromagnetic waves in a NLO medium.

First note that

- FWM processes are allowed in all media (inversion or non inversion symmetry)
- Multi-resonant processes can dramatically enhance the magnitude of $\chi^{(3)}$.

In general, when $\chi^{(2)}$ is allowed, $\left|\chi^{(2)}\right| >> \left|\chi^{(3)}\right|$, we therefore will consider NLO media with inversion symmetry such that $\chi^{(2)}$ effects can be neglected.

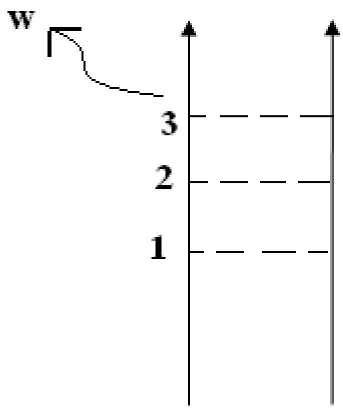
Useful applications with $\chi^{(3)}$ processes

- Tunable IR or UV coherent sources in all media
- Wave front reconstruction with DFWM (*e.g.*, Phase Conjugate Optics)
- Powerful spectroscopic techniques

7.1 Third-Order Nonlinear Optical Susceptibilities

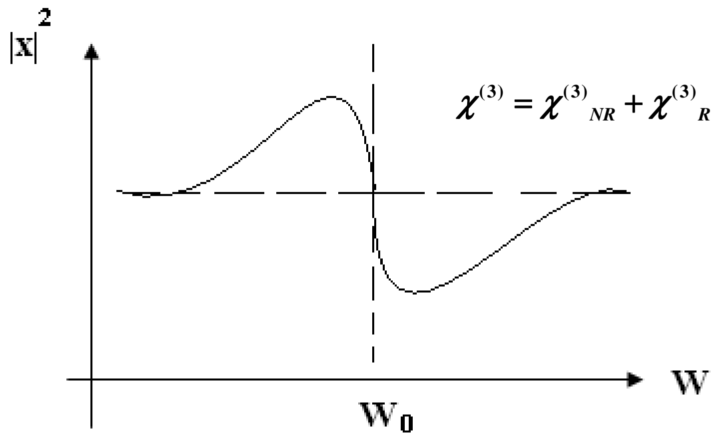
$\chi^{(3)}$ in a medium with inversion symmetry where $\chi^{(2)} = \mathbf{0}$, $\chi^{(3)}$ is the lowest nonlinear optical process.

- $\chi^{(3)}$ consists of 48 terms
- Near resonances, a few terms of $\chi^{(3)}$ are resonantly enhanced through the energy denominators



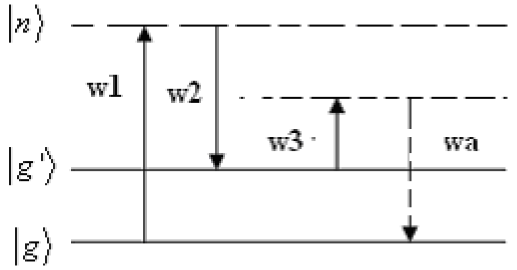
Note:
3 vertices on the left: C (3, 3) = 1
2 vertices on the left: C (3, 2) = 3
1 vertices on the left: C (3, 1) = 3
<u>0 vertices on the left: C (3, 0) = 1</u>
C (3, 3) + C (3, 2)+C (3, 1) +C (3,0)=8
Permutations of three vertices = 3! =6
➔ **3! 8 = 48**

- In principle, the resonant part of $\chi^{(3)}$ can be separated from the non resonant part through resonant dispersion



7.1.1 Singly Resonant Case

For the three input pump frequencies, ω_1, ω_2, ω_3, single resonance of $\chi^{(3)}$ can occur when any of the three frequencies or their algebraic sums approach a transition frequency of the medium, such as



($\omega_1 - \omega_2$) is resonant with $E_{g'g}$

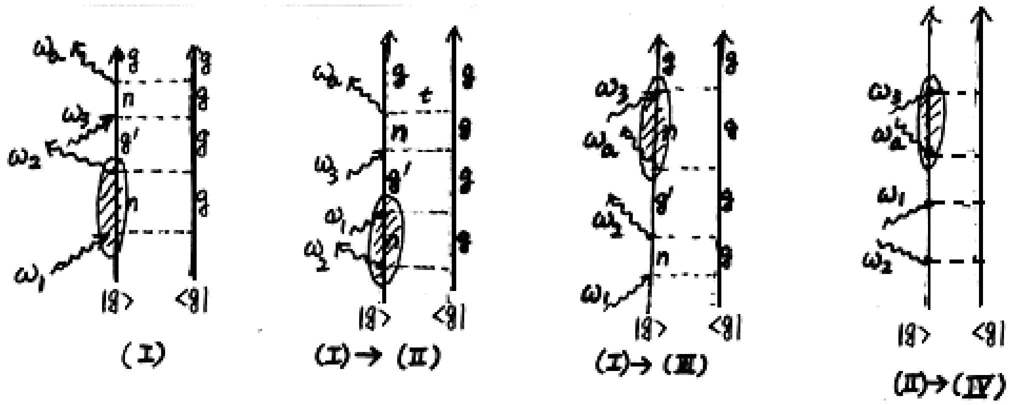
In this case,

$$\chi^{(3)} = \chi^{(3)}_{NR} + \chi^{(3)}_{R}$$

$$[\chi^{(3)}_R(\omega_a = \omega_1 - \omega_2 + \omega_3)]_{ijke} = -\frac{N}{\hbar}\frac{(M^a_{g'g})^*_{ij}(M^s_{g'g})_{kl}(\rho_g - \rho_{g'})}{(\omega_1 - \omega_2 - \omega_{gg'} - i\Gamma_{gg'})}$$

where $$(M^a_{g'g})_{ij} = \sum_n \left[\frac{\langle g'|er_j^{\omega_3}|n\rangle\langle n|er_i^{\omega_a}|g\rangle}{\hbar(\omega_a - \omega_{ng})} - \frac{\langle g'|er_i^{\omega_a}|n\rangle\langle n|er_j^{\omega_3}|g\rangle}{\hbar(\omega_3 + \omega_{ng})}\right]$$

$$(M^s_{g'g})_{kl} = \sum_n \left[\frac{\langle g'|er_k^{\omega_2}|n\rangle\langle n|er_e^{\omega_1}|g\rangle}{\hbar(\omega_1 - \omega_{ng})} - \frac{\langle g'|er_e^{\omega_1}|n\rangle\langle n|er_k^{\omega_2}|g\rangle}{\hbar(\omega_2 + \omega_{ng})}\right]$$



The expression for the I-*th* diagram

$$[\chi^{(3)}(\omega_a=\omega_1-\omega_2+\omega_3)]_{I-term}=\frac{N}{E_1E_2^*E_3}Tr(\mu\rho^{(3)})=\frac{N}{E_1E_2^*E_3}\left\{\sum_n\mu_{gn}\rho_{ng}^{(3)}\right\}$$

where

$$\rho_{ng}^{(3)}(I)=\sum_{g'ng}\rho_{gg}^{(0)}\langle n|\frac{H(\omega_3)}{i\hbar}|g'\rangle\langle g'|\frac{H^+(\omega_2)}{i\hbar}|n\rangle\langle n|\frac{H(\omega_1)}{i\hbar}|g\rangle\cdot$$

$$\frac{1}{i(\omega_1-\omega_2+\omega_3-\omega_{ng})}\cdot\frac{1}{i(\omega_1-\omega_2-\omega_{g'g}+i\Gamma_{g'g})}\cdot\frac{1}{i(\omega_1-\omega_{ng})}$$

The expression for the II-*th* diagram

$$\rho_{ng}^{(3)}(II)=\sum_{g'ng}\frac{\langle g'|\frac{H(\omega_1)}{i\hbar}|n\rangle\langle n|\frac{H^+(\omega_2)}{i\hbar}|g\rangle\rho_{gg}^{(0)}\langle n|\frac{H(\omega_3)}{i\hbar}|g'\rangle}{i^3(-\omega_2-\omega_{ng})(\omega_1-\omega_2-\omega_{g'g}+i\Gamma_{g'g})(\omega_3+\omega_1-\omega_2-\omega_{ng})}$$

$\therefore\quad \rho_{ng}^{(3)}(\mathrm{I})+\rho_{ng}^{(3)}(\mathrm{II})$

$$=\sum_{gg'n}\frac{\rho_{gg}^{(0)}}{(\omega_1-\omega_2-\omega_{g'g}+i\Gamma_{g'g})}\left\{\frac{(er_2)_{g'n}(er_1)_{ng}}{\omega_1-\omega_{ng}}-\frac{(er_1)_{g'n}(er_2)_{ng}}{\omega_2+\omega_{ng}}\right\}\frac{\langle n|er_s|g'\rangle}{\omega_a-\omega_{ng}}$$

$$=\sum_{gg'n}\frac{\rho_{gg}^{(0)}}{(\omega_1-\omega_2-\omega_{g'g}+i\Gamma_{g'g})}\left\{M_{g'g}^{s}\right\}\frac{\langle n|er_3|g'\rangle}{\omega_a-\omega_{ng}}$$

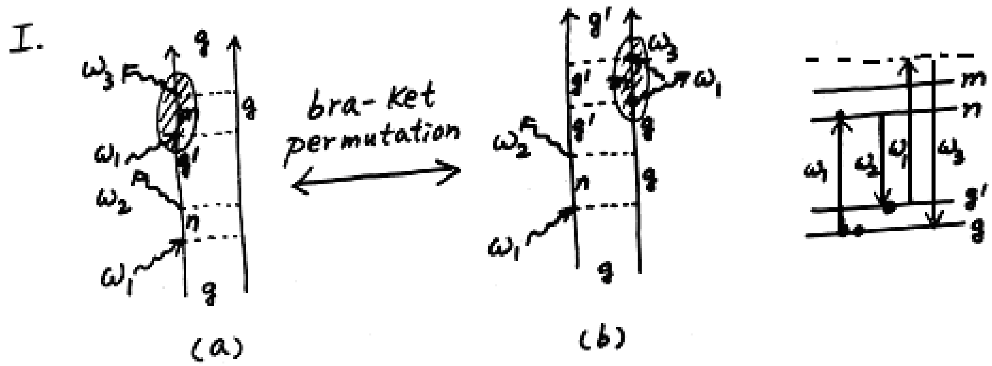
Simiarly,

$\therefore\quad \rho_{ng}^{(3)}(\mathbf{III})+\rho_{ng}^{(3)}(\mathbf{IV})$

$$=\sum_{gg'}\frac{\rho_{gg}^{(0)}}{(\omega_1-\omega_2-\omega_{g'g}+i\Gamma_{g'g})}\left\{M_{g'g}^{s}\right\}\frac{\langle n|er_a|g\rangle}{-(\omega_3+\omega_{ng})}]$$

7. 1. 2 Doubly Resonant Cases

- $\omega_1 - \omega_2$ resonant with $\omega_{g'g}$ (*i.e.*, two-photon process resonantly couples with the molecular vibrational transition), plus
- ω_1 single-photon resonance



Note the following photon energy conservation relations:

$\omega_3 = \omega_1 - \omega_2 + \omega_1 = 2\omega_1 - \omega_2$ and $\omega_3 = \omega_1 - \omega_2 + \omega_1 = 2\omega_1 - \omega_2$

$$\chi_R^{(3)}(\omega_3)|_a$$

$$= -\frac{Ne^4}{\hbar^3}\sum_m \frac{r^j_{gm} r^i_{mg'}}{(2\omega_1 - \omega_2 - \omega_{mg'})} \cdot \frac{r^k_{g'n} r^l_{ng}}{(\omega_1 - \omega_{ng} + i\Gamma_{ng})(\omega_1 - \omega_2 - \omega_{gg'} + i\Gamma_{g'g})}$$

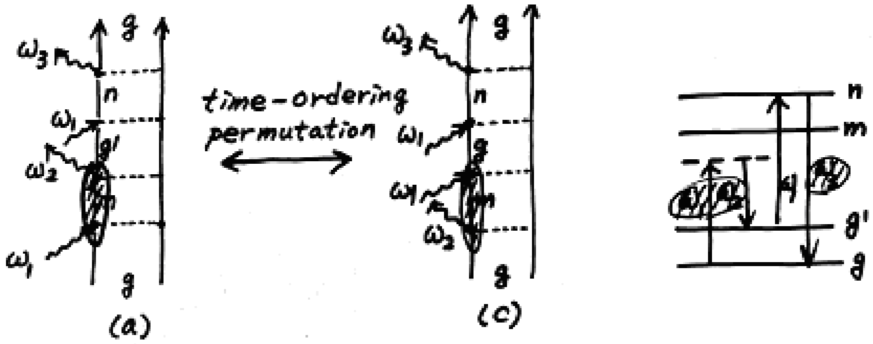
$$\chi_R^{(3)}(\omega_3)|_b$$

$$= -\frac{Ne^4}{\hbar^3}\sum_m \frac{r^j_{gm} r^i_{mg'}}{(2\omega_1 - \omega_2 - \omega_{mg'})} \cdot \frac{r^k_{g'n} r^l_{ng}}{(\omega_1 - \omega_{ng} + i\Gamma_{ng})(\omega_1 - \omega_2 - \omega_{g'g} + i\Gamma_{g'g})}$$

$$[\chi_R^{(3)}(\omega_3)]_{ijkl}(a+b)$$

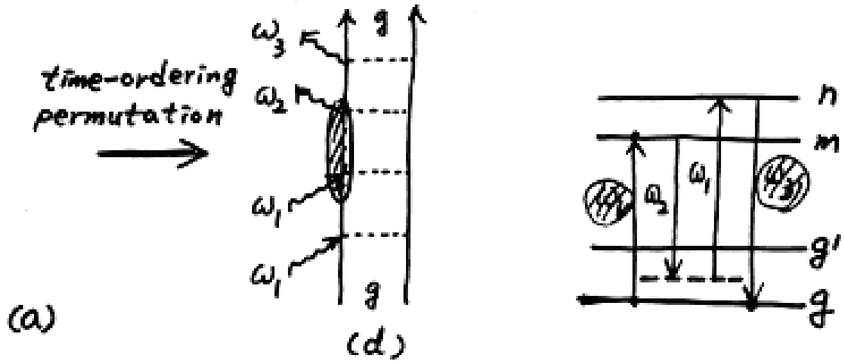
$$= -\frac{Ne^4}{\hbar^3}\sum_m \left[\frac{r^i_{gm} r^j_{mg'}}{(2\omega_1 - \omega_2 - \omega_{mg})} + \frac{r^j_{gm} r^i_{mg'}}{(2\omega_1 - \omega_2 + \omega_{mg'})}\right] \frac{r^k_{g'n} r^l_{ng}}{(\omega_1 - \omega_{ng} + i\Gamma_{ng})(\omega_1 - \omega_2 - \omega_{g'g} + i\Gamma_{g'g})}$$

II. Time-ordering Permutation



$$\chi_R^{(3)}(\omega_3)|_c$$
$$= -\frac{Ne^4}{\hbar^3}\sum_m \left[\frac{r^e_{g'm} r^k_{mg}}{(-\omega_2 - \omega_{mg})} \frac{r^i_{gn} r^j_{ng'}}{(2\omega_1 - \omega_2 - \omega_{ng} + i\Gamma_{ng})} \frac{\rho^{(0)}_{gg}}{(\omega_1 - \omega_2 - \omega_{g'g} + i\Gamma_{g'g})} \right]$$

$$\chi_R^{(3)}(\omega_3)|_{(a+c)}$$
$$= -\frac{Ne^4}{\hbar^3}\sum_m \left[\frac{r^K_{g'm} r^l_{mg}}{(\omega_1 - \omega_{mg})} - \frac{r^l_{g'm} r^k_{mg'}}{(\omega_2 + \omega_{mg})} \right] \frac{r^i_{gn} r^j_{ng'} \rho^{(0)}_{gg}}{(2\omega_1 - \omega_2 - \omega_{ng} + i\Gamma_{ng})(\omega_1 - \omega_2 - \omega_{g'g} + i\Gamma_{g'g})}$$

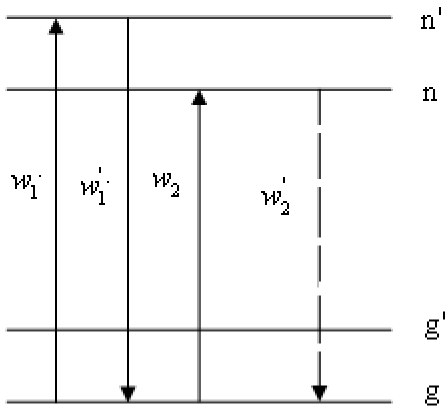


$$\chi_R^{(3)}(\omega_3)|_d = -\frac{Ne^4}{\hbar^3}\sum_m \rho^{(0)}_{gg} \left[\frac{r^i_{gn}}{(2\omega_1 - \omega_2 - \omega_{ng} + i\Gamma_{ng})} \cdot \frac{r^k_{nm} r^j_{mn}}{(2\omega_1 - \omega_{mg})} \cdot \frac{r^l_{ng}}{\omega_1 - \omega_{ng} + i\Gamma_{ng}} \right]$$

$$\chi_R^{(3)}(\omega_3)|_{a+d} = -\frac{Ne^4}{\hbar^3}\sum_m \rho^{(0)}_{gg} \left[\frac{r^i_{gn}}{(2\omega_1 - \omega_2 - \omega_{ng} + i\Gamma_{ng})} \frac{r^l_{ng}}{(\omega_1 - \omega_{ng} + i\Gamma_{ng})} \left\{ \frac{r^j_{nm} r^k_{mn}}{\omega_1 - \omega_2 - w_{mg}} + \frac{r^k_{nm} r^j_{mn}}{2\omega_1 - \omega_{mg}} \right\} \right]$$

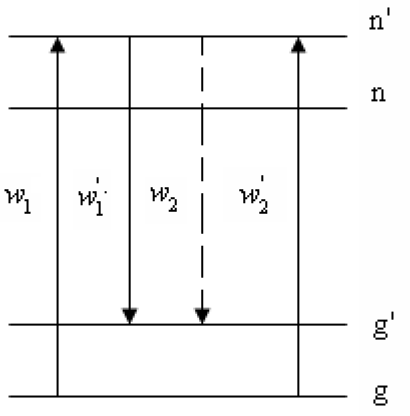
7.1.3 Triply Resonant Cases

All three energy denominators in $\chi_R^{(3)}$ are near resonant



$$\chi_R^{(3)}(\omega_2' = \omega_2 - \omega_1' + \omega_1)$$

$$= \frac{Ne^4}{\hbar^3} \underbrace{r_{gn}^{i} r_{ng}^{j} r_{gn'}^{k} r_{n'g}^{e}}_{\omega_2'\ \omega_2\ \omega_1'\ \omega_1} \rho_{gg}^{(0)} \left\{ \frac{(\omega_2 - \omega_{ng} + i\Gamma_{ng})^{-1} - (\omega_1' - \omega_{n'g} - i\Gamma_{n'g})^{-1}}{(\omega_2' - \omega_{ng} + i\Gamma_{ng}) - (\omega_1' - \omega_2 - i\Gamma_{n'n})} + \frac{(\omega_1 - \omega_{ng} + i\Gamma_{ng})^{-1} - (\omega_1' - \omega_{ng} - i\Gamma_{ng})^{-1}}{(\omega_2' - \omega_{ng} + i\Gamma_{ng}) - (\omega_1 - \omega_1' + i/T_{1g})} \right\}$$



$$\chi_R^{(3)}(\omega_2' = \omega_1 - \omega_1' + \omega_2)$$

$$= \frac{Ne^4}{\hbar^3} \underbrace{r_{g'n'}^{i} r_{n'g}^{j} r_{gn'}^{k} r_{n'g'}^{e}}_{\omega_2\ \omega_1\ \omega_1'\ \omega_2'} \rho_{gg}^{(0)} \cdot$$

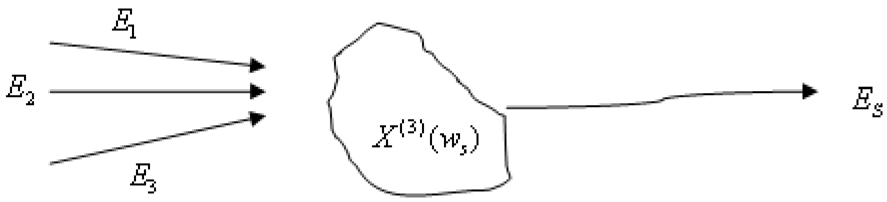
$$\left\{ \frac{1}{(\omega_2' - \omega_{n'g'} + i\Gamma_{n'g'})(\omega_1' - \omega_2 - \omega_{gg'} - i\Gamma_{g'g})(\omega_1' - \omega_{n'g} + i\Gamma_{n'g})} + \frac{(\omega_1 - \omega_{n'g} - i\Gamma_{n'g})^{-1} - (\omega_1' - \omega_{n'g} + i\Gamma_{n'g})^{-1}}{(\omega_2' - \omega_{n'g'} + i\Gamma_{n'g'})(\omega_1 - \omega_1' + i/T_{1n'})} \right\}$$

The effective $\chi_R^{(3)}$ of an ensemble of molecules or ions should be a weighted average of $\chi_R^{(3)}$ over the distribution of the resonant frequencies

$$\left[\chi_R^{(3)} \right]_H = \sum f\left(\omega_{ng}\right) \chi^{(3)}(\omega_{ng})$$

7-2 General Theory of Four-Wave Mixing

- For a cubic or isotropic medium



$$\boxed{P^{(3)}(w_s) = X^{(3)}(w_s) : E_1(w_1)E_2(w_2)E_3(w_3)}$$

$$[\nabla^2 + \tilde{\omega}_s^2 \varepsilon(\omega_s)]E_s = -4\pi\tilde{\omega}_s^2 P^{(3)}(\omega_s) \quad \textbf{where } \tilde{\omega}_s = \omega_s / c$$

Assuming

- SVA
- Negligible pump depletion
- Simplifying boundary condition

$$\frac{d\varepsilon_s}{dz} = \frac{2\pi i(\tilde{\omega}_s^2)}{K_s} \cdot P^{(3)} \cdot e^{i\Delta K \cdot Z}$$

$$\Rightarrow \therefore \quad \varepsilon_{si}(\omega_s, z) = -\frac{2\pi i(\tilde{\omega}_s^2)}{(\Delta K_z)K_s} \chi_{ijkl}^{(3)} \varepsilon_{lj} \varepsilon_{2k} \varepsilon_{3l} (1 - e^{i\Delta k \cdot z}) e^{-\alpha_{si} z}$$

$$where \ \Delta\vec{\mathbf{K}} = \vec{\mathbf{K}}_1 + \vec{\mathbf{K}}_2 + \vec{\mathbf{K}}_3 - \vec{\mathbf{K}}_s$$

Now further assuming

- Output Field in the same mode as one of the input field, $i.e.\ E_{si} = E_{3l}$

Then E_{3l} will experience gain or loss induced by the nonlinear wave interaction

$$\omega_s = \omega_3 \ \ \& \ \ \vec{\mathbf{K}}_s = \vec{\mathbf{K}}_3$$

$$\therefore \quad \omega_s = \omega_1 + \omega_2 + \omega_3 \ \Rightarrow \ \omega_1 = -\omega_2$$

$$\vec{\mathbf{K}}_s = \vec{\mathbf{K}}_1 + \vec{\mathbf{K}}_2 + \vec{\mathbf{K}}_3 \Rightarrow \vec{\mathbf{K}}_1 + \vec{\mathbf{K}}_2 = \Delta\vec{\mathbf{K}}$$

$$\frac{d\varepsilon_s}{dz} = \frac{2\pi i \tilde{\omega}_s^2}{K_s} \chi_{ijkl}^{(3)} \varepsilon_{lj} \varepsilon_{2k} \varepsilon_s e^{i\Delta k \cdot z}$$

$$\frac{1}{\varepsilon_s(z)} d\varepsilon_s(z) = \frac{2\pi i \tilde{\omega}_s^2}{K_s} \chi_{ijkl}^{(3)} \varepsilon_{lj} \varepsilon_{2k} \cdot e^{i\Delta k \cdot z}$$

$$\Rightarrow \quad \varepsilon_{si}(z) = \varepsilon_{si}(0) e^{g_i(z) - \alpha_{si} z}$$

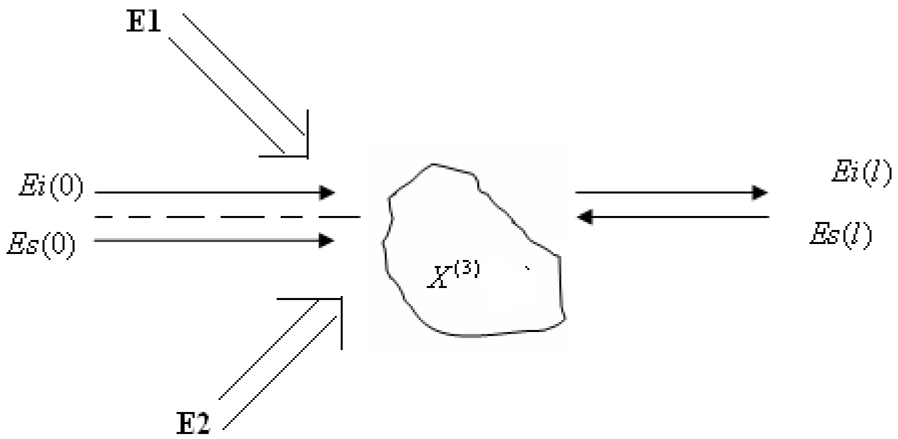
$$where \quad g_i(z) = \frac{2\pi \tilde{\omega}_s^2}{(\Delta K_z) K_s} \chi_{ijkl}^{(3)} \varepsilon_{ij}\, \varepsilon_{2k} (1 - e^{i\Delta \vec{K} \cdot \vec{Z}})$$

especially **when** $E_{1j} = E_{2k}^*$ **&** $\Delta K = 0$

$$g_i(z) = \frac{2\pi \tilde{\omega}_s^2}{K_s} \mathrm{Im}(\chi_{ijkl}^{(3)}) \left| \varepsilon_{ij} \right|^2 z$$

The result is similar to the case of stimulated Raman gain.

- **Backward Parametric Amplification**



In this case, two pump beams are used instead of one field as in optical parametric amplification based on $\chi^{(2)}$ effect.

Let us consider

(a) perfect phase matching: $\Delta \vec{K} = 0$

(b) negligible pump depletion:

$$\frac{d\varepsilon_z}{dz} = \frac{2\pi i \tilde{\omega}_s^2}{K_s} \chi^{(3)} \varepsilon_1 \varepsilon_2 \varepsilon_i^*$$

$$\frac{d\varepsilon_i}{dz} = \frac{2\pi i \tilde{\omega}_i^2}{K_i} \chi^{(3)*} \varepsilon_1^* \varepsilon_2^* \varepsilon_s$$

$$\varepsilon_s(z=0)=\varepsilon_s(z=l)/\cos(g_o l/2)+i\frac{\omega_s}{\omega_i}\sqrt{\frac{K_i}{K_s}}\varepsilon_i^*(0)\tan(g_o l/2)$$

$$\varepsilon_i^*(z=l)=-i\frac{\omega_i}{\omega_s}\sqrt{\frac{K_s}{K_i}}\varepsilon_s^*(l)\tan(g_o l/2)+\varepsilon_i^*(0)/\cos(g_o l/2)$$

$$\text{where}\quad g_0=\frac{4\pi\tilde{\omega}_s^2\tilde{\omega}_i^2}{KiKs}\cdot\left|\chi_{eff}^{(3)}\right|^2$$

$g_o\cdot l=\pi \quad \Rightarrow$ **Onset of Oscillation!**

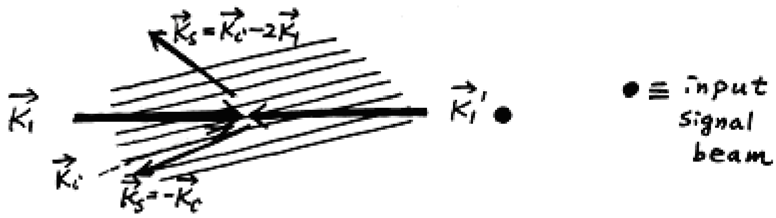
7.3 Degenerate Four-Wave Mixing (DFWM)

if $\omega_1=\omega_2=\omega_3=\omega_s=\omega,\quad then$

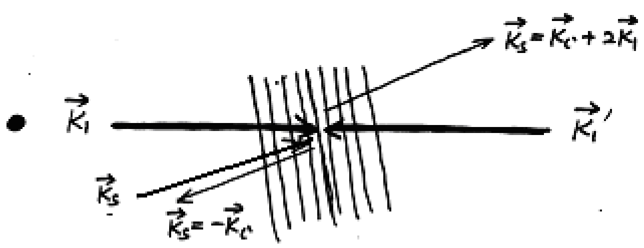
$P_s^{(3)}(\omega_s)$ is composed of three terms:

$$P_s^{(3)}(\omega_s)=P_A^{(3)}(\vec{K}_1+\vec{K}_1'-\vec{K}_i,\omega_s)+P_B^{(3)}(\vec{K}_1-\vec{K}_1'-\vec{K}_i,\omega_s)$$
$$+P_C^{(3)}(-\vec{K}_1+\vec{K}_1'+\vec{K}_i,\omega_s)$$

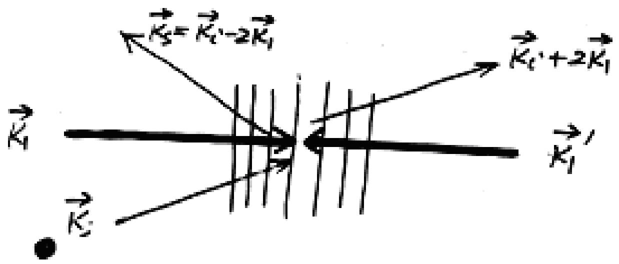
$$\text{where}\ P_A^{(3)}(\vec{K}_1+\vec{K}_1'-\vec{K}_i,\omega)=\chi^{(3)}(\omega):E_1(\vec{K}_1)E_1'(\vec{K}_1')E_i^*(\vec{K}_i)$$



$$P_B^{(3)}(\vec{K}_1-\vec{K}_1'+\vec{K}_i,\omega)=\chi^{(3)}(\omega):E_1(\vec{K}_1)E_1'^*(\vec{K}_1')E_i(\vec{K}_i)$$



$$P_C^{(3)}(-\vec{K}_1+\vec{K}_1'-\vec{K}_i,\omega)=\chi^{(3)}(\omega):E_1^*(\vec{K}_1)E_1'(\vec{K}_1')E_i(\vec{K}_i)$$



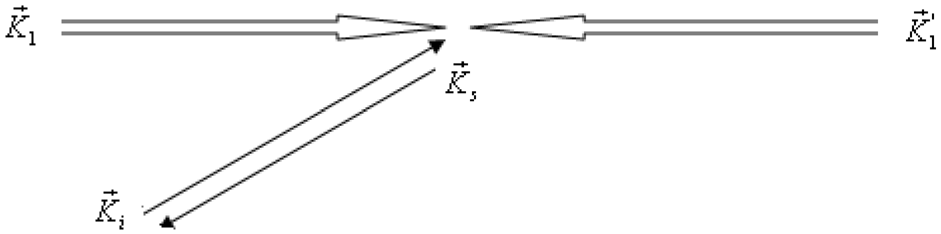
- $\chi^{(3)}(\omega)$ at least singly resonant arising from two-photon zero frequency (ω-ω=0) resonance (ω_1-ω_1 + i/T_1) or two-photon resonance if $\omega+\omega-\omega_{ng} \approx 0$.
- when $\omega-\omega_{ng} \approx 0$, $\chi^{(3)}$ is triply resonant. This implies very large resonant enhancement in DFWM.

We can understand DFWM as follows:
Two of the three input fields interfere and form a static grating, the third input wave is scattered by the grating to yield the output wave, *e.g.* grating formed by $\vec{K}_1$ and $\vec{K}_i$ scatters the $\vec{K}_1'$ wave to yield

$$\vec{\boldsymbol{K}}_s = \vec{\boldsymbol{K}}_1' \pm (\vec{\boldsymbol{K}}_1 - \vec{\boldsymbol{K}}_i) = \left\{ \begin{matrix} -\vec{\boldsymbol{K}}_i \\ -2\vec{\boldsymbol{K}}_1 + \vec{\boldsymbol{K}}_i \end{matrix} \right\} \quad \textit{when} \;\; \vec{\boldsymbol{K}}_1' = -\vec{\boldsymbol{K}}_1 .$$

Since $\left|\vec{K}_s\right| \neq \omega\sqrt{\varepsilon_s}/c$, the three output waves are not phase-matched in general.

But if $\vec{\boldsymbol{K}}_1 = -\vec{\boldsymbol{K}}_1'$, then $\vec{\boldsymbol{K}}_s = -\vec{\boldsymbol{K}}_i$ is always phase matched, *i.e.*



$$\boldsymbol{\rho}_s^{(3)}(\vec{\boldsymbol{K}}_s = -\vec{\boldsymbol{K}}_i, \boldsymbol{\omega}) = \boldsymbol{\chi}^{(3)}(\boldsymbol{\omega}) : \boldsymbol{E}(\vec{\boldsymbol{K}}_1)\boldsymbol{E}'(-\vec{\boldsymbol{K}}_1)\boldsymbol{E}_i^*(\vec{\boldsymbol{K}}_i)$$
$$= \underline{\boldsymbol{A}}(\boldsymbol{E}_1 \cdot \boldsymbol{E}_i^*)\boldsymbol{E}_{\underline{1}}' + \boldsymbol{B}(\boldsymbol{E}_1' \cdot \boldsymbol{E}_i^*)\boldsymbol{E}_{\underline{1}} + \boldsymbol{C}(\boldsymbol{E}_1 \cdot \boldsymbol{E}_1')\boldsymbol{E}_i^*$$

$\boldsymbol{B(\theta) = A(\pi - \theta)}$ **moving grating**

static grating

By properly arranging the polarizations of the input fields, only one term can remain.

Initial condition:

$\varepsilon_s(l) = 0 \quad \varepsilon_i(0) = \varepsilon_{io} =$ object wave

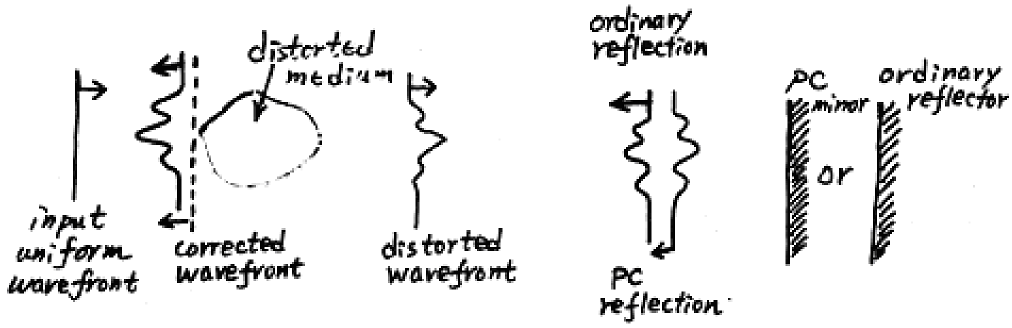
➔ from solution of the coupled wave eqs.

$$\varepsilon_s(0) = i\frac{\omega_s}{\omega_i}\sqrt{\frac{\mathrm{K_i}}{\mathrm{K_s}}}\varepsilon_i^*(0)\tan(g_o l/2)$$

$$= i\varepsilon_i^*(0)\tan(g_o l/2) = \text{complex conjugate wave of } \varepsilon_i(0)$$

8-4 Phase Conjugation by DFWM

- Output wave is complex conjugate to the phase of an input wave
- Can appear in SFG, DFG, OPA and FWM
- If the PC output propagates in the backward direction with respect to the corresponding input wave, it can be used to correct the "aberration" encountered by the input wave, such as



Methods to achieve PC

- DFWM by using

Photorefractive crystals; stimulated Brillouin scattering

7.5 Tunable IR & UV Generations

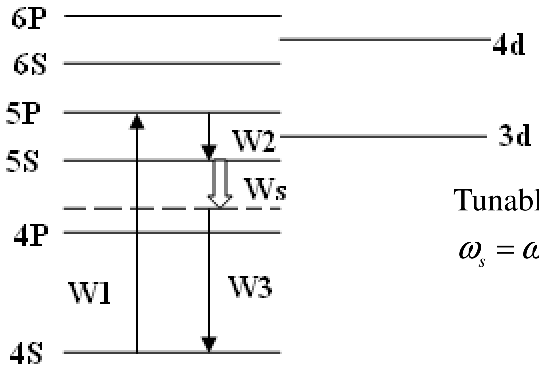
Objective: using FWM to extend laser output frequency to IR or UV.

Consider atomic vapor

$\chi^{(3)} \sim 10^{-33} esu/atom$

- Single resonance ➔ $\chi^{(3)} \sim 10^{-31} esu/atom$
- Can be doubly or triply resonant to increase $\chi^{(3)}$ further.

E.g.



Tunable IR output ω_s with $\omega_s = \omega_1 - \omega_2 - \omega_3$ by varying ω_3

$$\omega_s = \omega_1 - \omega_2 - \omega_3 \qquad\qquad \omega_3$$

$$(\chi_R^{(3)})_{ijkl} \approx \frac{Ne^4}{\hbar^3}\sum_{sp} A_{sp}\, \underline{\langle 4s|r_j|4p\rangle}\langle 4p|r_i|5s\rangle \underbrace{\langle 5s|r_k|5p\rangle}_{\omega_2} \underbrace{\langle 5p|r_e|4s\rangle}_{\omega_1}$$

where $A_{sp} = \dfrac{1}{(\omega_1 - \omega_{5p-4s} + i\Gamma_{5p})(\omega_1 - \omega_2 - \omega_{5s-4s} + i\Gamma_{5s})(\omega_3 - \omega_{4p-4s})}$

with

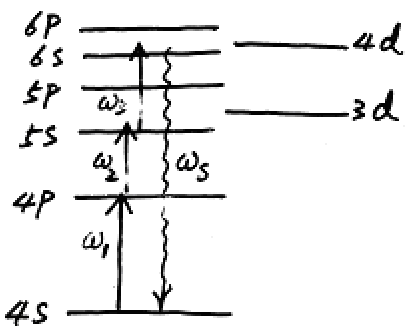
$$\omega_1 - \omega_{5p-4s} \approx 50\ \mathrm{cm}^{-1},\ \Gamma_{5s} \approx 0.1\, cm^{-1}$$

$$\omega_3 - \omega_{4p-4s} \approx 5000\ \mathrm{cm}^{-1}$$

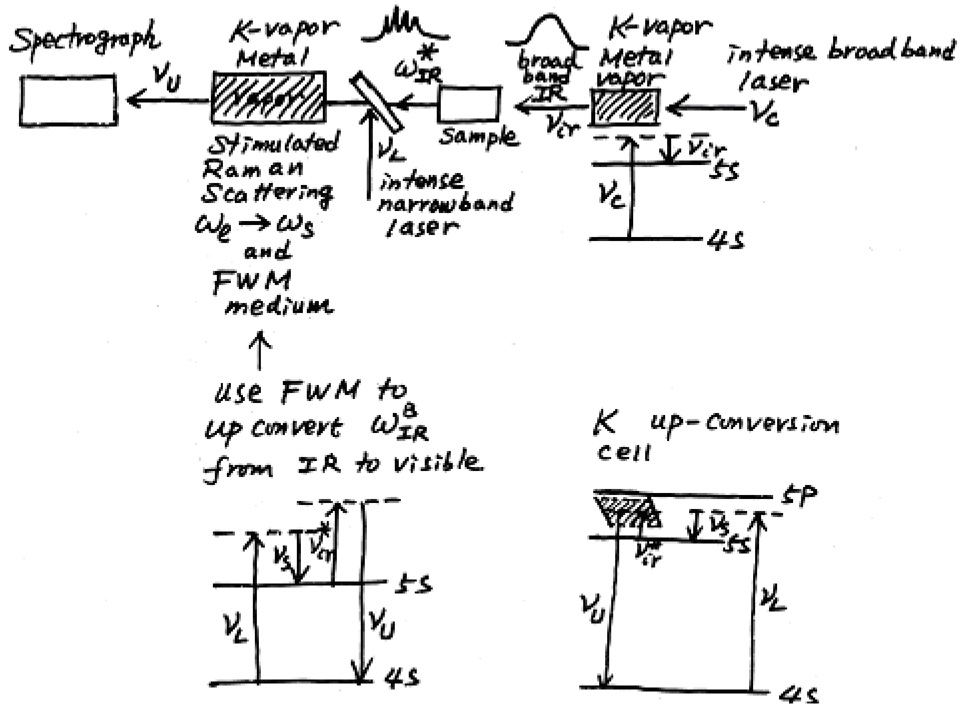
$$\Rightarrow \quad \chi_R^{(3)} / N \sim \ 6\times 10^{-27}\, esu / atom$$

$$when \quad \mathrm{N}\sim 10^{17}\, atoms / cm^3 \quad \Rightarrow \quad \chi_R^{(3)} \sim 6\times 10^{-10}\, esu!$$

Tunable UV output



e.g., FWM for time-resolved infrared spectroscopy



The conversion from IR to the visible is effectively uniform over a relatively wide spectral range. The up-converted signal thus provided a faithful reproduction of the spectral intensity.