Interaction of light with atoms: Line shapes and cross-sections

Summary of time-dependent perturbation theory approach

Fermi's Golden rule and lineshapes

Cross-sections

Reading: Svelto 2.4

Full QM approach

- Next level up in accuracy in QM is to approximately solve the Schrodinger equation in the presence of the incident field
  - QM representation of the electron wavefunction $\psi(\mathbf{r},t)$
  - Classical representation of the EM field as a perturbation

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \hat{H} = \hat{H}_0 + \hat{H}'$$

- Without external field: With external field (E-dipole):

$$\hat{H}_0\psi = i\hbar\frac{\partial\psi}{\partial t} \rightarrow \hat{H}_0\psi_n = E_n\psi_n \qquad \hat{H}' = \mu\cdot\mathbf{E} = -e\mathbf{r}\cdot\mathbf{E_0}\sin\omega t$$

- Assume wavefunction *with* field can be written in terms of a linear combination of wavefunctions *without* field

$$\psi(r,t) = \sum_n a_n(t)\psi_n(r,t) \qquad \psi_n(\mathbf{r},t) = u_n(\mathbf{r})e^{-E_n t/\hbar}$$

Framing the QM calculation

- Time-dependent SE with external field

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\hat{H}_0 + \hat{H}'\right)\psi = \left(\hat{H}_0 - e\,\mathbf{r}\cdot\mathbf{E_0}\sin\omega t\right)\psi$$

  - Applied field is built into the calculation
  - Dot product ensures r is along E
- Equation describes evolution of wavefunction
  - Independent of initial state
  - Absorption and stimulated emission are the same, only initial state is different

Spontaneous emission and QED

- What if there is no incident field?
- If atom is in an excited state, it is in an unstable equilibrium.
- But the vacuum fluctuations of the EM field (QED) “stimulate” emission spontaneously.
- Concept leads to “cavity QED” experiments, where an external cavity is used to shape/control the background radiation spectrum to enhance or suppress spontaneous emission.

Time-dependent perturbation theory

- Easiest to concentrate on 2 levels
- Assume input frequency is close to resonance:

$$\omega \approx \left(E_2 - E_1\right)/\hbar = \omega_{21}$$

- Assume weak probability of excitation:

$$a_1\left(t\right) \approx 1, \quad a_2\left(t\right) \ll 1$$

- Put form of solution into time-dependent SE (with field)
- Transition rate (in Hz) will be

$$W_{12} = \frac{d}{dt}\left|a_2\left(t\right)\right|^2$$

- Result: “Fermi’s Golden Rule”

$$W_{12}\left(\nu\right) = \frac{\pi^2}{3h^2}\left|\mu_{12}\right|^2 E_0{}^2 \delta\left(\nu - \nu_0\right)$$

$\delta\left(\nu - \nu_0\right)$ Dirac delta function

$$\int f\left(\nu\right)\delta\left(\nu - \nu_0\right)d\nu = f\left(\nu_0\right)$$

Using Fermi's golden rule

- Fermi's "Golden rule" $W_{12}(\nu) = \frac{\pi^2}{3h^2}|\mu_{12}|^2 E_0{}^2 \delta(\nu - \nu_0)$
  - To get a rate, we must integrate over frequency
  - Implicitly, the field^2 in this expression is connected to the spectral energy density:

    $$\rho_\nu = \tfrac{1}{2} n^2 \varepsilon_0 E_0^2$$

  - This way we get a total transition rate by integrating over frequency

    $$\rightarrow W_{12}(\nu) = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_\nu \delta(\nu - \nu_0)$$

- Total rate is obtained by integrating over all frequency:

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_\nu \delta(\nu - \nu_0) d\nu = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_{\nu_0}$$

Absorption with blackbody incident field

- Spectral energy density for blackbody:

$$\rho_\nu = \frac{8\pi\nu^2}{(c/n)^3}\frac{h\nu}{e^{h\nu/k_BT}-1}$$

- Integration with the delta function assigns $\nu \rightarrow \nu_0$

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_\nu \delta(\nu-\nu_0)d\nu = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_{\nu_0}$$

$$W_{12} = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \frac{8\pi\nu^2}{(c/n)^3}\frac{h\nu}{e^{h\nu/k_BT}-1}$$

– Check units:

$$W_{12} = \frac{2\pi^2}{3n^2h^2}\frac{e^2x^2}{\varepsilon_0}\frac{x}{x}\frac{8\pi\nu^2}{(c/n)^3}\frac{h\nu}{e^{h\nu/k_BT}-1} \rightarrow \frac{1}{(J\,s)^2}J\,m^3\frac{s^{-2}}{(m\,s^{-1})^3}J = s^{-1}$$

Working with spectral lineshapes

- For atomic system, replace Dirac delta with transition lineshape

$$\int g(\nu-\nu_0)\,d\nu = 1$$

- Lorentzian lineshape (radiative, collisional broadening)

$$\delta(\nu-\nu_0) \rightarrow g_L(\nu-\nu_0) = \frac{2}{\pi\,\Delta\nu_0}\frac{1}{1+\left(\dfrac{2(\nu-\nu_0)}{\Delta\nu_0}\right)^2}$$

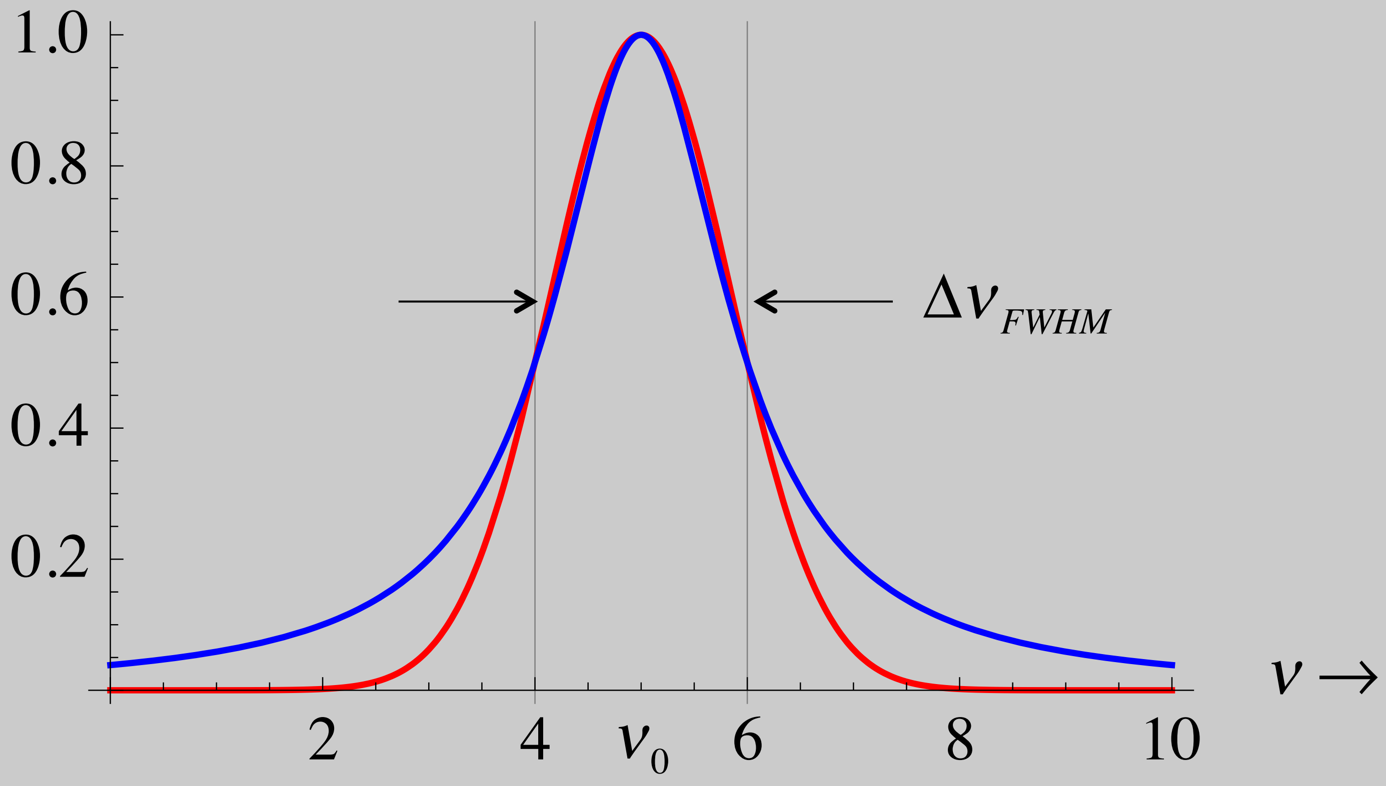
$\Delta\nu_0$ FWHM

- Doppler broadened (Gaussian) lineshape

$$\delta(\nu-\nu_0) \rightarrow g_G^{*}(\nu-\nu_0) = \frac{2}{\Delta\nu_0^{*}}\sqrt{\frac{\ln 2}{\pi}}\exp\left\{-4\ln 2\frac{(\nu-\nu_0)^2}{\Delta\nu_0^{*2}}\right\}$$

Lorentzian vs Gaussian lineshapes

- Lorentzian is much broader in spectral wings than Gaussian



Lorentzian lineshape

- Complex Lorentzian separated into Re and Im

$$\frac{1}{\gamma - i(\omega - \omega_0)} = \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} + i\frac{(\omega - \omega_0)}{(\omega - \omega_0)^2 + \gamma^2}$$

  – Real part corresponds to absorption effects

- Normalize

$$c\int \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} d\omega = c\gamma \frac{\pi}{\gamma} = 1 \quad \rightarrow g_L(\omega - \omega_0) = \frac{\gamma / \pi}{(\omega - \omega_0)^2 + \gamma^2}$$

- Convert ω to ν

$$c\int \frac{\gamma}{4\pi^2 (\nu - \nu_0)^2 + \gamma^2} d\nu = c\gamma \frac{1}{2\gamma} = 1$$

$$\rightarrow g_L(\nu - \nu_0) = \frac{2}{\gamma}\left[1 + \left(\frac{2(\nu - \nu_0)}{\gamma / \pi}\right)^2\right]^{-1} = \frac{2}{\pi \Delta\nu_0}\left[1 + \left(\frac{2(\nu - \nu_0)}{\Delta\nu_0}\right)^2\right]^{-1}$$

Natural broadening

- Radiative broadening results directly from the spontaneous emission lifetime of the state
- Fourier transforms
  - Forward: FT $$F(\omega)=\int_{-\infty}^{\infty} f(t)e^{i\omega t}\,dt$$
  - Inverse: FT^{-1} $$f(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega)e^{-i\omega t}\,d\omega$$
- Suppose exponential, oscillating decay in time domain

$$f(t)= \begin{matrix} e^{-\gamma t}e^{-i\omega_0 t} & \text{for } t \geq 0 \\ 0 & \text{for } t < 0 \end{matrix}$$

$$F(\omega)=\int_0^{\infty} e^{-\gamma t - i\omega_0 t}e^{i\omega t}\,dt = \left.\frac{e^{(-\gamma+i(\omega-\omega_0))t}}{-\gamma+i(\omega-\omega_0)}\right|_0^{\infty} = \frac{1}{\gamma-i(\omega-\omega_0)}$$

Complex Lorentzian

Fermi's golden rule generalized

- To account for the transition lineshape:

$$W_{12}(\nu) = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \rho_\nu \,\delta(\nu-\nu_0) \rightarrow \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{21}|^2 \rho_\nu \,g(\nu-\nu_0)$$

- Example: narrow linewidth laser incident on atom

$$\rho_\nu = \frac{n}{c} I\,\delta(\nu-\nu_L)$$

- Total transition rate:

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}|\mu_{12}|^2 \frac{n}{c} I\,\delta(\nu-\nu_L)\,g(\nu-\nu_0)\,d\nu$$

$$W_{12}(\nu_L) = \frac{2\pi^2}{3n\varepsilon_0 c h^2}|\mu_{12}|^2 I\,g(\nu_L-\nu_0)$$

Cross sections

- It is inconvenient to carry around all these constants and to use the dipole moments
  - Use values that connect to what we can measure
- Consider a beam passing through a gas of atoms with number density N_t (atoms/unit volume)
- Power absorbed/unit volume: $$\frac{dP_a}{dV} = W_{12} N_t h\nu$$
- Photon flux (photons/area/sec) $$F = \frac{I}{h\nu}$$
- Power in beam: $$P = I\,A = h\nu\,F\,A$$
- Evolution of flux: $$\frac{dF}{dz} = \frac{1}{h\nu}\frac{1}{A}\frac{dP}{dz} = -\frac{1}{h\nu}\frac{dP_a}{dV} = -W_{12} N_t$$

Cross sections

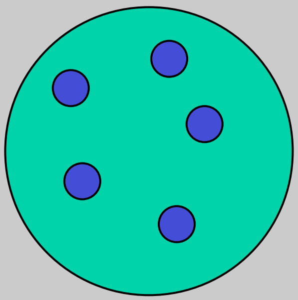
- Flux decreases as beam propagates in medium

$$\frac{dF}{dz} = -W_{12} N_t$$

- Define total absorption cross-section: $\sigma_{12} = \frac{W_{12}}{F}$

- So that: $\frac{dF}{dz} = -N_t \sigma_{12} \rightarrow F(z) = F_0 e^{-N_t \sigma_{12} z}$

- Physically, the cross-section is an effective area of the atom. In a low density gas, the beam of photons sees a collection of spheres:



$$\frac{dF}{F} = -N_t A dz \frac{\sigma_{12}}{A}$$

Frequency-dependent cross section

- Total cross section is obtained by integrating over lineshape (*h* for homogeneous):

$$\sigma_{12} = \int \sigma_h(\nu)\, d\nu$$

- Suppose we have a narrowband laser beam with a frequency that we can tune

$$W_{12}(\nu_L) = \frac{2\pi^2}{3n\varepsilon_0 c h^2} |\mu_{12}|^2 I\, g(\nu_L - \nu_0)$$

$$\sigma_h(\nu_L) = \frac{W_{12}(\nu_L)}{F} = \frac{W_{12}(\nu_L)}{I / h\nu_L} = \frac{h\nu_L}{I} \frac{2\pi^2}{3n\varepsilon_0 c h^2} |\mu_{12}|^2 I\, g(\nu_L - \nu_0)$$

$$\sigma_h(\nu_L) = \frac{2\pi^2}{3n\varepsilon_0 c h} |\mu_{12}|^2 \nu_L\, g(\nu_L - \nu_0)$$