Interaction of light with atoms

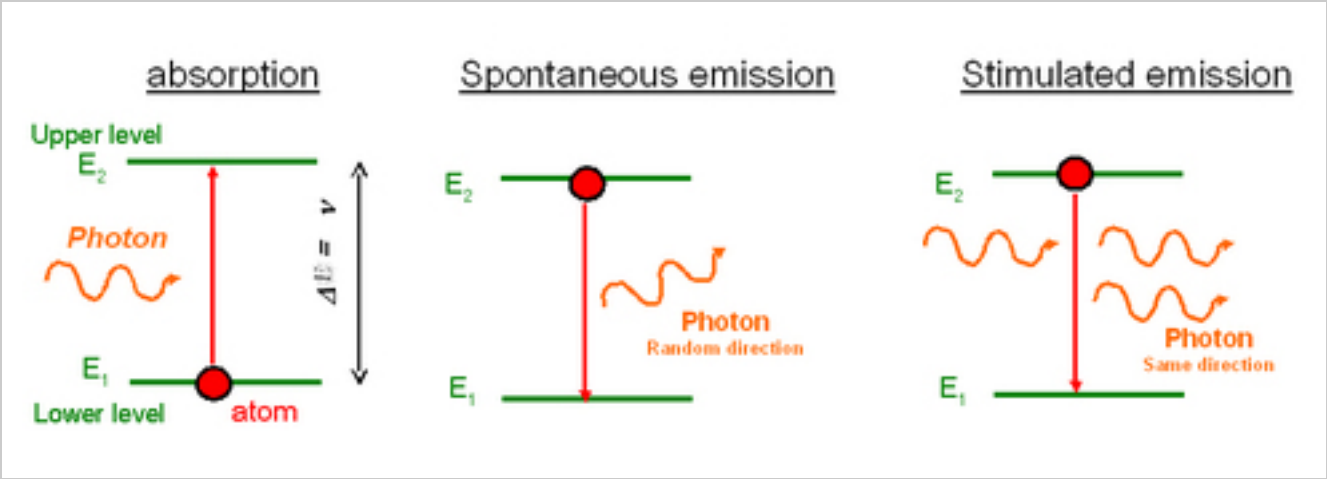
QM estimation of dipole radiation and lifetime

Summary of time-dependent perturbation theory approach

Reading: Svelto 2.3-2.4

Interaction of light with a 2-level system

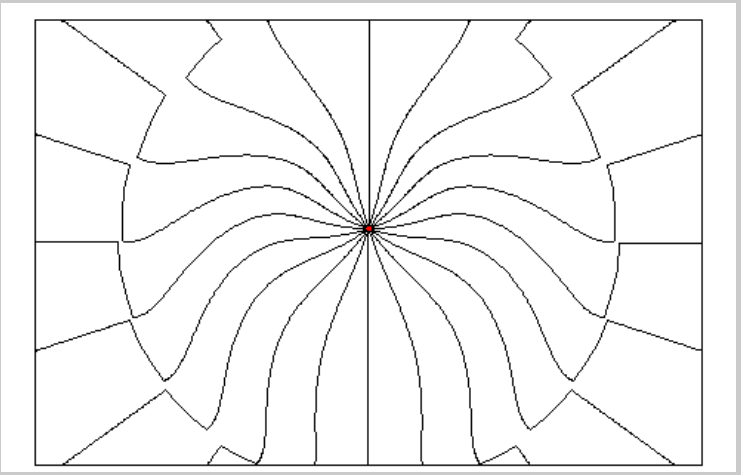
- Three allowed processes:



  - Note photon energy matches transition energy
  - All three process are related in the quantum picture
- First look at spontaneous emission: how do we get emission from a stationary state?

Radiation from accelerating charge

- An accelerating charge “shakes” the field lines, creating radiating EM waves.



See link to physlet animation of radiation field lines from an oscillating charge:

http://www.compadre.org/Physlets/optics/prob32_6.cfm

- Larmor formula for radiated power:

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2 a^2}{c^3} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2 \ddot{x}^2}{c^3} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{\ddot{p}^2}{c^3}$$

Dipole:

$$p(t) = -e\,x(t)$$

  - Antennas, bremsstrahlung, cyclotron radiation…

Radiation from an oscillating charge

- Larmor formula for radiated power:

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2\ddot{x}^2}{c^3} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{\ddot{p}^2}{c^3}$$

  - If the charge is moving as $x(t) = x_0 \cos\omega t$
  - The dipole is $p(t) = -e\,x_0 \cos\omega t$
  - Then the radiated power is

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2\ddot{x}^2(t)}{c^3} = -\frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2}{c^3}\omega^4 x_0^2 \cos^2\omega t = -\frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2\omega^4}{c^3}p^2(t)$$

  - Power is proportional to E^2, so radiated field is proportional to p(t)

- Charge distribution must oscillate to radiate
- Applied field induces oscillating dipoles, which re-radiate the field.

QM atomic transitions

We'll take an approach to understanding transitions from the quantum perspective

- An isolated atom in a pure energy eigenstate is in a *stationary* state: $\psi_n(\mathbf{r},t) = u_n(\mathbf{r})e^{-E_n t/\hbar}$
  - There is time dependence to the phase, but the amplitude remains constant. So, no radiation, no transitions.
- An applied EM field of the right frequency can induce a mixture of two states:

  $\psi_1(\mathbf{r},t) = u_1(\mathbf{r})e^{-E_1 t/\hbar}$ $\psi_2(\mathbf{r},t) = u_2(\mathbf{r})e^{-E_2 t/\hbar}$

  - Superposition: $\psi(\mathbf{r},t) = a_1(t)\psi_1(\mathbf{r},t) + a_2(t)\psi_2(\mathbf{r},t)$
  - w/ normalization: $|a_1(t)|^2 + |a_2(t)|^2 = 1$

QM charge distribution

- The electron is not localized in QM.
- The *charge* density can be calculated from ψ:

$$\rho(\mathbf{r},t) = -e\left|\psi(\mathbf{r},t)\right|^2$$

- For a stationary state:

$$\rho(\mathbf{r},t) = -e\left|\psi_n(\mathbf{r},t)\right|^2 = -e\left|u_n(\mathbf{r})e^{-E_n t/\hbar}\right|^2 = -e\left|u_n(\mathbf{r})\right|^2$$

  - No time dependence, charge is not moving!

- For a superposition state:

$$\rho(\mathbf{r},t) = -e\left|\psi(\mathbf{r},t)\right|^2 = -e\left|a_1\psi_1 + a_2\psi_2\right|^2$$

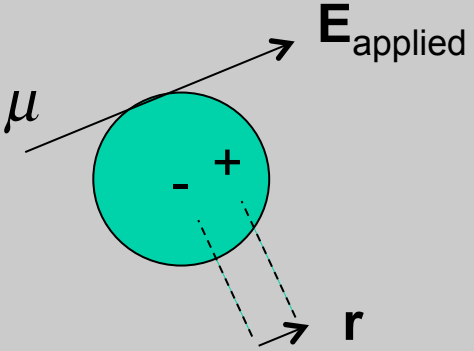
$$= -e\left(\left|a_1\psi_1\right|^2 + \left|a_2\psi_2\right|^2 + a_1 a_2{}^{*}\psi_1\psi_2{}^{*} + a_1{}^{*}a_2\psi_1{}^{*}\psi_2\right)$$

  - Cross terms will lead to time dependence in the charge.

QM dipole moment calculation

- The nucleus is localized, but the electron charge is spread over a probability distribution.
- The effective position is calculated like the center of mass, so dipole moment is:

$$\mu(t) = -e\int \mathbf{r}\,|\psi(\mathbf{r},t)|^2\,dV \qquad \mathbf{p} = q\,\mathbf{r} = \mu$$



  - Note displacement r is in the direction of E

$$\mu(t) = -e\left(\begin{array}{l}\int \mathbf{r}\,|a_1\psi_1|^2\,dV + \int \mathbf{r}\,|a_2\psi_2|^2\,dV \\ +\int a_1 a_2^{*}\,\mathbf{r}\,\psi_1\psi_2^{*}\,dV + \int a_1^{*} a_2\,\mathbf{r}\,\psi_1^{*}\psi_2\,dV\end{array}\right)$$

  - Terms in red go to zero by parity: $|\psi_n(\mathbf{r})|^2$ is even

Time dependent dipole moment

- The *cross* terms (which are like interference terms in optics), lead to time dependent oscillation:

$$\mu_{osc}(t) = -e\left(a_1 a_2^{*}\int \mathbf{r}\psi_1\psi_2^{*}\,dV + a_1^{*}a_2\int \mathbf{r}\psi_1^{*}\psi_2\,dV\right)$$

$$= -e\left(a_1 a_2^{*}\int \mathbf{r}\,u_1(\mathbf{r})u_2^{*}(\mathbf{r})e^{+i(E_2-E_1)t/\hbar}\,dV + a_1^{*}a_2\int \mathbf{r}\,u_1^{*}(\mathbf{r})u_2(\mathbf{r})e^{-i(E_2-E_1)t/\hbar}\,dV\right)$$

  - Oscillation frequency: $\omega_{21} = (E_2 - E_1)/\hbar$

$$\mu_{osc}(t) = a_1 a_2^{*}\mu_{21}e^{i\omega_{21}t} + a_1^{*}a_2\mu_{12}e^{-i\omega_{21}t} = \mathrm{Re}\left[2a_1 a_2^{*}\mu_{21}e^{i\omega_{21}t}\right]$$

$$\mu_{21} = \int u_1(\mathbf{r})(-e\mathbf{r})u_2^{*}(\mathbf{r})\,dV$$ Dipole "matrix element"

- μ_{21} is the part that depends on the atomic structure, independent of the populations.
- This is a vector: the direction of **r** is along the **E**-field direction,
- The atom or molecule may have any orientation to this.

QM dipole radiated power

- Use classical Larmor expression to estimate the radiated power from this oscillating dipole.

$$\langle P_{rad} \rangle = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{e^2\langle \ddot{x}^2(t)\rangle}{c^3} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{1}{c^3}\int \ddot{\mu}^2(t)\,dt$$

Note: μ = p

Integrate over one period

$$\mu_{osc}(t) = a_1 a_2^{*}\mu_{21}e^{i\omega_{21}t} + a_1^{*}a_2\mu_{12}e^{-i\omega_{21}t}$$

$$\ddot{\mu}_{osc}(t) = \omega_{21}^{2}\left(a_1 a_2^{*}\mu_{21}e^{i\omega_{21}t} + a_1^{*}a_2\mu_{12}e^{-i\omega_{21}t}\right)$$

$$\ddot{\mu}_{osc}^{2}(t) = \omega_{21}^{4}\left(\left(a_1 a_2^{*}\mu_{21}e^{i\omega_{21}t}\right)^2 + \left(a_1^{*}a_2\mu_{12}e^{-i\omega_{21}t}\right)^2 + 2|a_1|^2|a_2|^2|\mu_{21}|^2\right)$$

$$\langle \ddot{\mu}_{osc}^{2} \rangle = \omega_{21}^{4}\,2|a_1|^2|a_2|^2|\mu_{21}|^2$$

Let $|\mu_{21}| \rightarrow \mu_{21}$

$$P_{rad} = \frac{1}{4\pi\varepsilon_0}\frac{2}{3}\frac{1}{c^3}\omega_{21}^{4}\mu_{21}^{2}\,2|a_1|^2|a_2|^2$$

QM dipole radiation: rate of decay

- Simplify the cycle-averaged radiated power

$$\langle P_{rad} \rangle = \frac{\omega_{21}^{\ 4} \mu_{21}^{\ 2}}{3\pi\varepsilon_0 c^3} |a_1|^2 |a_2|^2 = \hbar\omega_{21} \frac{\omega_{21}^{\ 3} \mu_{21}^{\ 2}}{3\hbar\pi\varepsilon_0 c^3} |a_1|^2 |a_2|^2$$

Photon energy

Rate (frequency)

- If we assume that the excitation probability of the upper level is small, then

$$|a_1|^2 = 1 - |a_2|^2 \approx 1$$

- We can then deduce the change in upper level population:

$$\frac{dE}{dt} = -\langle P_{rad} \rangle = \hbar\omega_{21} \frac{d}{dt} |a_2(t)|^2$$

Define:

$$\tau_{sp} = \frac{1}{A_{21}} = \frac{3\pi\hbar\varepsilon_0 c^3}{\omega_{21}^{\ 3} \mu_{21}^{\ 2}}$$

$$\frac{d}{dt} |a_2(t)|^2 \approx -\frac{1}{\tau_{sp}} |a_2(t)|^2 \rightarrow |a_2(t)|^2 \approx |a_2(0)|^2 \exp\left[-t/\tau_{sp}\right]$$

This connects the spontaneous emission rate to a quantum calculation of the dipole moment.

Selection rules

- In Dirac notation, the dipole matrix element is:

$$\mu_{21} = \int u_1(\mathbf{r})(-e\mathbf{r})u_2^*(\mathbf{r})dV = \langle 2|-e\mathbf{r}|1\rangle$$

- Working with the symmetries of wavefunctions leads to selection rules about which transitions can take place.
  - Parity: r is odd, so u_1 must be opposite parity of u_2
  - Angular momentum: $\Delta l = \pm 1$. Photon has1 unit of ang. mom.
    $\Delta m = 0, \pm 1$
- Exceptions:
  - Transition might take place under other moments:
    - Magnetic dipole, electric quadrupole, etc.
    - Leads to longer lifetimes.
  - States might not be “pure”, mixture of eigenstates
    - External or internal perturbations

HeNe laser transitions

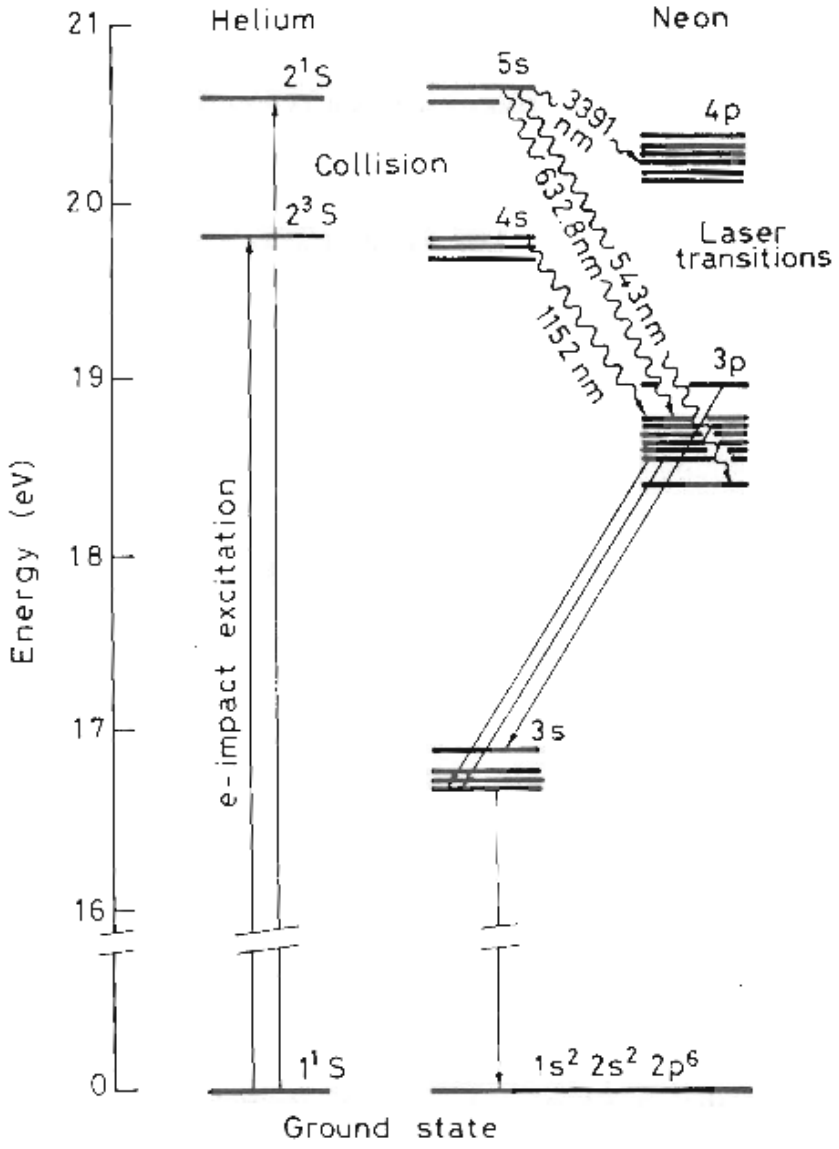


FIG. 10.1. Relevant energy levels of the He-Ne laser.

Transition	Wavelength [nm]	A_{ik} [10^8 s^{-1}]	Gain [%/m]	
3s2→2p1	730.5 ③	0,00255	1,2	
3s2→2p2	640.1 ①	0,0139	4,3	
3s2→2p3	635.2 ①	0,00345	1,0	
3s2→2p4	632.8 ①	0,0339	10,0	→ main red line
3s2→2p5	629.4 ①	0,00639	1,9	
3s2→2p6	611.8 ①	0,00226	1,7	→ orange line
3s2→2p7	604.6	0,00200	0,6	
3s2→2p8	593.9	0,00255	0,5	→ yellow line
3s2→2p9	★			
3s2→2p10	543.3	0,00283	0,52	
2s2→2p1	1523.1 ②			
2s2→2p2	1177.0 ③			
2s2→2p3	1160.5			
2s2→2p4	1152.6 ③			
2s2→2p5	1141.2 ③			
2s2→2p6	1084.7 ③			
2s2→2p7	1062.3			
2s2→2p8	1029.8			
2s2→2p9	★			
2s2→2p10	886.5			
2s3→2p2	1198.8 ③			
2s3→2p5	1161.7 ③			
2s3→2p7	1080.1 ③			

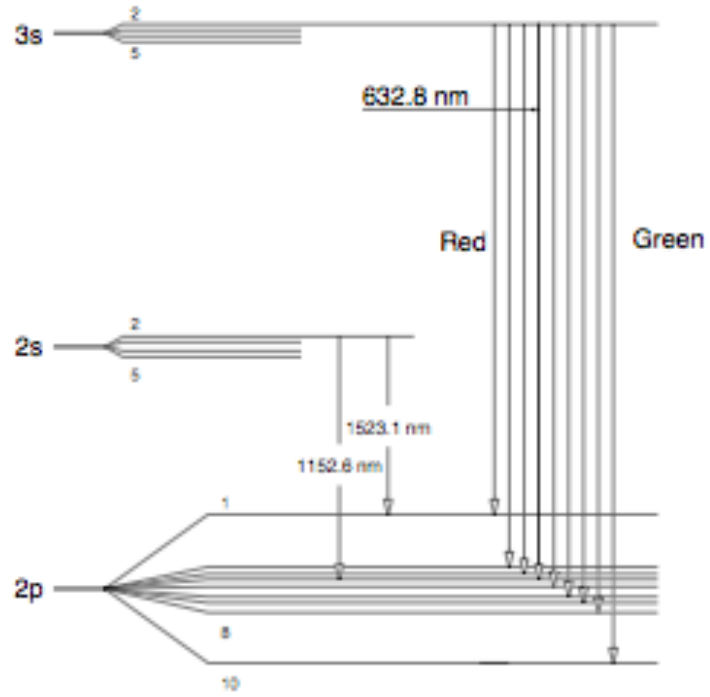


Fig. 3: The most important laser transitions in the neon system

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:

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

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

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

- Result: "Fermi's Golden Rule"

$$W_{12}(\nu) = \frac{\pi^2}{3h^2}\left|\mu_{21}\right|^2 {E_0}^2 \delta(\nu - \nu_0)$$

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

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

Fermi's golden rule

- Express field^2 in terms of (total) energy density:

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

For other lineshape:

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

- When EM source varies in frequency, energy density btw v' and v'+dv' is $d\rho = \rho_{\nu'} d\nu'$
- So the contribution to the rate at v' is

$$dW_{12}(\nu') = \frac{2\pi^2}{3n^2\varepsilon_0 h^2}\left|\mu_{21}\right|^2 \rho_{\nu'}\, g(\nu-\nu_0)\, d\nu'$$

- Total rate is:

$$W_{12} = \int \frac{2\pi^2}{3n^2\varepsilon_0 h^2}\left|\mu_{21}\right|^2 \rho_{\nu'}\, g(\nu-\nu_0)\, d\nu'$$

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)

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

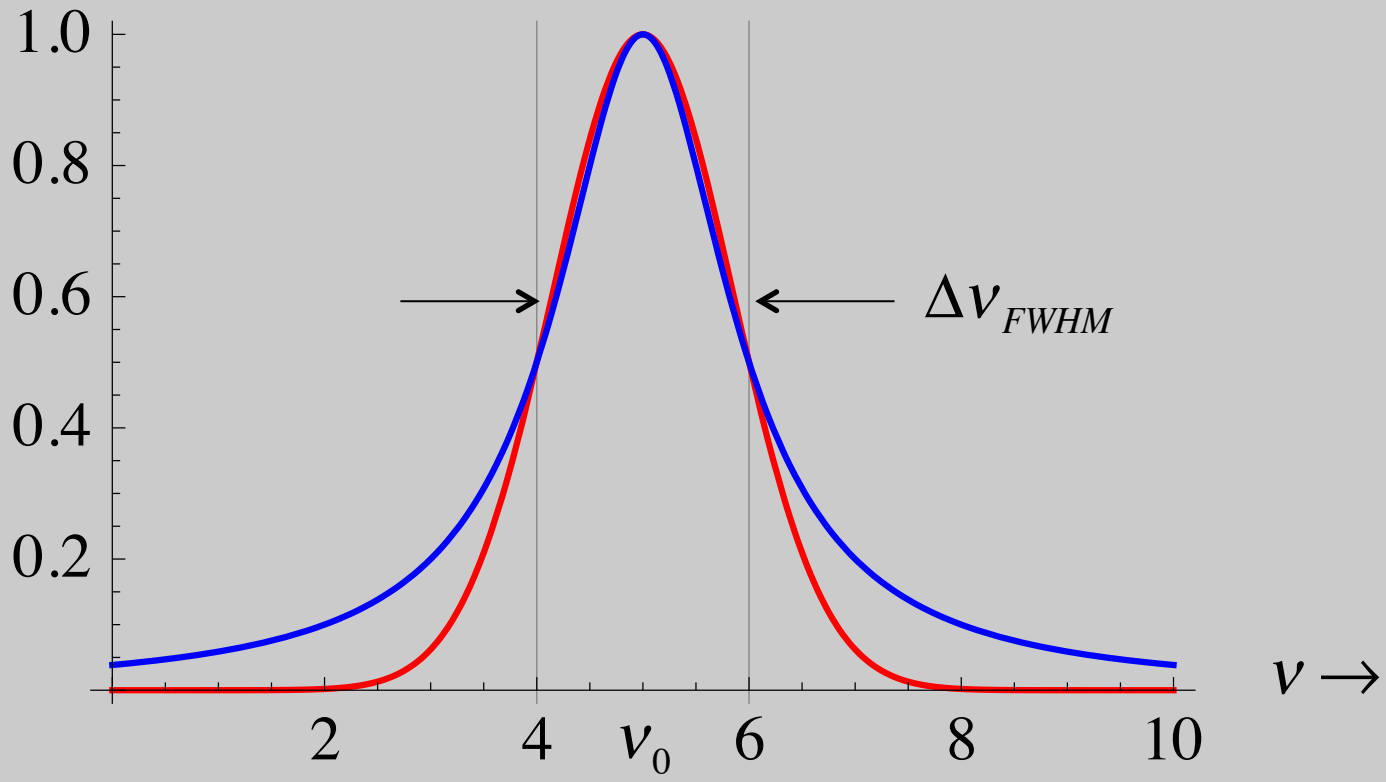
$\Delta\nu_0$ FWHM

- 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



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

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

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

Complex Lorentzian

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

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

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