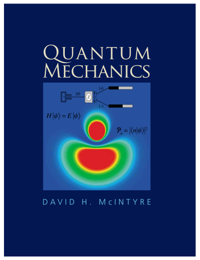
Time-dependent perturbation theory

Read McIntyre 14.1-14.3

PH451/551



Time-dependent perturbation

1. Schrödinger Equation $$H\left|\psi\right\rangle = i\hbar\frac{d}{dt}\left|\psi\right\rangle$$

2. Initial state: $$\left|\psi(t=0)\right\rangle = \sum_n c_n \left|\varphi_n\right\rangle$$

3. Usual time-development: $$\left|\psi_{H'=0}(t)\right\rangle = \sum_n c_n e^{-i\frac{E_n}{\hbar}t}\left|\varphi_n\right\rangle$$

4. Add perturbation: $H = H_0 + H'(t)$

5. Time-dep coefficients: $$\left|\psi_{H'\neq 0}(t)\right\rangle = \sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t}\left|\varphi_n\right\rangle$$

Solve for $c_n(t)$

1. Start:

$$\left(H_0 + H'(t)\right)\left|\psi(t)\right\rangle = i\hbar \frac{d}{dt}\left|\psi(t)\right\rangle$$

$$\left(H_0 + H'(t)\right)\sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t}\left|\varphi_n\right\rangle = i\hbar \frac{d}{dt}\sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t}\left|\varphi_n\right\rangle$$

2. Crunch …. Crank …
3. 1st order result:

$$c_k(t) = \frac{1}{i\hbar}\int_0^t \left\langle k\right| H'(t') \left|i\right\rangle e^{i\frac{E_k - E_i}{\hbar}t'}\, dt' \qquad \omega_{ki} = \frac{E_k - E_i}{\hbar}$$

Transition probability

1. Start:

$$P_{i\to f}(t) = \left|\langle \psi_f | \psi(t)\rangle\right|^2$$

$$= \left|\langle \psi_f \middle| \sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t} \middle| \psi_n\rangle\right|^2$$

$$= \left|c_f(t)\right|^2$$

2. Result:

$$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\int_0^t \langle f | H'(t') | i\rangle e^{i\frac{E_f - E_i}{\hbar}t'} dt'\right|^2$$

3. Examples: constant H', Gaussian H', harmonic H'

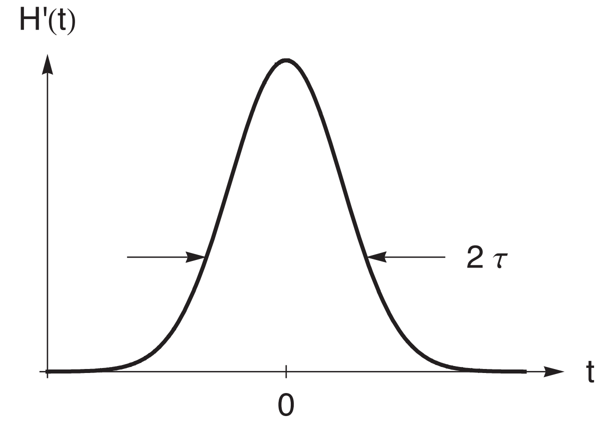
Constant H'

1. Turns on for a time, then off:

$$P_{i\to f}(t)=\left|c_f(t)\right|^2=\frac{4\left|\langle f|H'|i\rangle\right|^2}{\hbar^2\omega_{fi}^2}\sin^2\left(\omega_{fi}t/2\right)$$

2. Like Rabi result from Ch3.

Gaussian H'



1. H':

$$H'(t) = V_0 e^{-\frac{t^2}{\tau^2}}$$

2. Change time origin, sin integral is 0:

$$c_f(\infty) = \frac{1}{i\hbar}\langle f|V_0|i\rangle \int_{-\infty}^{\infty} e^{-\frac{t'^2}{\tau^2}} \cos(\omega_{fi} t')\,dt'$$

$$= \frac{1}{i\hbar}\langle f|V_0|i\rangle \sqrt{\pi}\tau e^{-\frac{\omega_{fi}^2\tau^2}{4}}$$

3. Transition probability:

$$P_{i\to f} = \frac{\pi\tau^2}{\hbar^2}\left|\langle f|V_0|i\rangle\right|^2 e^{-\frac{\omega_{fi}^2\tau^2}{2}}$$

Perturbations turned on slowly do not change the state of the system. What is “slow” for the 1s-2p H transition? 1yr? 1ms? 1ns? Calculate!

$$\tau \sim \frac{1}{\omega_{fi}}$$

Harmonic H'

1. H': $$H'(t) = 2V(\vec{\mathbf{r}})\cos\omega t$$
$$= V(\vec{\mathbf{r}})\left(e^{i\omega t} + e^{-i\omega t}\right)$$

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

2. Coefficient:

$$c_f(t) = \frac{1}{i\hbar}\int_0^t \langle f|V(\vec{\mathbf{r}})\left(e^{i\omega t} + e^{-i\omega t}\right)|i\rangle e^{i\boxed{\frac{E_f - E_i}{\hbar}}t'}\,dt'$$

$$= \frac{1}{i\hbar}\langle f|V|i\rangle\int_0^t \left[e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'}\right]dt'$$

$$= \frac{1}{i\hbar}\langle f|V|i\rangle\left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{i(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi}-\omega)}\right]$$

$$= \frac{1}{i\hbar}\langle f|V|i\rangle\left[e^{i\frac{\omega_{fi}+\omega}{2}t}\frac{\sin\frac{\omega_{fi}+\omega}{2}t}{\frac{\omega_{fi}+\omega}{2}} + e^{i\frac{\omega_{fi}-\omega}{2}t}\frac{\sin\frac{\omega_{fi}-\omega}{2}t}{\frac{\omega_{fi}-\omega}{2}}\right]$$

Harmonic H'

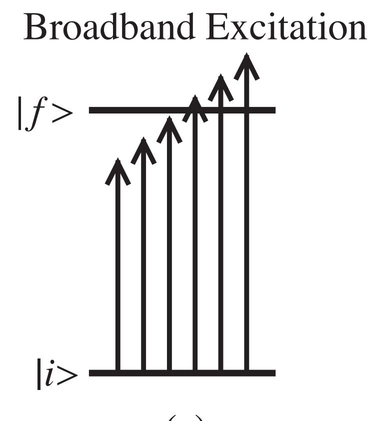
1. Electric dipole approximation: ignore spatial variation of E field when atoms excited by visible light. Why?
2. Transition rate (absorption):

$$R_{i\to f} = \frac{2\pi e^2 E_0^2}{\hbar^2} \left| \hat{\varepsilon} \bullet \langle f | \mathbf{r} | i \rangle \right|^2 \delta\left(\omega_{fi} - \omega\right)$$

3. Field energy density
4. Stimulated emission, absorption (B_{12}=B_{21}). Spontaneous absorption
5. Detailed balance

Harmonic H' - broadband

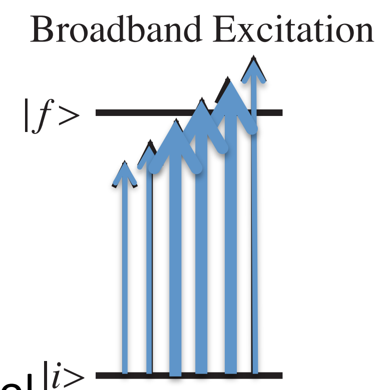
1. Broadband excitation, dipole approx



(a)

2. Transition rate (absorption):

$$R_{i\to f} = \frac{2\pi e^2 E_0^2}{\hbar^2}\left|\hat{\varepsilon}\bullet\langle f|\mathbf{r}|i\rangle\right|^2 \delta\left(\omega_{fi}-\omega\right)$$



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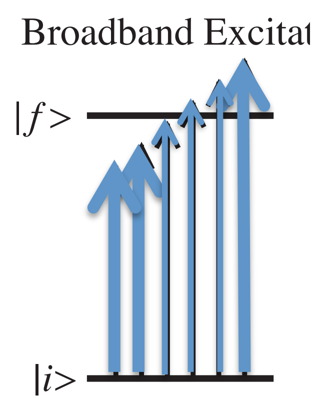


(a)

3. Field energy density:

$$2\varepsilon_0^2 E_0^2 = \rho\left(\omega\right)d\omega$$

Photons per unit vol per unit frequency range

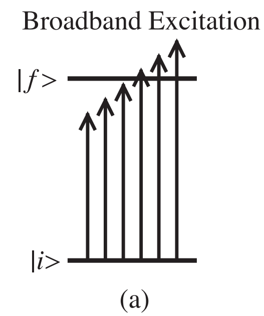
4. Pol. Avg.:

$$\hat{\varepsilon}\bullet\langle f|\mathbf{r}|i\rangle = \frac{1}{3}$$

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

$$u = \frac{\varepsilon_0}{2}E^2 + \frac{1}{2\mu_0}B^2$$

Harmonic H' - broadband



1. Sum rates for different frequencies:

$$R_{i\to f} = \frac{\pi e^2}{3\varepsilon_0 \hbar^2}\rho\left(\omega_{fi}\right)\left|\langle f|\mathbf{r}|i\rangle\right|^2$$

2. Transition rate (absorption):

$$R_{i\to f} = B_{if}\,\rho\left(\omega_{fi}\right)$$

3. Einstein *B* coefficient:

$$B_{if} = \frac{\pi e^2}{3\varepsilon_0 \hbar^2}\left|\langle f|\mathbf{r}|i\rangle\right|^2$$

Eqn 14.54

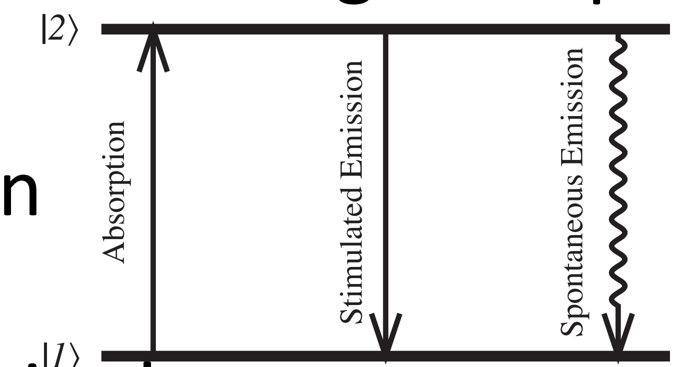
$$B_{if} = \frac{\pi\left(1.6\times 10^{-19} C\right)^2}{3\left(8.85\times 10^{-12} m^{-3} kg^{-1} s^4 A^2\right)\left(1.05\times 10^{-34} m^2 kg s^{-1}\right)^2}\left|\langle f|\mathbf{r}|i\rangle\right|^2$$

$$\begin{aligned}\mathbf{E}(t) &= 2E_0\hat{\varepsilon}\cos\omega t\\ &= \hat{\varepsilon}\left(E_0 e^{i\omega t} + E_0 e^{-i\omega t}\right)\end{aligned}$$

$$u = \frac{\varepsilon_0}{2}E^2 + \frac{1}{2\mu_0}B^2$$

Harmonic H' - broadband

1. Stimulated absorption and stimulated emission coefficients are the same (go back to original eqns and see symmetry):
2. Stimulated abs = stim. emission
   => no relaxation (unphysical)
   => propose spontaneous emission!:



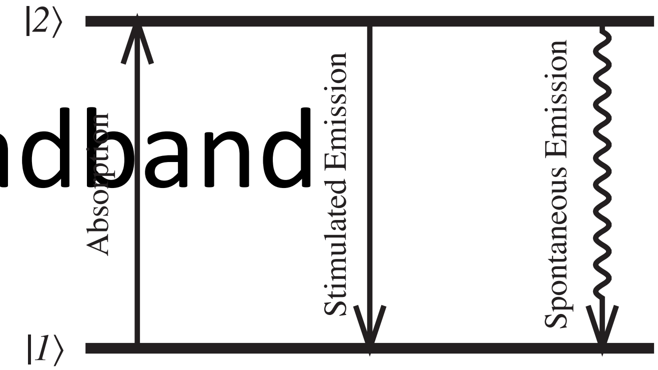
$$\frac{dN_1}{dt} = -N_1 B_{12}\rho(\omega_{21}) + N_2 B_{21}\rho(\omega_{21}) + N_2 A_{21}$$

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/kT} - 1}$$

$$\frac{dN_2}{dt} = +N_1 B_{12}\rho(\omega_{21}) - N_2 B_{21}\rho(\omega_{21}) - N_2 A_{21}$$

$$\frac{N_1}{N_2} = \frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_2}{k_B T}}} = e^{\frac{E_2 - E_1}{k_B T}} = e^{\frac{\hbar\omega_{21}}{k_B T}}$$

Harmonic H' - broadband



$$0=-N_1 B_{12}\rho(\omega_{21})+N_2 B_{21}\rho(\omega_{21})+N_2 A_{21}$$

$$\rho(\omega_{21})=\frac{A_{21}}{B_{12}}\frac{1}{N_1/N_2-1}$$

$$=\frac{A_{21}}{B_{12}}\frac{1}{e^{\frac{\hbar\omega_{21}}{k_B T}}-1}$$

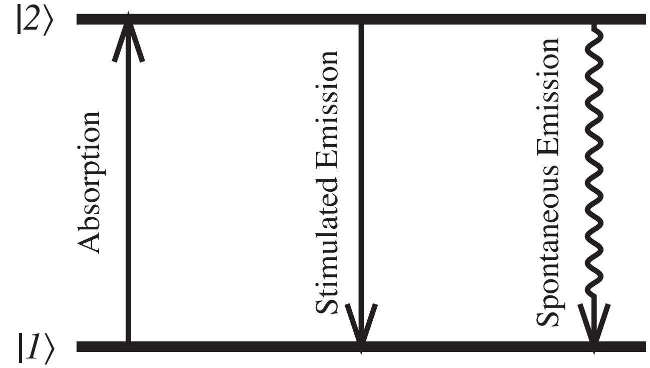
$$\frac{N_1}{N_2}=\frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_2}{k_B T}}}=e^{\frac{E_2-E_1}{k_B T}}=e^{\frac{\hbar\omega_{21}}{k_B T}}$$

$$\rho(\omega)=\frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/kT}-1}$$

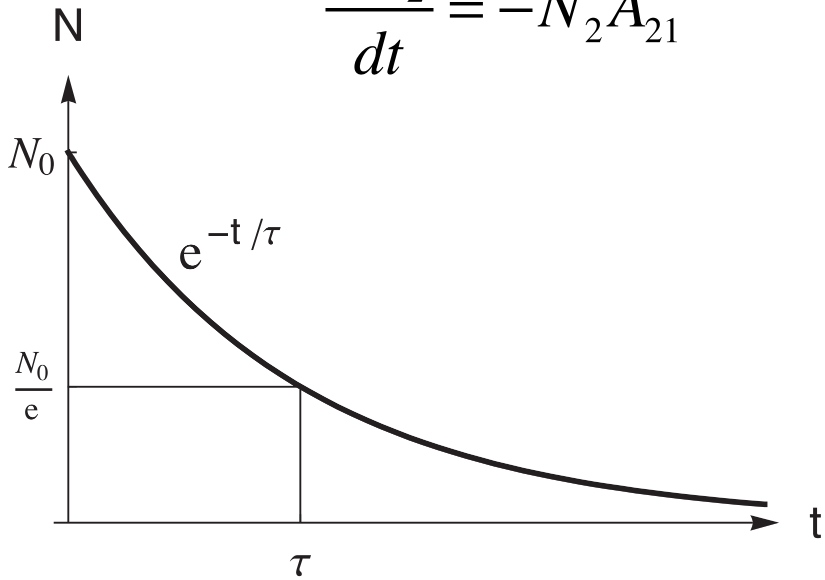
$$A_{21}=\frac{\hbar\omega_{21}^3}{\pi^2 c^3}\frac{\pi e^2}{3\varepsilon_0\hbar^2}\left|\langle f|\mathbf{r}|i\rangle\right|^2=\frac{e^2\omega_{21}^3}{3\pi\varepsilon_0\hbar c^3}\left|\langle f|\mathbf{r}|i\rangle\right|^2$$

Harmonic H' - broadband

1. Einstein *A* coefficient:
   (no field =>



$$\frac{dN_2}{dt} = -N_2 A_{21}$$



$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1}$$

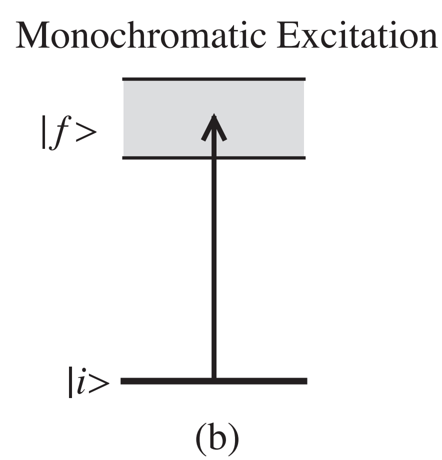
$$\frac{N_1}{N_2} = \frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_2}{k_B T}}} = e^{\frac{E_2 - E_1}{k_B T}} = e^{\frac{\hbar\omega_{21}}{k_B T}}$$

$$A_{21} = \frac{e^2 \omega_{21}^3}{3\pi\varepsilon_0 \hbar c^3} \left| \langle 2 | \mathbf{r} | 1 \rangle \right|^2$$

$$\tau = \frac{1}{A_{21}}$$

Harmonic H' – laser excitation

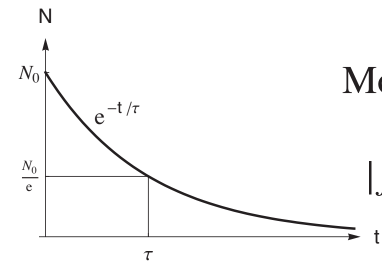
1. Take-home message:
   For atom - (resonant) light interactions, the atom acts as an efficient antenna, despite its small size.
2. Monochromatic excitation:
3. Transition rate (absorption),
   sum over rates to all final states:

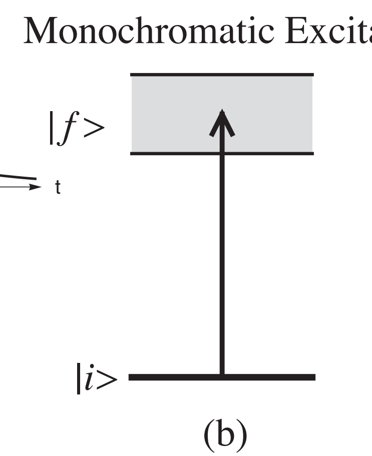


$$R_{i\to f} = \frac{2\pi}{\hbar^2}\left|V_{fi}\right|^2 \int_{E_f-\varepsilon}^{E_f+\varepsilon} \delta\left(\omega_{fi}-\omega\right) g\left(E\right)\hbar\, d\omega$$

Eqn 14.37

Harmonic H' – laser excitation





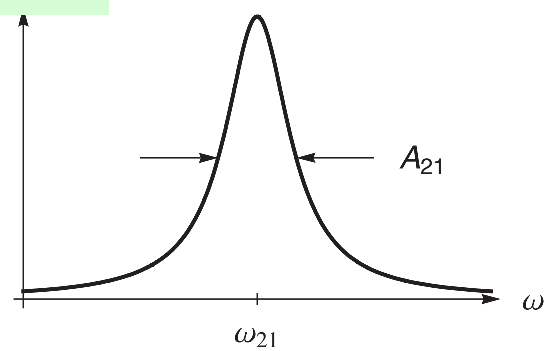
1. Excited state emits like this-> and has a Lorentzian density of states.
2. Lorentzian DoS normalized :

$$g(E) = \frac{\hbar A_{21}/2\pi}{\left(E - \hbar\omega_{21}\right)^2 + \left(\frac{\hbar A_{21}}{2}\right)^2}$$

$$f(\omega)d\omega = g(E)dE$$

$$f(\omega) = \frac{A_{21}/2\pi}{\left(\omega - \omega_{21}\right)^2 + \left(\frac{A_{21}}{2}\right)^2}$$

Eqn 14.68



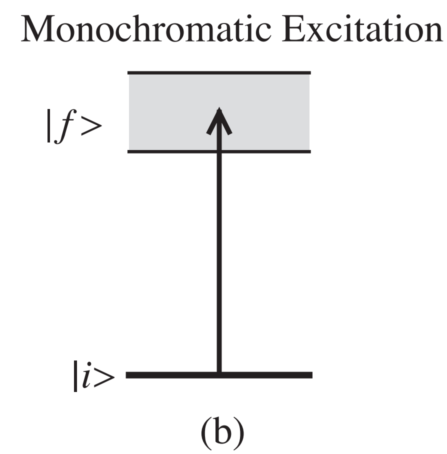
Harmonic H' – laser excitation

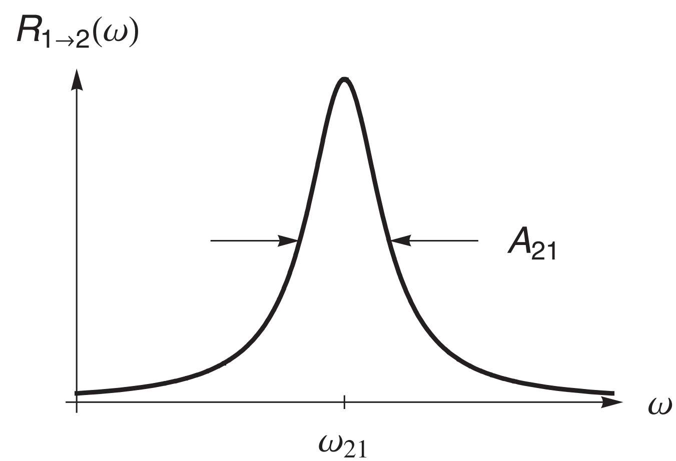
1. Intensity $I = 2c\varepsilon_0 E_0^2$

$$\left|V_{fi}\right|^2 = e^2 E_0^2 \left|\hat{\varepsilon} \bullet \langle 2|\mathbf{r}|1\rangle\right|^2$$

$$B_{if} = \frac{\pi e^2}{3\varepsilon_0 \hbar^2}\left|\langle f|\mathbf{r}|i\rangle\right|^2$$

2. Rate: $R_{1\to 2} = 3\frac{I}{c}B_{12}f(\omega)$





Harmonic H' – cross section

1. Efficiency: dimensions?

$$\text{efficiency} = \frac{\text{output}}{\text{input}}$$

2. examples:
   miles out, gallons in
   calories out, calories in
   grades out, hours in
3. Here: transitions made per time (out), number of photons per area per time (dimensions?)

Harmonic H' – cross section

1. Efficiency: area

$$\text{efficiency} = \frac{R_{1\to2}}{I/\hbar\omega} = \frac{\#\text{ per unit time}}{\#\text{ per unit time per unit area}}$$

$$\sigma = \frac{R_{1\to2}}{I/\hbar\omega} = \frac{3(I/c)B_{12}f(\omega_{21})}{I/\hbar\omega_{21}}$$

$$= \frac{3(I/c)B_{12}(2/\pi A_{21})}{I/\hbar\omega_{21}}$$

$$= \frac{6\hbar\omega_{21}}{\pi c}\frac{B_{12}}{A_{21}}$$

$$\sigma = 3\frac{\lambda_{21}^2}{2\pi}$$

2. Plug in B/A ratio

$$\sigma = 3\frac{\lambda_{21}^2}{2\pi}$$

3. Atom "looks like" it has a radius about the size of the wavelength of light, whereas is is about 100-1000 times smaller (numbers?)
4. For atom - (resonant) light interactions, the atom acts as an efficient antenna, despite its small size