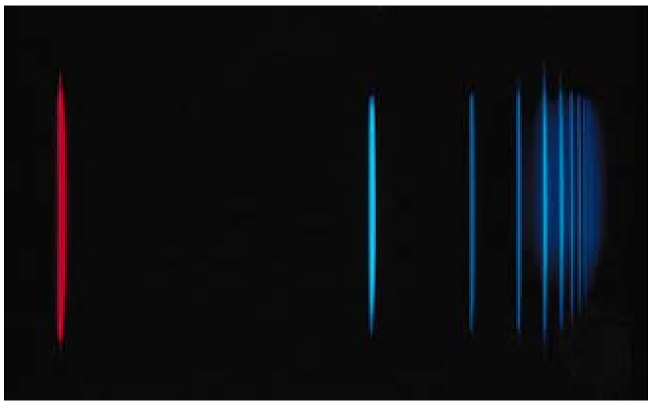
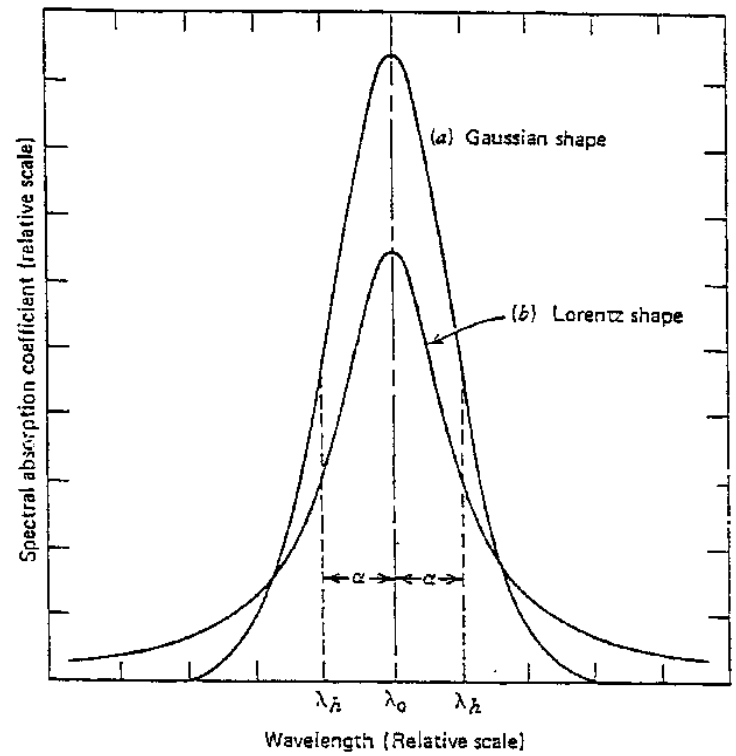
Line shapes





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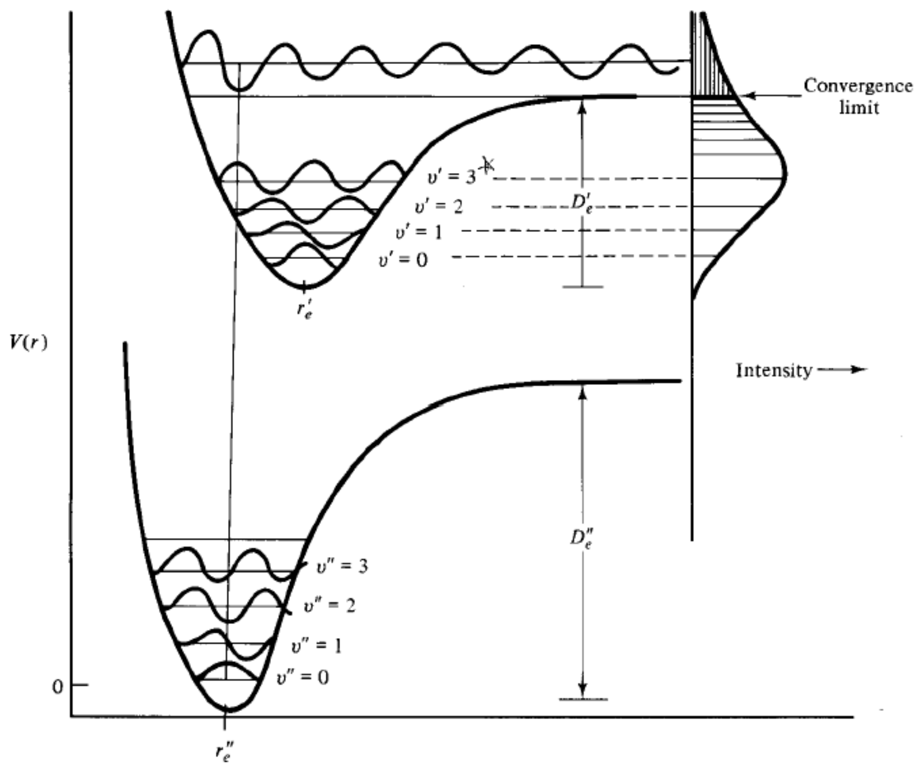
What determines the line width ?



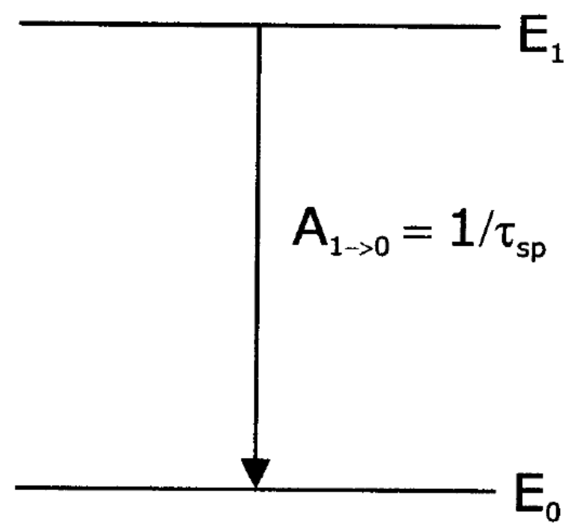


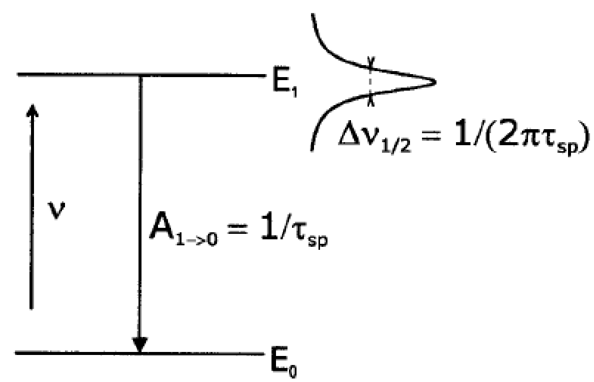
Figure 1.15: Spontaneous emission in a two-level system.

Line shapes: Homogeneous vs inhomogeneous

- Homogeneous line shape:
  - All molecules behave in the same way
  - Lorentz line shape
  - Examples are:
    - Pressure broadening — $\Delta\nu_{1/2} = bp$ b=10 MHz/Torr
    - Natural lifetime broadening — $\tau_{\rm sp} \equiv 1/A_{1\to 0}$ $\quad \tau_{\rm sp} = \dfrac{1}{\sum A_{n\to j}}$
    - Transit time broadening

Heissenberg's uncertainty principle:

$$\Delta E \Delta t \geq \hbar \qquad \text{or} \qquad \Delta\nu\Delta t \geq \frac{1}{2\pi}$$



Line shapes (cont): Homogeneous vs inhomogeneous

- Inhomogeneous line shape:
  - All molecules behave differently (distribution)
  - Gaussian line shape
  - Examples are:
    - Doppler broadening $\Delta\nu = \frac{v}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2}$
    - Power broadening $\Delta\nu \sim \frac{\mu_{10}E}{2\pi h} = \frac{\omega_R}{4\pi^2}$

Line shapes: Homogeneous vs inhomogeneous

- Homogeneous line shape:
  - All molecules behave in the same way
  - Lorentz line shape
  - Examples are:
    - Natural lifetime broadening $\tau_{\mathrm{sp}} \equiv 1/A_{1\to 0} \qquad \tau_{\mathrm{sp}} = \dfrac{1}{\sum A_{n\to j}}$
    - (Transit time broadening)
    - (Power broadening) $\Delta\nu \sim \dfrac{\mu_{10}E}{2\pi h} = \dfrac{\omega_{\mathrm{R}}}{4\pi^2}$

Heissenberg's uncertainty principle:

$$\Delta E \Delta t \geq \hbar \qquad \text{or} \qquad \Delta\nu\Delta t \geq \frac{1}{2\pi}$$

Lorentzian line shape function

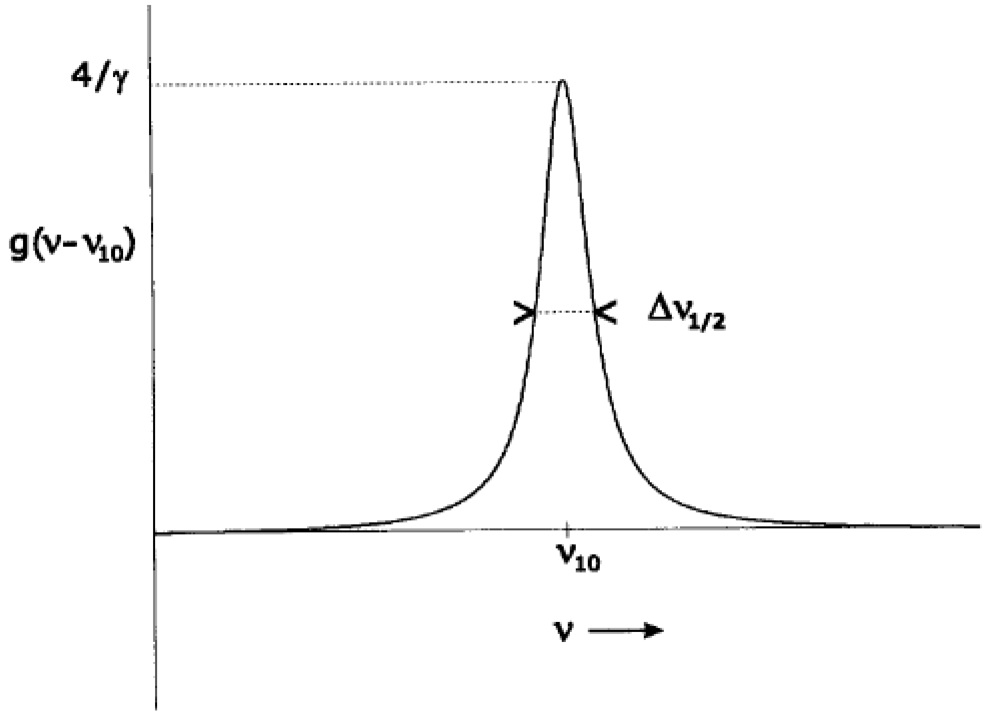
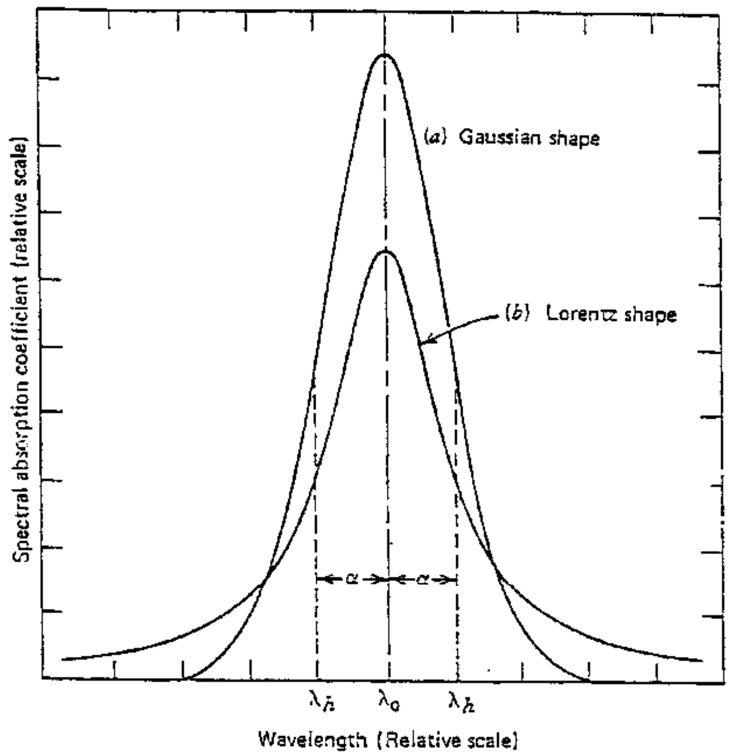


Figure 1.18: A normalized Lorentzian function.

$$g(\nu - \nu_0) = \frac{\Delta\nu_{1/2}/(2\pi)}{(\Delta\nu_{1/2}/2)^2 + (\nu - \nu_0)^2}$$

Gaussian lineshape function



$$g(\nu-\nu_0) = A \exp -[(\nu-\nu_0)^2 / (2\,\alpha^2)]$$

Voigt lineshape function

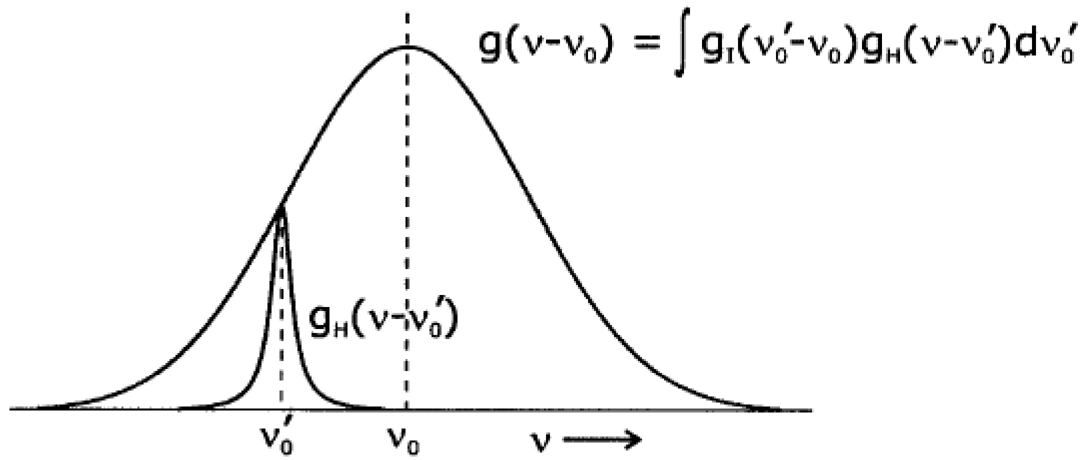


Figure 1.21: The Voigt lineshape is a convolution of an inhomogeneous Gaussian lineshape function with a homogeneous Lorentzian lineshape function.

http://scienceworld.wolfram.com/physics/topics/SpectralLineshapes.html

- At what pressure will the Doppler broadening (FWHM) equal the pressure broadening (FWHM) for a room temperature (20C) sample of CO gas for a pure rotational transition at 115 GHz, a vibrational-rotational transition at 2140 cm^{-1}, and an electronic transition at 1537 Å ? Use a “typical” pressure-broadening coefficient of 10 MHz/Torr in all three cases.

Example CO

	115 GHz	$2140 cm^{-1}$	1537 A
• Doppler	10^{-8} Hz	$5\ 10^{-3}\ cm^{-1}$	$0.15\ cm^{-1}$
• Pressure		15 Torr	450 Torr

- M = 28 amu
- T = 20 C
- b = 10 MHz $Torr^{-1}$ = $3.33\ 10^{-4}\ cm^{-1}\ Torr^{-1}$

- The absorption cross section of Mercury atoms is $3.3\ 10^{-14}$ cm^2 (measured at 253.65nm with a spectral resolution of 0.015nm). Your instrument is capable of detecting an optical density of 10^{-4}, and measures over a pathlength of 1 m. What Hg concentration is detectable ?
- A: $10^5 < x < 10^6$ molec m^{-3}
- B: $10^6 < x < 10^7$ molec m^{-3}
- C: $10^7 < x < 10^8$ molec m^{-3}
- D: $10^8 < x < 10^9$ molec m^{-3}
- E: $> 10^{10}$ molec m^{-3}