

Interaction of light with atoms

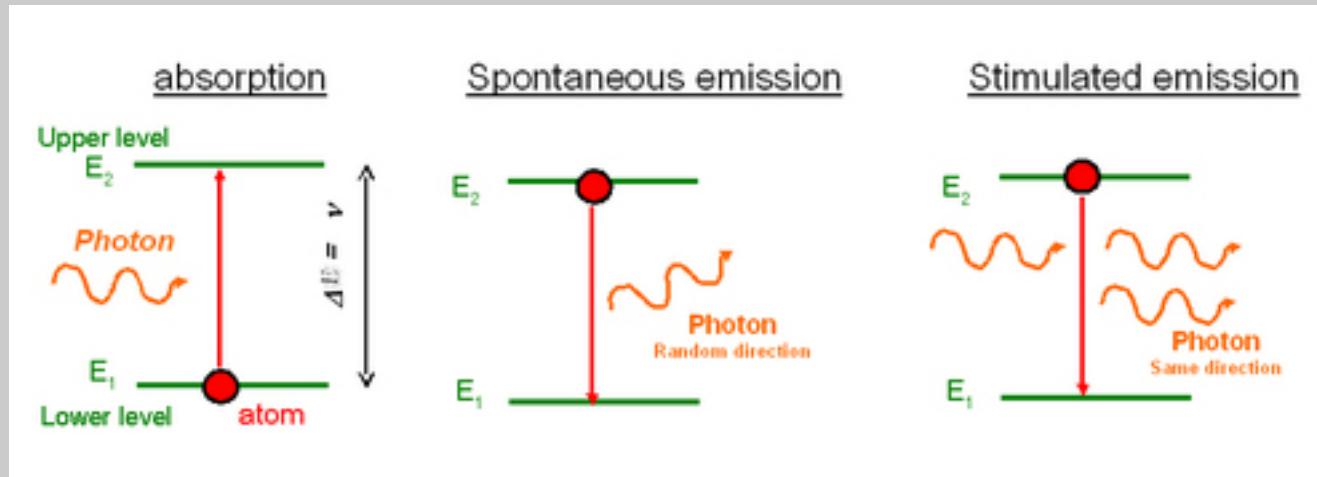
QM estimation of dipole radiation and lifetime

Summary of time-dependent perturbation theory approach

Reading: Svelto 2.3-2.4

Interaction of light with a 2-level system

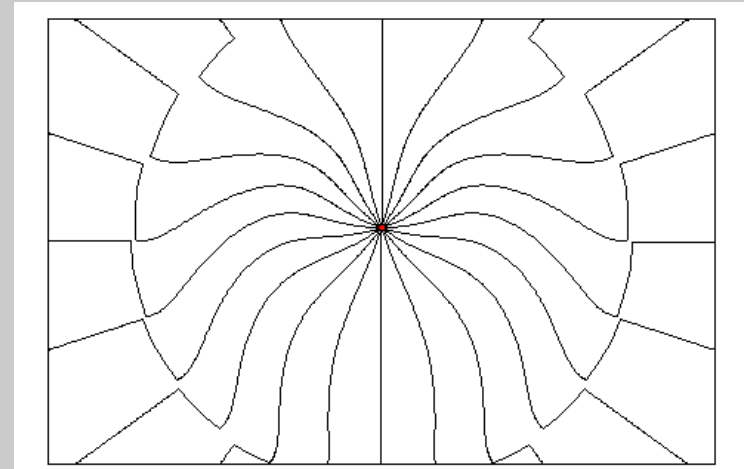
- Three allowed processes:



- Note photon energy matches transition energy
- All three processes 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:

$$P_{rad} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2 a^2}{c^3} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2 \ddot{x}^2}{c^3} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{\dot{p}^2}{c^3}$$

Dipole:

$$p(t) = -ex(t)$$

- Antennas, bremsstrahlung, cyclotron radiation...

Radiation from an oscillating charge

- Larmor formula for radiated power:

$$P_{rad} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2 \ddot{x}^2}{c^3} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{\ddot{p}^2}{c^3}$$

- 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

$$P_{rad} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2 \ddot{x}^2(t)}{c^3} = -\frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2}{c^3} \omega^4 x_0^2 \cos^2 \omega t = -\frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2 \omega^4}{c^3} p^2(t)$$

- 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:

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

- 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 :

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

- For a stationary state:

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

- No time dependence, charge is not moving!

- For a superposition state:

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

$$= -e\left(|a_1\psi_1|^2 + |a_2\psi_2|^2 + a_1a_2^*\psi_1\psi_2^* + a_1^*a_2\psi_1^*\psi_2\right)$$

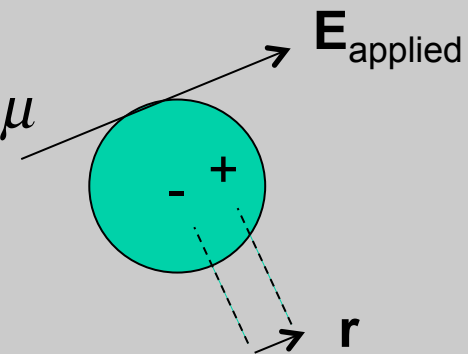
- Cross terms will lead to time dependence in the charge.

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:

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

- Note displacement r is in the direction of E



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

- 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:

$$\begin{aligned}\mu_{osc}(t) &= -e \left(a_1 a_2^* \int \mathbf{r} \psi_1 \psi_2^* dV + a_1^* a_2 \int \mathbf{r} \psi_1^* \psi_2 dV \right) \\ &= -e \left(a_1 a_2^* \int \mathbf{r} u_1(\mathbf{r}) u_2^*(\mathbf{r}) e^{+i(E_2 - E_1)t/\hbar} dV + a_1^* a_2 \int u_1^*(\mathbf{r}) u_2(\mathbf{r}) e^{-i(E_2 - E_1)t/\hbar} dV \right)\end{aligned}$$

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

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

$$\mu_{21} = \int u_1(\mathbf{r}) (-e\mathbf{r}) u_2^*(\mathbf{r}) dV \quad \text{Dipole “matrix element”}$$

- μ_{21} is the part that depends on the atomic structure, independent of the populations.
- This is a vector: the direction of \mathbf{r} is along the \mathbf{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.

$$\langle P_{rad} \rangle = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{e^2 \langle \ddot{x}^2(t) \rangle}{c^3} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{1}{c^3} \int \ddot{\mu}^2(t) dt$$

Note: $\mu = p$

Integrate over one period

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

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

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

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

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

$$P_{rad} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{1}{c^3} e^2 \omega_{21}^4 \mu_{21}^2 2|a_1|^2 |a_2|^2$$

QM dipole radiation: rate of decay

- Simplify the cycle-averaged radiated power

$$\langle P_{rad} \rangle = \frac{e^2 \omega_{21}^4 \mu_{21}^2}{3\pi\epsilon_0 c^3} |a_1|^2 |a_2|^2 = \hbar\omega_{21} \frac{e^2 \omega_{21}^3 \mu_{21}^2}{3\hbar\pi\epsilon_0 c^3} |a_1|^2 |a_2|^2$$

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:

$$\tau_{sp} = \frac{1}{A_{21}} = \frac{3\pi\hbar\epsilon_0 c^3}{e^2 \omega_{21}^3 \mu_{21}^2}$$

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

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 has 1 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

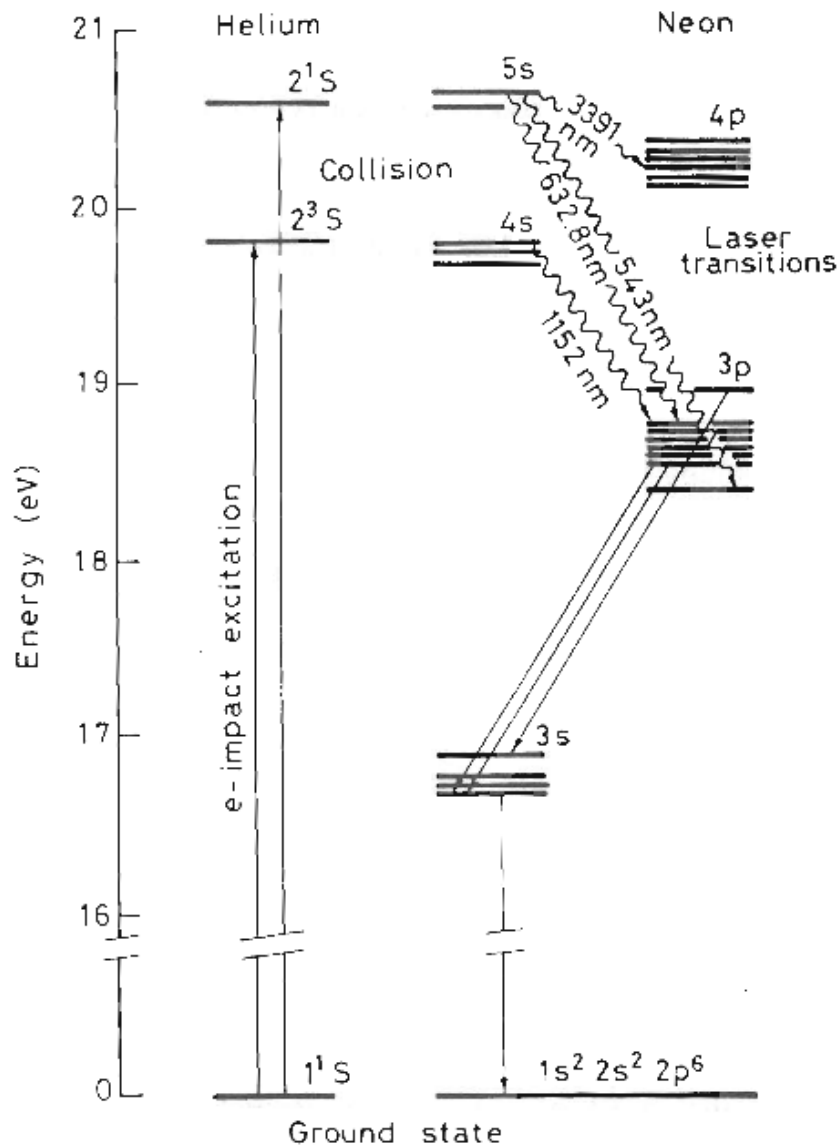


FIG. 10.1. Relevant energy levels of the He-Ne laser.

Transition	Wavelength [nm]	A_{ik} [10^8 s^{-1}]	Gain [%/m]
3s ₂ →2p ₁	730.5 ①	0,00255	1,2
3s ₂ →2p ₂	640.1 ①	0,0139	4,3
3s ₂ →2p ₃	635.2 ①	0,00345	1,0
3s ₂ →2p ₄	632.8 ①	0,0339	10,0
3s ₂ →2p ₅	629.4 ①	0,00639	1,9
3s ₂ →2p ₆	611.8 ①	0,00226	1,7
3s ₂ →2p ₇	604.6	0,00200	0,6
3s ₂ →2p ₈	593.9	0,00255	0,5
3s ₂ →2p ₉	★		
3s ₂ →2p ₁₀	543.3	0,00283	0,52
2s ₂ →2p ₁	1523.1 ②		
2s ₂ →2p ₂	1177.0 ③		
2s ₂ →2p ₃	1160.5		
2s ₂ →2p ₄	1152.6 ①		
2s ₂ →2p ₅	1141.2 ③		
2s ₂ →2p ₆	1084.7 ③		
2s ₂ →2p ₇	1062.3		
2s ₂ →2p ₈	1029.8		
2s ₂ →2p ₉	★		
2s ₂ →2p ₁₀	886.5		
2s ₃ →2p ₂	1198.8 ③		
2s ₃ →2p ₅	1161.7 ③		
2s ₃ →2p ₇	1080.1 ③		

→ main red line
 → orange line
 → yellow line

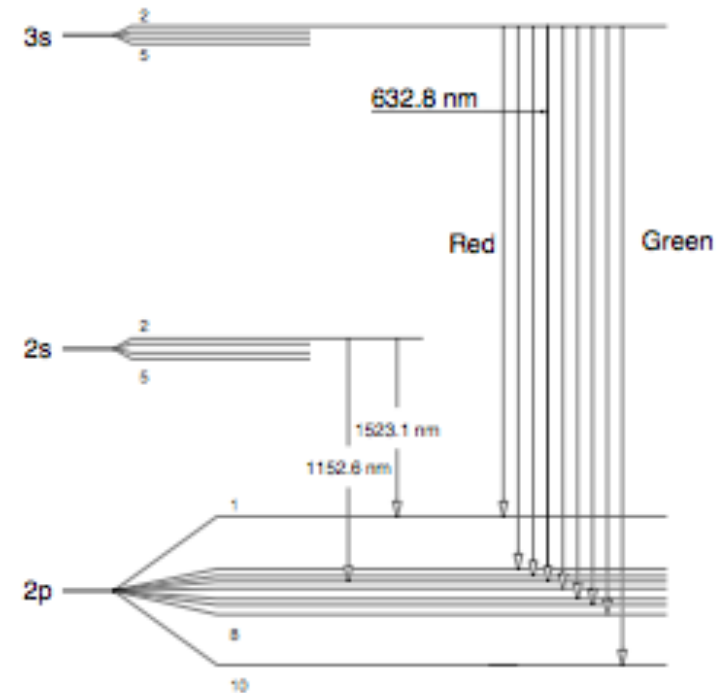


Fig. 3: The most important laser transitions in the neon system

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

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

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

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

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

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

Framing the QM calculation

- Time-dependent SE with external field

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

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

- 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:

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

- 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

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

- Result: “Fermi’s Golden Rule”

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

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

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

Fermi's golden rule

- Express field² in terms of (total) energy density:

$$\rho = \frac{1}{2} n^2 \epsilon_0 E_0^2$$

For other lineshape:

$$\rightarrow W_{12}(\nu) = \frac{2\pi^2}{3n^2 \epsilon_0 h^2} |\mu_{21}|^2 \rho \delta(\nu - \nu_0) = \frac{2\pi^2}{3n^2 \epsilon_0 h^2} |\mu_{21}|^2 \rho g(\nu - \nu_0)$$

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

$$dW_{12}(\nu') = \frac{2\pi^2}{3n^2 \epsilon_0 h^2} |\mu_{21}|^2 \rho_{\nu'} g(\nu - \nu_0) d\nu'$$

- Total rate is:

$$W_{12} = \int \frac{2\pi^2}{3n^2 \epsilon_0 h^2} |\mu_{21}|^2 \rho_{\nu'} g(\nu - \nu_0) d\nu'$$

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)

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

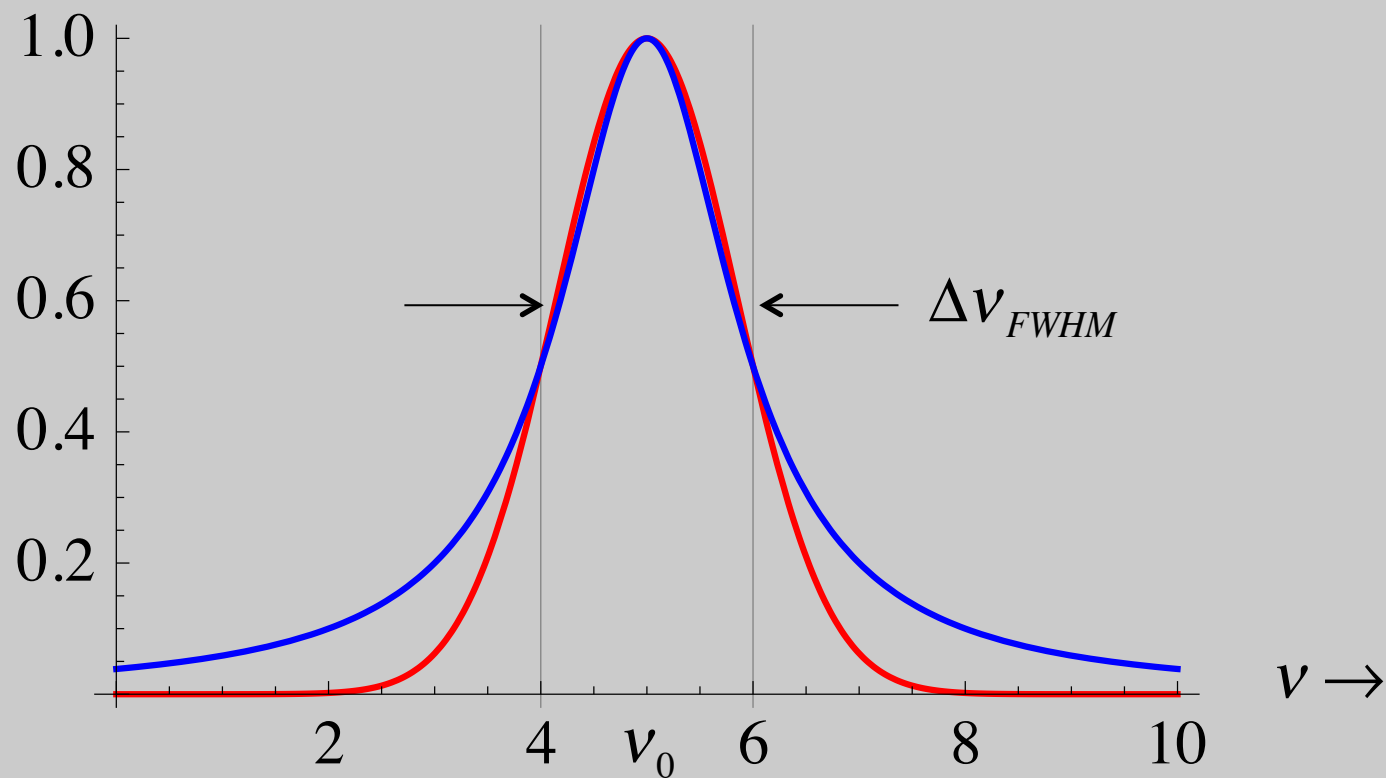
$\Delta\nu_0$ FWHM

- 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

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

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

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

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

- Convert ω to ν

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

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