Now look at emission & absorption from a microscopic, quantum point of view

Consider two isolated atomic levels $|e\rangle, |g\rangle$, assume they interact via the electric dipole term : $\vec{d}\cdot\vec{E}$

$$E_e - E_g = \hbar\omega_0$$

<u>Emission</u>: assume the initial state is the excited atomic state, with no photons excited, and the final state is the atomic ground state, plus one photon in some direction $\vec{k}$

$$|e, 0, 0, 0 \ldots\rangle \rightarrow |g, 0, 0, 1_{k\lambda}, 0, 0 \ldots\rangle$$

Use fermis golden rule: In principle, there is an angular dependence to the matrix elements $\vec{d}\cdot\vec{E}$, so one should calculate the rate into a solid angle & integrate

treating the sum over $\vec{k}$ as an integral →
$$R_{eg} = \int \frac{\partial R_{eg}}{\partial\Omega\, \partial E}\, d\Omega\, dE$$
the integral over $d\Omega$ is over directions $\vec{k}$, and we must sum $\lambda = 1, 2$

where
$$\frac{dR_{eg}}{d\Omega\, dE} = \frac{2\pi}{\hbar} \left| \langle g\, 1_{k\lambda} | \vec{d}\cdot\hat{\vec{E}}_{k\lambda} | e, 0\rangle \right|^2 \rho(E)\, \delta(E - \hbar\omega_0)$$

$\rho(E) \rightarrow$ density of photon modes $\dfrac{V}{(2\pi)^3} \dfrac{E^2}{\hbar^3 c^3}$

$$\rho(\hbar\omega_0) = \frac{V}{(2\pi)^3} \frac{\omega_0^2}{\hbar c^3}$$
} do the E integral, $|\vec{k}| = \dfrac{\omega_0}{c}$

$$R_{eg} = \sum_\lambda \int \frac{2\pi}{\hbar} \underbrace{|\langle g\, 1_{k\lambda}| \hat{\vec{d}} \cdot \hat{\vec{E}}_k | e\, 0\rangle|^2}\ \frac{V}{(2\pi)^3} \frac{\omega_0^2}{\hbar c^3}\, d\Omega_k$$

take $R=0$ in $e^{i\vec{k}\cdot\vec{R}}$

$$\underbrace{|\langle g|\vec{d}\cdot\vec{\epsilon}_k|e\rangle|^2}_{\text{replace this with}} \left(|E_{0k}|^2 \underbrace{|\langle 1_{k\lambda}| \underset{0}{\hat{a}_{k\lambda}} - \underset{1}{\hat{a}^\dagger_{k\lambda}} |0\rangle|^2}_{=1}\right)$$

replace this with its average over orientations: (which turns out to be)

$$\frac{1}{3}\underbrace{|\langle g|\vec{d}|e\rangle|^2}_{e^2 M_{eg}^2}, \quad \hat{\vec{M}} = \sum_i \hat{\vec{r}}_i$$

now the isotropic integral over $d\Omega \Rightarrow 4\pi$, sum over polarization $\Rightarrow 2$

$$R_{eg} = \frac{2\pi}{\hbar} \frac{e^2 M_{eg}^2}{3} \frac{\hbar\omega_0}{2\epsilon_0 V} \frac{V}{(2\pi)^3} \frac{\omega_0^2}{\hbar c^3}\ 2\times 4\pi$$

$$= \boxed{\frac{e^2 M_{eg}^2\, \omega_0^3}{3\pi\, \hbar\, \epsilon_0\, c^3} = A_{eg}}$$

note how easy this was with the quantized field!

Also note that $A_{eg} = \frac{1}{\tau} \propto \omega_0^3$

excited state lifetime

this is because the phase space $\propto \omega_0^2$ and the coupling strength $\propto \omega_0$ (at least for a fixed size atom)

What if there had been a large number of photons in one mode to start with?

$\longrightarrow$ stimulated emission

e.g. $|\text{initial state}\rangle = |e, 0, \ldots n_{k'\lambda'}, 0 \ldots\rangle$

then for that mode, $\hat{\vec{d}} \cdot \hat{\vec{E}}_{k\lambda} = \hat{\vec{d}} \cdot \vec{\epsilon}_{k\lambda'} \left(\hat{a}_{k\lambda'} - \hat{a}^{\dagger}_{k\lambda'} \right) E_{0k}$ will couple

$$\langle g, 0, \ldots n_{k'\lambda'}+1, 0 \ldots | \hat{a}^{\dagger}_{k\lambda'} | e, 0, \ldots n_{k\lambda'}, 0 \ldots \rangle \rightarrow \text{conserves energy}$$

and

$$\langle g, 0, \cdots n_{k\lambda'} - 1, 0 \ldots | \hat{a}_{k\lambda'} | e, 0 \ldots n_{k\lambda'}, 0 \ldots \rangle \rightarrow \text{doesn't conserve energy.}$$

the full $\hat{a}^{\dagger}_{k\lambda'}$ term gives

$$|E_{0k}|^2 \left| \langle g | \vec{d} | e \rangle \cdot \vec{\epsilon}_{k\lambda'} \right|^2 \underbrace{\left| \langle 0, \cdots n_{k\lambda'}+1, 0 \ldots | \hat{a}^{\dagger}_{k\lambda'} | e, 0 \ldots n_{k\lambda'}, 0, \ldots \rangle \right|^2}_{\left|\sqrt{n_{k\lambda'}+1}\right|^2 \; = \; n_{k\lambda'}+1.}$$

We have to be careful using Fermi's Golden Rule, because these are <u>two</u> states coupled, not a continuum of states. Fermi's Golden rule only works when coupling to a continuum of states.

We can discuss the problem is several ways:

1) Solve the two-state problem, which will be described by Rabi oscillations, not Fermis Golden Rule. This assumes we ignore the coupling of $|e\rangle$ to other modes.
2) assume the input radiation is broad-band in energy, filling a continuum in energy around the resonant frequency of the atom. (Similar to Einsteins approach)
3) Ask "How did the atom get to $|e\rangle$ in the first place?", and consider the full scattering process: $|g\rangle \xrightarrow{\text{photon}} |e\rangle \xrightarrow{\text{photon}} |g\rangle$

(Note for next weeks lecture: the Optical Bloch equations provide a framework for discussing Spontaneous processes (Fermis Golden Rule) and Rabi oscillations between 2 levels simultaneously)

For now take approach #2

assume the light propagates along a direction $\vec{k}'$, but has a spread in frequency (energy/$\hbar$) with a constant # of photons in each mode n_0:

$$\#\text{ of photons between } \omega, \omega+\delta\omega, \text{ in solid angle } d\Omega_k = n_0\, \rho_{1d}(\omega)\, \delta(\Omega_k - \Omega_{k'})\, \delta\omega$$

$$= \frac{n_0}{\hbar}\, \rho_{1d}\left(\frac{E}{\hbar}\right) \delta(\Omega_k - \Omega_{k'})\, \delta E.$$

Here, $\rho_{1d}(E)$ is the 1d mode density, n_0 is the average number of photons in the mode (along $\vec{k}$)

Now apply Fermis Golden Rule

$$R_{eg} = \int \frac{2\pi}{\hbar} \left| \langle \text{final} \right| \vec{d} \cdot \vec{E} \left| e, 0, .. n_{k'\lambda'}, 0.. \rangle \right|^2 \rho(E)^{\delta(E-\hbar\omega_0)} \, dE \, d\Omega_k$$

there are two different types of final states:

1) $\vec{k}_f$ along $\vec{k}'$, for which the matrix element involves the state $|g, 0, .. n_{k'\lambda'} - 1, 0 ... \rangle$:

$$|\langle g|\vec{d}|e\rangle \cdot \vec{\epsilon}_{k'\lambda'}|^2 \, E_{0k}^2 \, (n_0 + 1) \, \rho_{1D}(\omega_0)$$

2) $\vec{k}_f$ not along $\vec{k}'$, for which the matrix element involves the state $|g, 0, .. 1_{k_f\lambda_f}, n_{k'\lambda'}, 0 .. \rangle$

$$|\langle g|\vec{d}|e\rangle \cdot \vec{\epsilon}_{k_f\lambda_f}|^2 \, E_{0k}^2 \, 1 \, \rho_{3D}(\omega_0)$$

When we do the integral over dE + $d\Omega_k$, include the +1 from $(n_0 + 1)$ with the other single photon spontaneous events:

the +1 term from this integral goes here

$$R_{eg} = \underbrace{\frac{2\pi}{\hbar} |\langle g|\vec{d}|e\rangle \cdot \vec{\epsilon}_{k\lambda'}|^2 E_{0k}^2 \, n_0 \, \rho_{1D}(\hbar\omega_0)}_{\text{this is stimulated emission}} + \underbrace{\frac{e^2 M_{eg}^2 \, \omega_0^3}{3\pi \hbar \epsilon_0 c^3}}_{\text{this is just the spontaneous emission } A_{eg} \text{ from before.}}$$

assume that the ensemble of scattering atoms are pointed in random directions:

$$|\langle g|\vec{d}|e\rangle \cdot \vec{\epsilon}_k|^2 = \frac{1}{3} e^2 M_{eg}^2 \, , \quad \hat{\vec{M}}_{eg} = \sum_i \hat{\vec{r}}_i$$

$$R_{eg} = \frac{2\pi}{\hbar} \frac{e^2 M_{eg}^2}{3} \frac{\hbar \omega_0}{2\epsilon_0 V} n_0 \rho_{1d} + A_{eg}$$

$$= \frac{\pi e^2 M_{eg}^2}{\epsilon_0 \hbar^2} \frac{\hbar \omega_0 n_0 \rho_{1d}}{V \hbar} + A_{eg}$$

$$\left.\begin{aligned} \text{but } \hbar\omega &= \text{Energy per photon} \\ n_0 \frac{\rho_{1d}}{\hbar} &= \text{\# of photons per } \delta\omega \\ V &= \text{volume} \end{aligned}\right\} \quad \frac{\hbar \omega_0 n_0 \rho_{1d}}{V \hbar} = W(\omega)$$

the energy density per $\delta\omega$

$$R_{eg} = \underbrace{\frac{\pi e^2 M_{eg}^2}{\epsilon_0 \hbar^2}}_{B_{eg}} W(\omega) + A_{eg}$$

and $\dfrac{A_{eg}}{B_{eg}} = \dfrac{\hbar \omega_0^3}{\pi^2 c^3}$

as ω_0 increase, spontaneous emission becomes stronger relative to stimulated emission for fixed $W(\omega)$

Since A & B both depend on $e^2 M_{eg}^2$, the ratio is independent → a fundamental result.

$\frac{\hbar\omega_0^3}{\pi^2 c^3}$ has units of energy density per $d\omega$

define a saturation energy density per $d\omega$:

$$W_s = \frac{\hbar\omega_0^3}{\pi^2 c^3}$$

There will be a corresponding saturation intensity per $\delta\omega$

$$\rho_s = \underbrace{c}_{\text{speed of light}} W_s$$

Imagine shining (broad band) light on the atom from one direction. What are the steady state energy level populations? What are the average scattering rates? (as a function of incoming energy density)

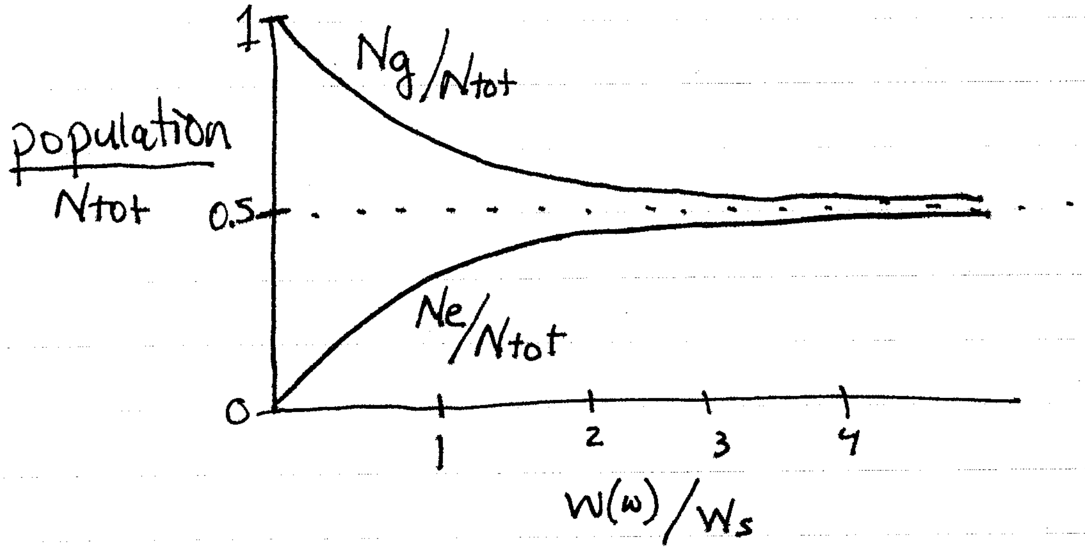
Rate equations: $\dot{N}_g = \underbrace{A}_{\substack{\text{spontaneous} \\ \text{from } |e\rangle}} N_e + B\,W(\omega)(\underset{\text{stimulated}}{N_e} - \underset{\text{absorbed}}{N_g})$

$\dot{N}_e = -\dot{N}_g$

in steady state, $\dot{N}_e = \dot{N}_g = 0$ $\qquad N_{tot} = N_g + N_e$

$$N_g = \frac{A + B\,W(\omega)}{A + 2B\,W(\omega)} = \frac{W_s + W(\omega)}{W_s + 2W(\omega)} N_{tot}$$

$$N_e = \frac{B\,W(\omega)}{A + 2B\,W(\omega)} = \frac{W(\omega)}{W_s + 2W(\omega)} N_{total}$$



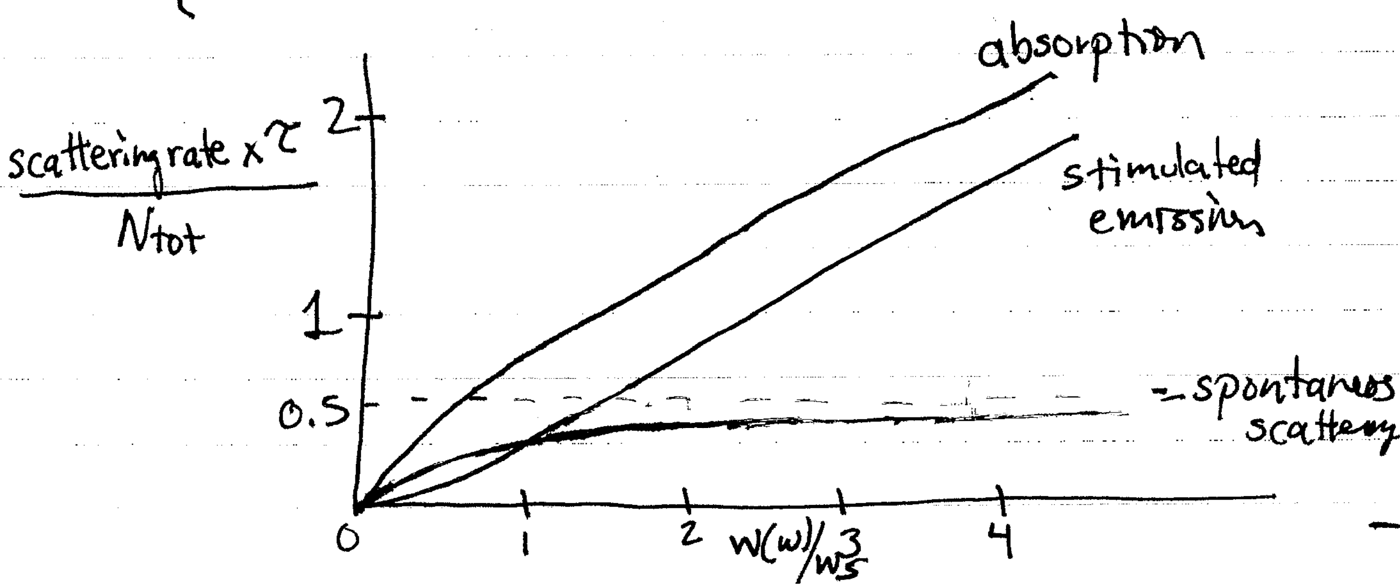
What about the total scattering rates?

absorption : $N_g \, B \, W(\omega) = N_{tot} A \left(\frac{W_s + W(\omega)}{W_s + 2W(\omega)} \right) \left(\frac{W(\omega)}{W_s} \right)$

stimulated emission : $N_e \, B \, W(\omega) = N_{tot} A \left(\frac{W(\omega)}{W_s + 2W(\omega)} \right) \left(\frac{W(\omega)}{W_s} \right)$

spontaneous emission : $N_e \, A = N_{tot} A \left(\frac{W(\omega)}{W_s + 2W(\omega)} \right)$

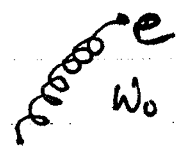
$A = \frac{1}{\tau}$



See Bill's lecture notes from lecture # 3 for a discussion of the cross section.

I did not get to this in class, but there is a useful classical analogy to scattering:

imagine an electron on a spring subject to an oscillating $\vec{E}$ - field:



(Gaussian units, sorry) $\longrightarrow$ $\vec{F} = e\vec{E}\cos(\omega t)$

take $\hat{x}$ to be along the polarization direction for $\vec{E}$, $\vec{r}\cdot\vec{E} = xE$

$$\boxed{\ddot{x} - \gamma\dot{x} + \omega_0^2 x = \frac{e}{m} E\cos(\omega t).}$$

(allow for damping, since we know it should radiate)

this has classical solutions (in steady state)

$$x(t) = -\frac{eE}{m}\cos(\omega t)\,\frac{\omega_0^2-\omega^2}{(\omega_0^2-\omega^2)^2+4\gamma^2\omega^2}$$

$$-\frac{eE}{m}\sin(\omega t)\,\frac{2\gamma\omega}{(\omega_0^2-\omega^2)^2+4\gamma^2\omega^2}$$

$$\dot{x}(t) = \frac{eE}{m}\sin(\omega t)\ \omega(\omega_0^2-\omega^2)\Big/\left((\omega_0^2-\omega^2)^2+4\gamma^2\omega^2\right)$$

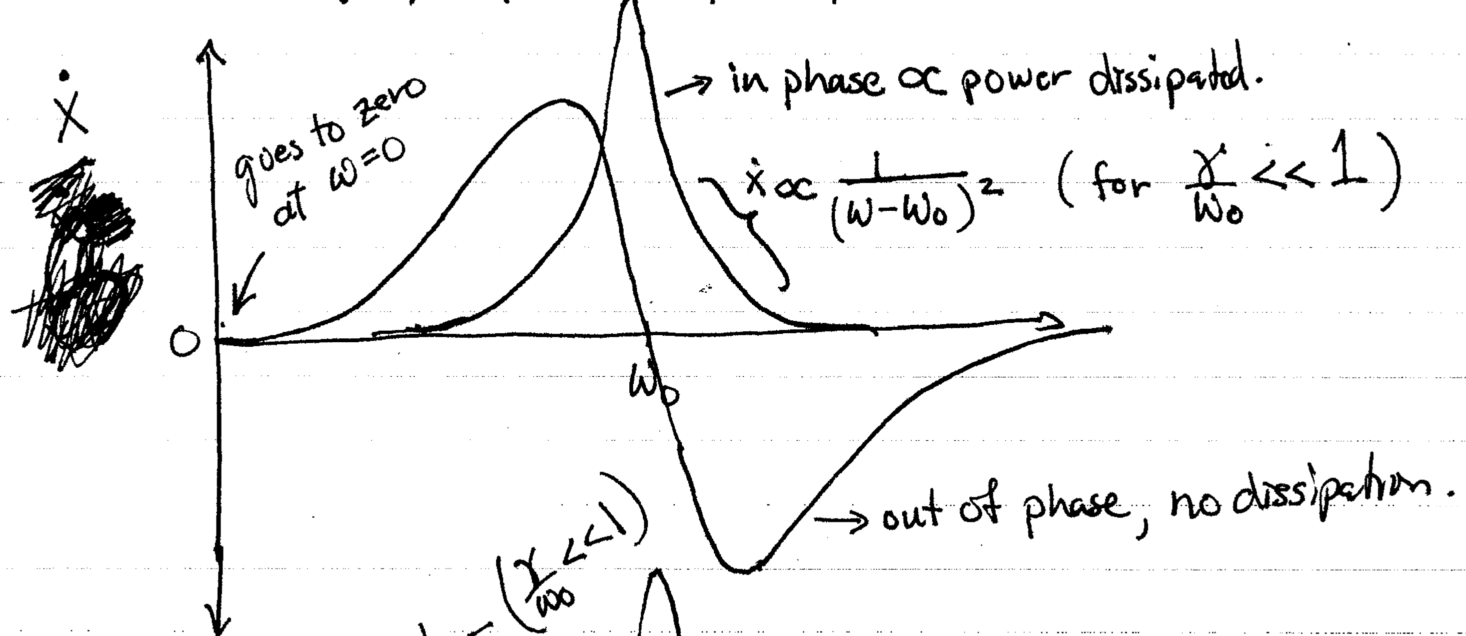
$$-\frac{eE}{m}\cos(\omega t)\ 2\gamma\omega^2\Big/\left((\omega_0^2-\omega^2)^2+4\gamma^2\omega^2\right)$$

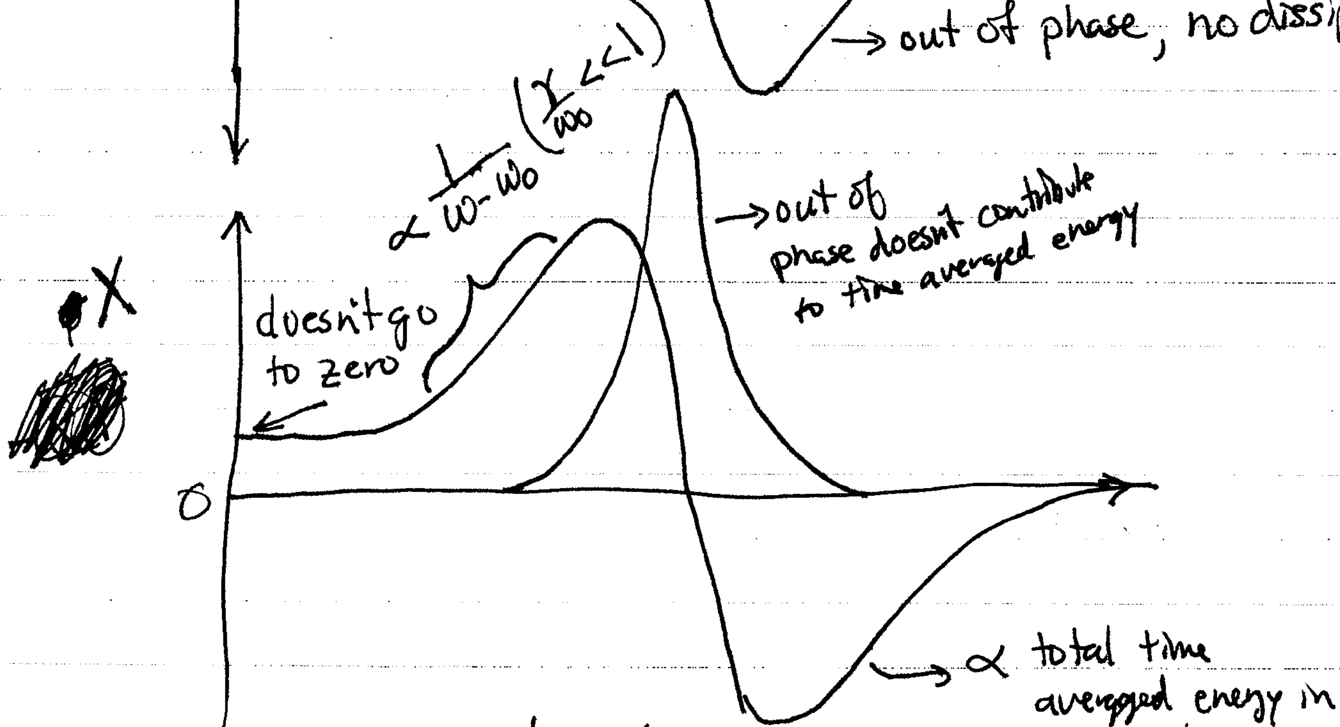
Note: the power dissipated is $\int_0^T \dot{x}(t) F(t)\, dt \equiv \overline{\dot{x} F}$

only the in-phase parts will contribute to the time-average.

the time average electrostatic energy is $\int_0^T x F\, dt = \overline{xF}$

again, only the in phase part will contribute.





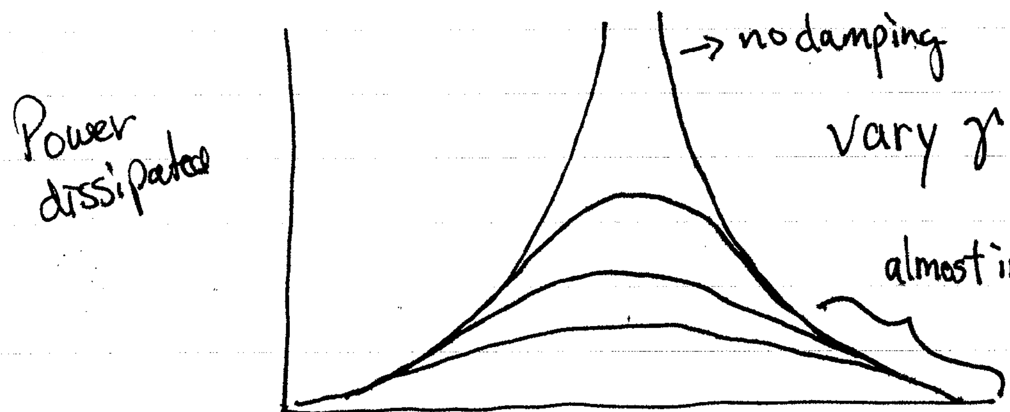
Many properties of atoms will look similar.

Look on resonance:

$$\dot{x}F = \frac{e^2E^2}{m}\,\frac{1}{4\gamma}$$

if ~~[scribbled]~~ $\frac{e^2E^2}{m}$ and γ are independent,

We can get different widths and heights of the dissipation ("scattering") resonance:



vary γ at fixed $\frac{e^2E}{m}$

almost independent of damping, except at very large damping.

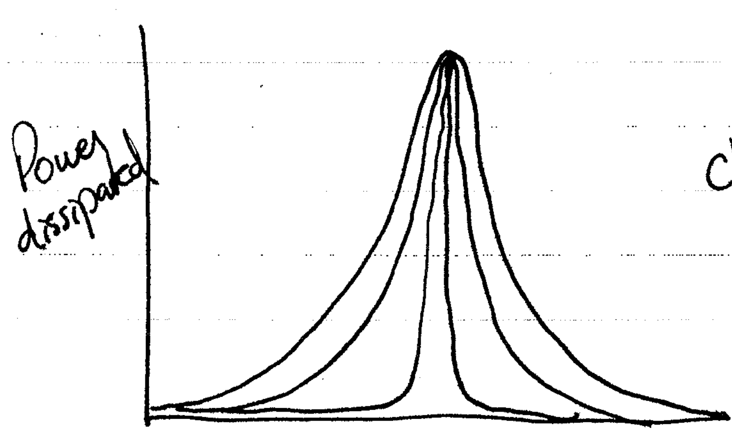
But for an electron oscillating, we know it classically radiates,

$$\gamma = \frac{e^2\omega_0^2}{3mc^3}\,\frac{1}{4\pi\epsilon_0}$$

(see Jackson for dipole radiation)

$$\dot{x}F = \frac{e^2E^2}{4m}\,\frac{3mc^3\epsilon_0 4\pi}{e^2\omega_0^2} = \frac{3}{4}\,\underbrace{\epsilon_0 E^2 c}_{\text{intensity = energy density}\times c}\,\underbrace{\frac{c^2}{\omega_0^2}}_{1/k^2}4\pi \propto I\,\lambda^2$$

depends only on wavelength.



Changing γ also changes the coupling $\frac{eE}{m}$, so on resonance dissipation is the same. → more like atoms.