Emission and Absorption – Population Rate Equations

02-27-2025

So far we have derived a set of Eqs. of Motion for the elements of the Density Matrix:

$$\dot{\rho}_{11} = -\Gamma_1 \rho_{11} + A_{21}\rho_{22} - \frac{i}{2}\left(\chi\rho_{12} - \chi^*\rho_{21}\right)$$

$$\dot{\rho}_{22} = -\Gamma_2 \rho_{22} - A_{21}\rho_{22} + \frac{i}{2}\left(\chi\rho_{12} - \chi^*\rho_{21}\right)$$

$$\dot{\rho}_{12} = (i\Delta - \beta)\rho_{12} + \frac{i\chi^*}{2}\left(\rho_{22} - \rho_{11}\right) = \dot{\rho}_{21}^*$$

where $\beta = \frac{1}{\tau} + \frac{A_{21}}{2} + \frac{\Gamma_1 + \Gamma_2}{2}$

(Non-trivial Steady State Solution requires $\Gamma_1 = \Gamma_2 = 0$)

(*) These eqs. are difficult to solve in the general case. See, e. g., Allen & Eberly for discussion of some special cases and a reference to original work by Torrey et al.

(*) For ≥ 3 levels the Density Matrix Equations get very cumbersome and it is desirable to simplify the description when possible.

(*) One such simplification takes the form of Rate Equations for the populations only.

Steady State Solutions: (requires $\Gamma_1 = \Gamma_2 = 0$)

Let $\dot{\rho}_{12} = 0$ $\Rightarrow$

$$\rho_{12} = \frac{i\chi^*/2}{\beta - i\Delta}\left(\rho_{22} - \rho_{11}\right)$$

$$\rho_{21} = \frac{-i\chi/2}{\beta + i\Delta}\left(\rho_{22} - \rho_{11}\right)$$

$\Downarrow$

$$\chi\rho_{12} - \chi^*\rho_{21} = \frac{i|\chi|^2\beta}{\Delta^2 + \beta^2}\left(\rho_{22} - \rho_{11}\right)$$

Plug into eqs for populations to get

$$\dot{\rho}_{11} = A_{21}\rho_{22} + \frac{|\chi|^2\beta/2}{\Delta^2 + \beta^2}\left(\rho_{22} - \rho_{11}\right) = 0$$

$$\dot{\rho}_{22} = -A_{21}\rho_{22} - \frac{|\chi|^2\beta/2}{\Delta^2 + \beta^2}\left(\rho_{22} - \rho_{11}\right) = 0$$

From these eqs. we can find <u>steady state values</u> for the populations and coherences in terms of $\chi, \Delta, A_{21}, \beta$ when (and only when) $\dot{\rho}_{11} = \dot{\rho}_{22} = 0$

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Steady State Solutions: (requires $\Gamma_1 = \Gamma_2 = 0$)

Let $\dot{\rho}_{12} = 0 \Rightarrow$

$$\begin{cases} \rho_{12} = \dfrac{i\chi^*/2}{\beta - i\Delta}(\rho_{22} - \rho_{11}) \\ \rho_{21} = \dfrac{-i\chi/2}{\beta + i\Delta}(\rho_{22} - \rho_{11}) \end{cases}$$

$$\chi\rho_{12} - \chi^*\rho_{21} = \frac{i|\chi|^2\beta}{\Delta^2 + \beta^2}(\rho_{22} - \rho_{11})$$

Plug into eqs for populations to get

$$\dot{\rho}_{11} = A_{21}\rho_{22} + \frac{|\chi|^2\beta/2}{\Delta^2 + \beta^2}(\rho_{22} - \rho_{11}) = 0$$

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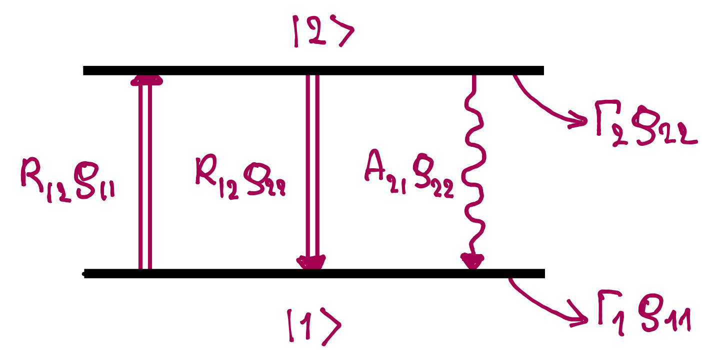
<u>Note</u>: The terms remaining after elimination of ρ_{12}, ρ_{21} are commonly identified with <u>induced</u> or <u>stimulated</u> processes. They are proportional to $|\chi|^2, |E_0|^2$ and thus the <u>intensity</u> of the light field.

<u>Def</u>: Absorption Rate = Stimulated Emission Rate

$$R_{12} = \frac{|\chi|^2\beta/2}{\Delta^2 + \beta^2} = \frac{|\vec{r}_{12}\cdot\vec{\varepsilon}E_0/\hbar|^2\beta/2}{(\omega_{21} - \omega)^2 + \beta^2}$$

Schematic:



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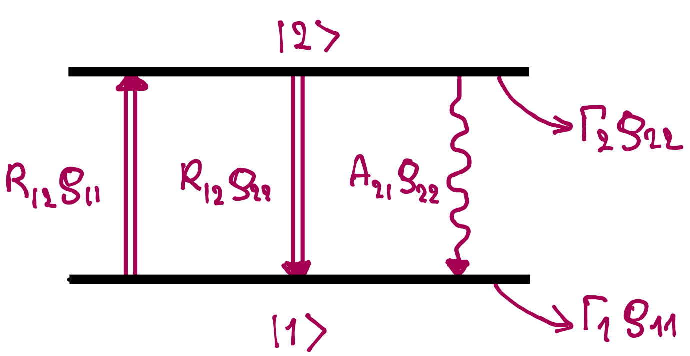

Elastic Collision Broadening

In hot and dense gases the dominant source of relaxation is often elastic collisions between atoms

Let $\beta \gg \Gamma_1, \Gamma_2, A_{21}$ ⇨ ρ_{12} reaches steady state much faster than ρ_{11}, ρ_{22}

We can solve the eq. for $\dot{\rho}_{12}$ assuming it is in steady state for given values of ρ_{11}, ρ_{22}

This yields Rate Equations for the populations only, valid in the collision broadened regime

$$\dot{\rho}_{11} = -\Gamma_1\rho_{11} + A_{21}\rho_{22} + R_{12}(\rho_{22}-\rho_{11}) \neq 0$$

$$\dot{\rho}_{22} = -\Gamma_2\rho_{22} - A_{21}\rho_{22} - R_{12}(\rho_{22}-\rho_{11}) \neq 0$$

(*) This is another example of adiabatic elimination of a fast variable (the coherence), leaving us with simpler equations for the slower variables.

(*) From these we can find the transient behavior of the coherences ρ_{11}, ρ_{22}

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(∗) From these we can find the <u>transient</u> behavior of the coherences ρ_{11}, ρ_{22}

<u>Note</u>: When collisions are very frequent the dipole $\langle \hat{\vec{\mu}} \rangle$ is oriented at random relative to the driving field. In that case

$$\langle |\vec{\mu}_{12} \cdot \vec{\varepsilon} E_0|^2 \rangle_{angles} = \frac{1}{3} \mu_{12}^2 |E_0|^2 \Rightarrow$$

$$R_{12} = \frac{\langle |\vec{\mu}_{12} \cdot \vec{\varepsilon} E_0/\hbar|^2 \rangle_{angles} \beta/2}{\Delta^2 + \beta^2} = \frac{1}{3} \frac{|\chi|^2 \beta/2}{\Delta^2 + \beta^2}$$

Photon Flux and Cross Section

Let $R_{12} \equiv \sigma(\Delta)\phi$ where $\hbar\omega\phi = \underbrace{\frac{1}{2} c \varepsilon_0 |E_0|^2}_{\text{intensity}}$

"photon flux" (ϕ)

This allows us to recast the Rate Eqs

$$\dot{\rho}_{11} = -\Gamma_1 \rho_{11} + A_{21}\rho_{22} + \sigma(\Delta)\phi(\rho_{22} - \rho_{11})$$

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We see that per atom, per unit time

# of absorption events	=	$\sigma(\Delta)\phi\rho_{11}$
# of stim. emission events	=	$\sigma(\Delta)\phi\rho_{22}$

Note: Given N atoms, the total # of events are $N\rho_{11}, N\rho_{22}$. This is useful when we care about the total power in the light field, e. g., in the context of laser theory

Solution of the Rate Equations

Let $\Gamma_1 = \Gamma_2 = 0$ and plug in $\rho_{11} = 1-\rho_{22}$

$$\dot{\rho}_{22} = -A_{21}\rho_{22} - \sigma(\Delta)\phi(2\rho_{22}-1)$$

$$= -\underbrace{(A_{21}+2\sigma(\Delta)\phi)}_{\gamma}\rho_{22} + \sigma(\Delta)\phi$$

The solution is a damped approach to Steady State!

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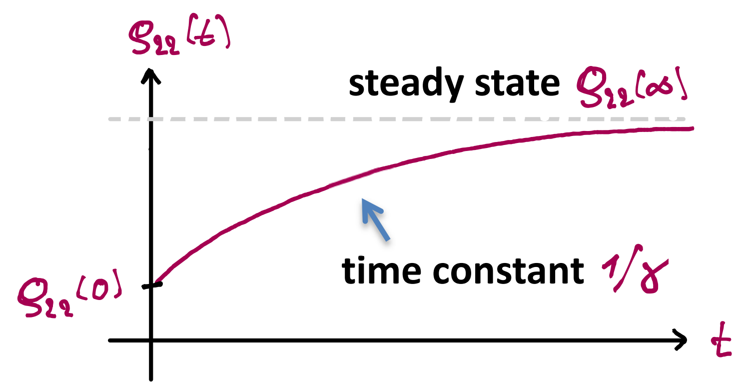
The solution is a damped approach to Steady State!

$$\rho_{22}(t) = [\rho_{22}(0) - \rho_{22}(\infty)]e^{-\gamma t} + \rho_{22}(\infty)$$

where

$$\gamma = (A_{21} + 2\sigma(\Delta)\phi), \quad \rho_{22}(\infty) = \frac{\sigma(\Delta)\phi}{A_{21} + 2\sigma(\Delta)\phi}$$



(∗) This transient behavior is valid in the collision broadened regime only.

(∗) Without collisions the transient regime Is one of damped Rabi oscillations.

(∗) The steady state value $\rho_{22}(\infty)$ is good regardless

Emission and Absorption – Population Rate Equations

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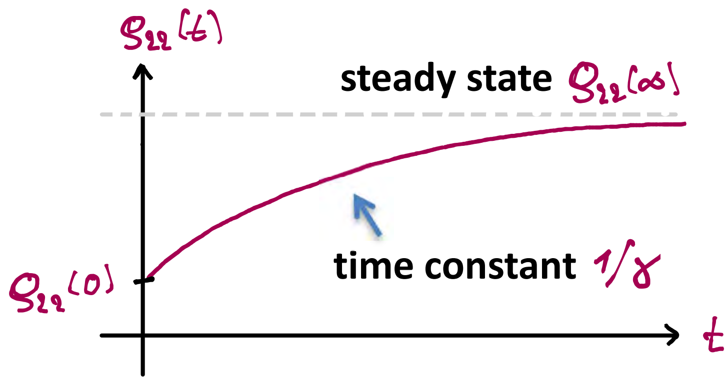

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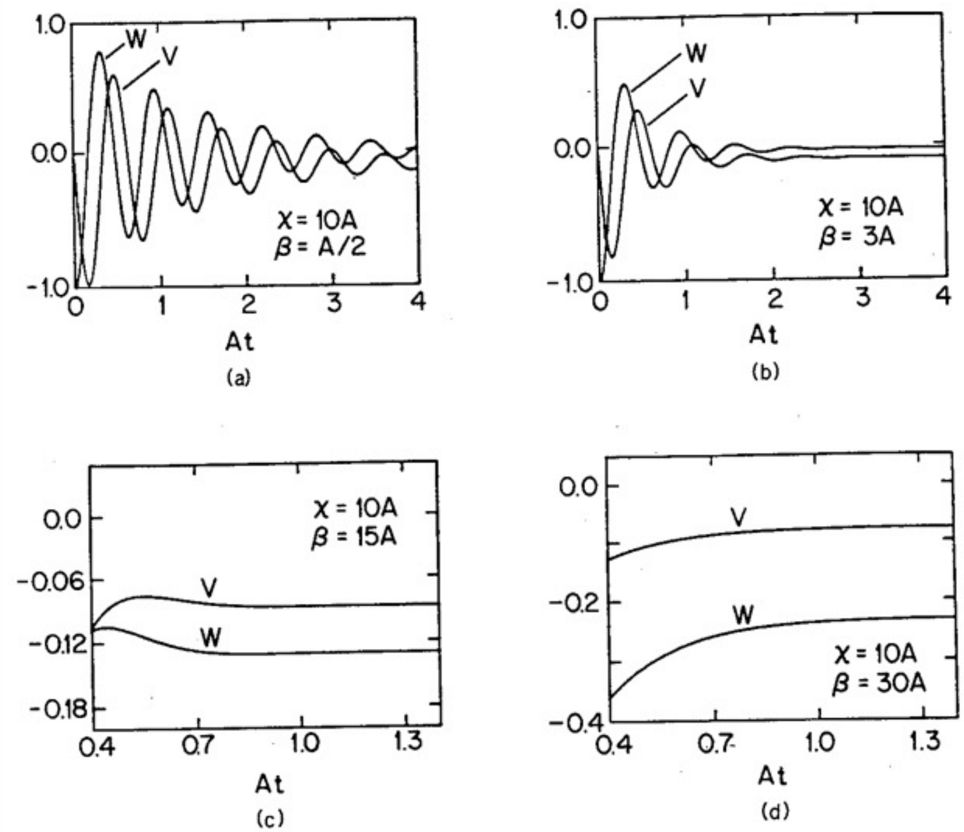
Numerical simulation of Density Matrix Eqs (Optical Bloch Picture).

Figure from Milloni & Eberly



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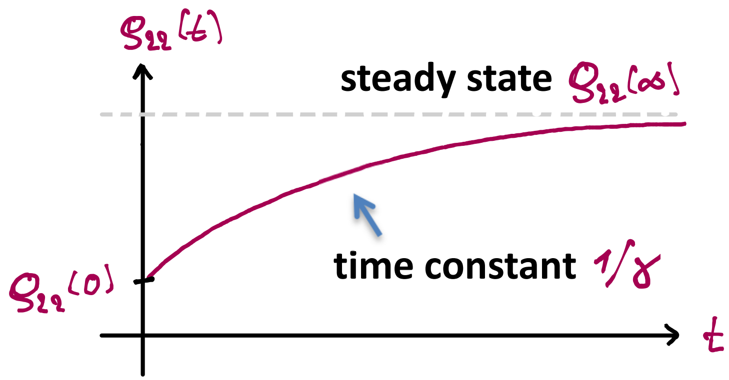

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Limiting cases:

$\sigma(\Delta)\phi = 0 \Rightarrow \rho_{22}(\infty) = 0$

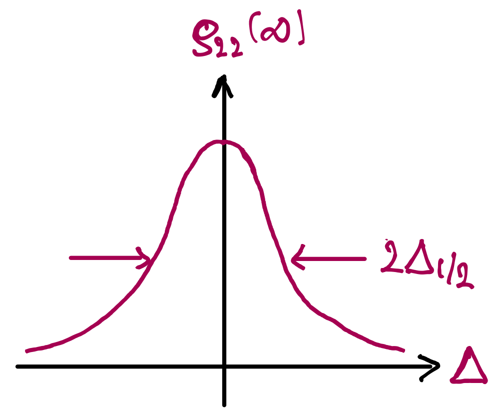
$\sigma(\Delta)\phi \ll A_{21} \Rightarrow \rho_{22}(\infty) = \frac{\sigma(\Delta)\phi}{A_{21}}$

$\sigma(\Delta)\phi \gg A_{21} \Rightarrow \rho_{22}(\infty) = 1/2$ ← Saturation!

Rewrite $\rho_{22}(\infty)$ using $R_{12} = \sigma(\Delta)\phi = \frac{|X|^2\beta/2}{\Delta^2 + \beta^2}$

$$\Rightarrow \rho_{22}(\infty) = \frac{|X|^2\beta/2A_{21}}{\Delta^2 + \beta^2 + |X|^2\beta/A_{21}}$$

Plot $\rho_{22}(\infty)$ vs Δ:



HWHM line width $\Delta_{1/2}$:

$$\Delta_{1/2} = \sqrt{\beta^2 + |X|^2\beta/A_{21}} = \beta\sqrt{1 + \frac{2\sigma(0)\phi}{A_{21}}}$$

$\left(\text{used } \sigma(0)\phi = \frac{|X|^2}{2\beta}\right)$

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Limiting cases:

$\sigma(\Delta)\phi = 0$	⇨	$\rho_{22}(\infty) = 0$
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Rewrite $\rho_{22}(\infty)$ **using** $R_{12} = \sigma(\Delta)\phi = \dfrac{|X|^2\beta/2}{\Delta^2+\beta^2}$

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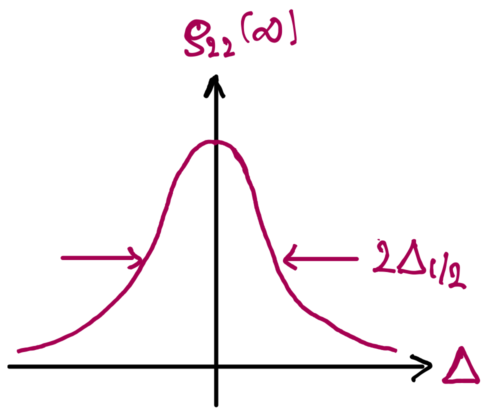


HWHM line width:

$$\Delta_{1/2} = \sqrt{\beta^2+|X|^2\beta/A_{21}}$$

$$= \beta\sqrt{1+\frac{2\sigma(0)\phi}{A_{21}}}$$

(used $\sigma(0)\phi = \dfrac{|X|^2}{2\beta}$)

Power Broadening: Rewrite

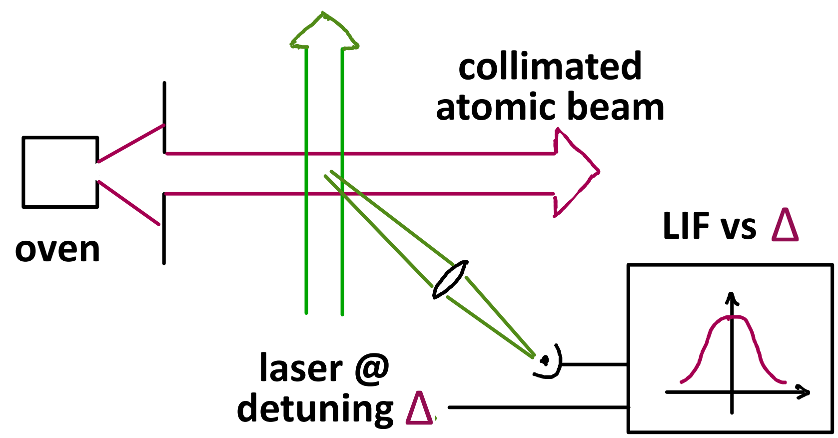
$$\Delta_{1/2} = \beta\sqrt{1+\phi/\phi_{SAT}} = \beta\sqrt{1+I/I_{SAT}}$$

where

$$\phi_{SAT} \equiv \frac{A_{21}}{2\sigma(0)}, \qquad I_{SAT} \equiv \frac{\hbar\omega A_{21}}{2\sigma(0)}$$

β : natural linewidth

Power Broadening in molecular beam spectroscopy:



Keep $I \ll I_{SAT}$ for best spectroscopic resolution

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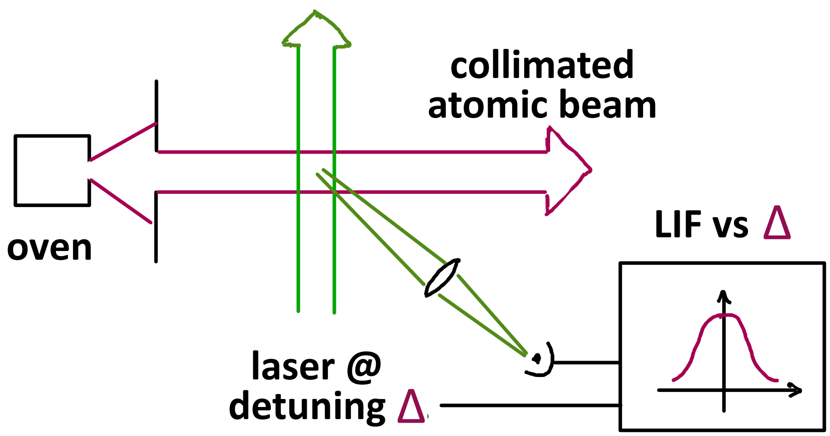

Keep $I \ll I_{SAT}$ for best spectroscopic resolution

More about the Photon Scattering Cross Section

By Definition

$$R_{12} = \frac{|\chi|^2\beta/2}{\Delta^2+\beta^2} = \sigma(\Delta)\phi = \sigma(\Delta)\frac{\frac{1}{2}c\varepsilon_0|E_0|^2}{\hbar\omega}$$

where $|\chi|^2 = |\vec{r}_{12}\cdot\vec{\varepsilon}E_0/\hbar|^2 = f\,\dfrac{|\vec{r}_{12}|^2|E_0|^2}{\hbar^2}$

and Collision free → $1 \geq f \geq 1/3$ ← Collision broadened

This gives us

$$\sigma(\Delta) = f\,\frac{\omega r_{12}^2}{\hbar c\varepsilon_0\beta}\,\frac{\beta^2}{\Delta^2+\beta^2} \equiv \sigma(0)\frac{\beta^2}{\Delta^2+\beta^2}$$

Let $\beta = A_{21}/2$, $\Gamma_1 = \Gamma_2 = 0$ (collision free)

$$\sigma(0) = f\,\frac{2\omega r_{12}^2}{\hbar c\varepsilon_0 A_{21}} = f\,\frac{4\pi}{\hbar\varepsilon_0\lambda}\,\frac{r_{21}^2}{A_{21}} \quad *$$

The connection between A_{21} and r_{21}^2 is intuitive, derived rigorously during the QED part of OPTI 544

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where $|X|^2 = |\vec{\mu}_{12}\cdot\vec{\varepsilon}E_0/\hbar|^2 = f\frac{|\vec{\mu}_{12}|^2|E_0|^2}{\hbar^2}$

and Collision free $\rightarrow$ $1 \geq f \geq 1/3$ $\leftarrow$ Collision broadened

This gives us

$$\sigma(\Delta) = f\frac{\omega\mu_{12}^2}{\hbar c\varepsilon_0\beta}\frac{\beta^2}{\Delta^2+\beta^2} \equiv \sigma(0)\frac{\beta^2}{\Delta^2+\beta^2}$$

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The connection between A_{21} and μ_{21}^2 is intuitive, derived rigorously during the QED part of OPTI 544

Here we simply note the result :

$$A_{21} = \frac{\mu_{12}^2\omega^3}{3\pi\varepsilon_0\hbar c^3}$$

Substituting in $*$ we get

$$\sigma(0) = f\frac{2\omega}{\hbar c\varepsilon_0}\frac{3\pi\varepsilon_0\hbar c^3}{\omega^3} = f\frac{3\lambda^2}{2\pi}$$

$$\frac{3\lambda^2}{2\pi} \geq \sigma(0) \geq \frac{\lambda^2}{2\pi}$$

Collision free, polarized light ($\frac{3\lambda^2}{2\pi}$); Collision broadened or un-polarized light ($\frac{\lambda^2}{2\pi}$)

– Remarkably simple result –
easy to remember

Why ?