Radiative broadening (Loudon 2.5)

- go from quantum states → macroscopic refr. index

incident field

$$E(t) = E_0 \cos(\omega t) = \tfrac{1}{2} E_0 \left(e^{-i\omega t} + e^{+i\omega t} \right)$$

induced polarization (linear)

$$P(t) = \tfrac{1}{2} \varepsilon_0 E_0 \left\{ \chi(\omega) e^{-i\omega t} + \chi(-\omega) e^{i\omega t} \right)$$

from $P = \varepsilon_0 E \chi$

then $\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E} + \varepsilon_0 \chi \vec{E} = \varepsilon(\omega) \vec{E}$

with $\varepsilon(\omega) = 1 + \chi(\omega)$ dielectric fcn (can be tensor)

finally the refractive index is:

$$n(\omega) = \sqrt{\frac{\varepsilon(\omega)\mu(\omega)}{\varepsilon_0 \mu_0}} = \sqrt{\frac{\varepsilon(\omega)}{\varepsilon_0}}$$ for non magnetic materials

the polarization is related to the quantum system through

$P(t) = N_A \mu(t)$ where $\mu(t)$ is the induced dipole moment,

N_A = number density of atoms (gas)

in condensed matter - acct. for local fields.

$$\mu(t) = C_1^* C_2 \mu_{12} e^{-i\omega_0 t} + C_1 C_2^* \mu_{21} e^{i\omega_0 t}$$

(assuming $\mu_{11} = \mu_{22} = 0$) also $\mu_{12} = \mu_{21}$ (real, true for bound states) check this

C_1, C_2 depend on time.

include all processes.

$$i\hbar \frac{dC_2}{dt} = C_1 V_{21} \cos(\omega t) e^{i\omega_0 t} \underbrace{- i\hbar \gamma_{sp} C_2}_{\text{spontan. decay}}$$

$$V_{21} = -\mu_{12} E_0$$

w/o applied field

$$C_2(t) = C_2(0)\, e^{-\gamma_{sp} t}$$

for a population,

$$N_2(t) \propto |C_2(t)|^2 = N_2(0)\, e^{-2\gamma_{sp} t}$$

$$\therefore\ 2\gamma_{sp} = A_{21}$$

we'll assume $C_1 \approx 1$ and constant $\therefore$ $\boxed{\text{term in eqn is a driving term.}}$

$$\rightarrow\ C_2(t) = -\frac{1}{2}\frac{V_{21}}{\hbar}\left[\frac{e^{i(\omega_0+\omega)t}}{\omega_0+\omega-i\gamma_{sp}} + \frac{e^{i(\omega_0-\omega)t}}{\omega_0-\omega-i\gamma_{sp}}\right]$$

now calc. $\mu(t) = \dfrac{\mu_{12}^2 E_0}{2\hbar}\left[e^{-i\omega t}\left(\dfrac{1}{\omega_0+\omega+i\gamma_{sp}} + \dfrac{1}{\omega_0-\omega-i\gamma_{sp}}\right) + e^{+i\omega t}\left(\dfrac{1}{\omega_0+\omega-i\gamma_{sp}} + \dfrac{1}{\omega_0-\omega+i\gamma_{sp}}\right)\right]$

avg over random orientations : 1/3

now compare w/ exp for $\chi(\omega)$

$$\rightarrow\ \chi(\omega) = \frac{N_a \mu_{12}^2}{3\epsilon_0\hbar}\left(\frac{1}{\omega_0-\omega-i\gamma_{sp}} + \frac{1}{\omega_0+\omega+i\gamma_{sp}}\right)$$

and

$$\chi(-\omega) = \chi^*(\omega)$$

express χ in terms of $\gamma_{sp} \rightarrow A_{21} \rightarrow \mu_{12}^2$

$$\rightarrow\ \chi(\omega) = N_a \frac{2\pi c^3}{\omega_0^3}\left(\frac{\gamma_{sp}}{\omega_0-\omega-i\gamma_{sp}} + \frac{\gamma_{sp}}{\omega_0+\omega+i\gamma_{sp}}\right)$$

compare to classical electron-on-spring model:

$$\chi(\omega) = N_a \frac{e^2}{m\epsilon_0}\frac{f_{21}}{\omega_0^2-\omega^2-i\gamma_{sp}\omega}$$

Absorption coefficient

complex $\chi(\omega)$

$\epsilon(\omega) = \epsilon_0(1 + \chi(\omega))$ for dilute gas.

$$n(\omega) = \sqrt{\frac{\epsilon(\omega)}{\epsilon_0}} \quad \text{non magnetic}$$

$$= \sqrt{1 + \chi(\omega)}$$

write $n = n_R + i n_I$

$$n^2 = n_R^2 - n_I^2 + 2 i n_R n_I = 1 + \chi_R + i \chi_I$$

$$n_I = \chi_I / 2 n_R$$

attenuation coeff. compare

$$I(z) = I_0 e^{-\alpha z}$$

$$= I_0 e^{+2 i k_0 (n_I i) z}$$

$$\alpha = 2 k_0 n_I = 2 \frac{\omega}{c} \frac{\chi_I}{2 n_R} = \frac{\omega}{c} \frac{\chi_I(\omega)}{n_R}$$

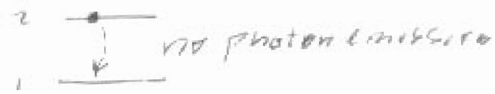
take im. part of χ, in RWA.

$$\chi(\omega) \approx N_a \frac{2\pi c^3}{\omega_0^3} \gamma_{sp} \frac{\omega_0 - \omega + i \gamma_{sp}}{(\omega_0 - \omega)^2 + \gamma_{sp}^2}$$

$$\mathrm{Im}\, \chi = N_a \frac{2\pi c^3}{\omega_0^3} \frac{\gamma_{sp}^2}{(\omega_0 - \omega)^2 + \gamma_{sp}^2}$$

lineshape $g(\omega_0 - \omega) \equiv \dfrac{\gamma_{sp}/\pi}{(\omega_0 - \omega)^2 + \gamma_{sp}^2}$ Lorentzian.

Nonradiative decay



several mechanisms for energy transfer → other species

- collisional de-excitation
  - → KE, excitation transfer, phonons.
- dipole interaction

collisional processes

<u>KE</u> excited species B^* electron, atom, molecule: A

$$B^* + A \to B + A + \Delta KE \quad \text{de-excite}$$

$$B + A \to B^* + A - \Delta KE \quad \text{excite.}$$

total:

$$\frac{d}{dt} N_{B^*} = -\underbrace{k_{B^*A} N_A}_{\text{rate } W_{nr} \,\propto\, N_A} N_{B^*} + k_{BA} N_A N_B$$

in thermal eqm: no ΔN_{B^*} on average (detailed balance)

and

$$k_{B^*A} = k_{BA}\, e^{\Delta E / kT}$$

since $\Delta E \gg kT$ typically k_{B^*A} is high.
and if $N_{B^*} \approx N_B$ b/c of pumping, we can ignore thermal excitation.

<u>internal ΔE</u>

$$B^* + A \to B + A^* - \Delta E \quad \text{kinetic}$$

- here $\Delta E \ll kT$ typically, so that excitation energy of B^* and A^* are ~ same - "near resonant"
- back transfer: $A^* + B \to B^* + A - \Delta E$