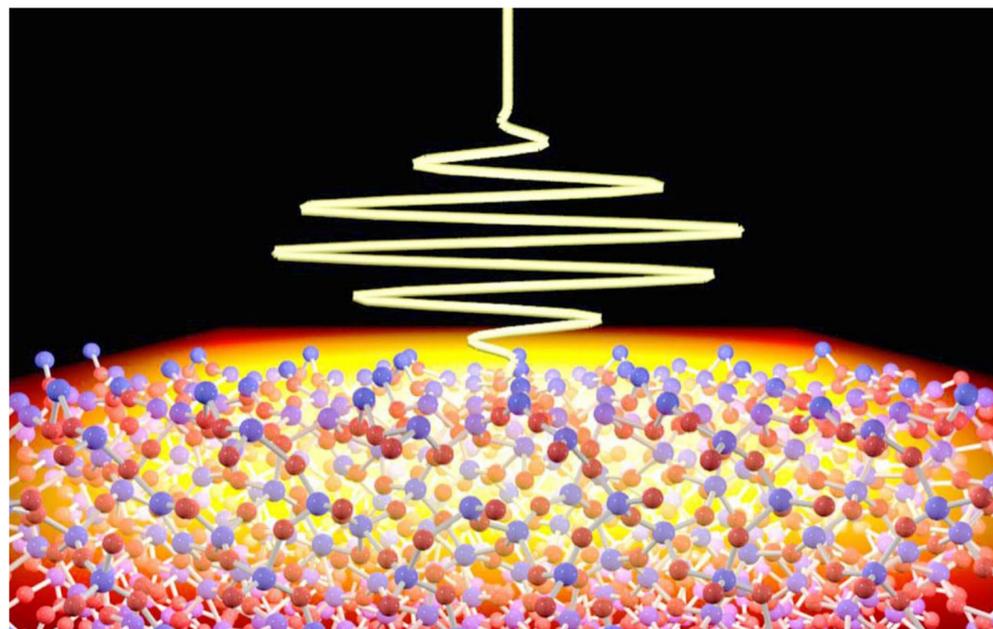


# **Theoretical basics of light-matter interactions and spontaneous emission**

**Laboratorio di Fisica della Materia Condensata, a.a. 2025/26**

# Atom-light interactions

- \* Laser light is generated by radiation emitted by atoms
- \* Spectroscopy measurements depend on the light absorbed and emitted by atoms, molecules, nanostructure, atoms in a crystal (electronic bands rather than levels)...
  - it is essential to look at the fundamental processes underlying **atom-light interactions**



# Fermi's golden rule

[see e.g. Bransden pp. 111-116]

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | \hat{V} | i \rangle|^2 \delta(E_f - E_i) \quad (\text{perturbative} \rightarrow \text{linear response})$$

$|i\rangle, |f\rangle$  : initial and final energy eigenstates that become coupled by perturbation

$\langle f | \hat{V} | i \rangle$  : matrix element of the perturbation, i.e. field-matter interaction

→ If the final discrete level is replaced by a continuum of states within a window  $[E_f, E_f + dE]$ , use the density of states  $\rho(E_f)$  instead of Dirac's delta

→ E.m. vacuum is also a perturbation!

# Physical principle, molecular case

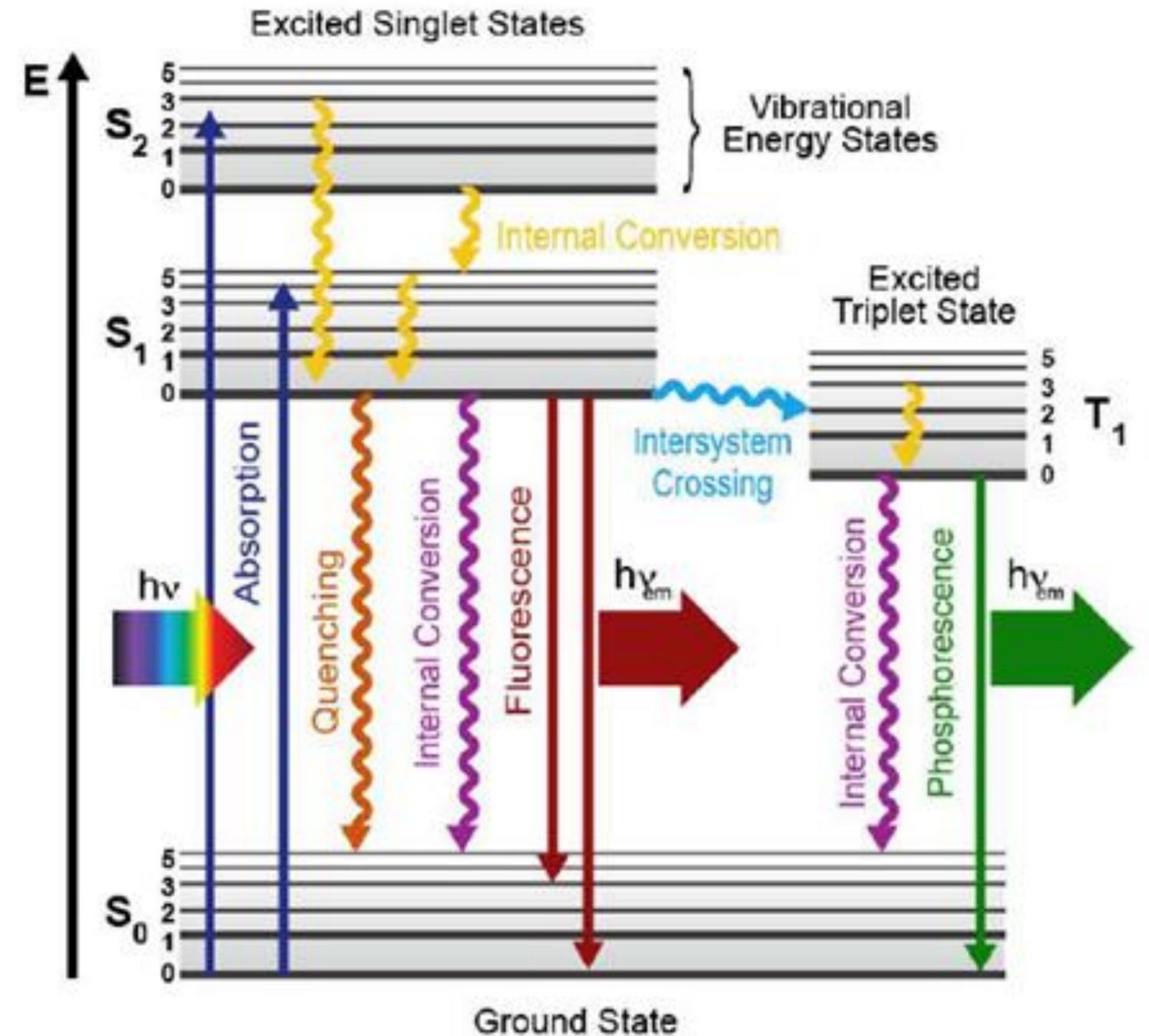
## Jablonski diagram

By stimulating the sample with a photon of sufficient energy ( $> E_{\text{gap}}$ ), we promote an electron into an excited state ( $\tau_{\text{abs}} \sim \text{fs}$ ).

The electron relaxes by internal conversion (non radiative,  $\tau_{\text{NR}} \sim 10 \text{ fs} - 10 \text{ ps}$ ) to reach the excited state with minimum energy (Kasha rule).

From there the electron can:

1. Keep relaxing non radiatively (energy dissipated as heat);
2. Decay to the ground state by emitting a photon (**luminescence**);
3. Reach an excited triplet state via *inter-system crossing* (ISC).

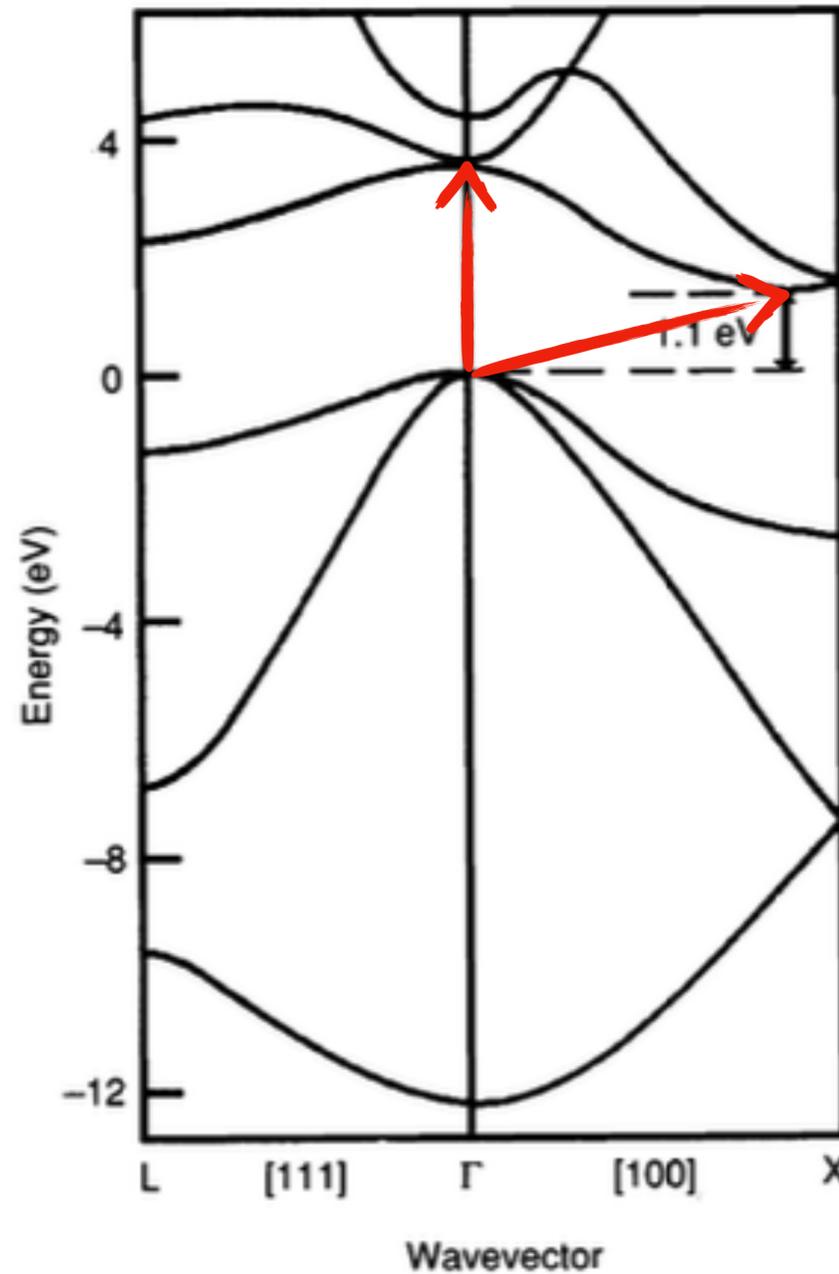


# Photoluminescence in solids

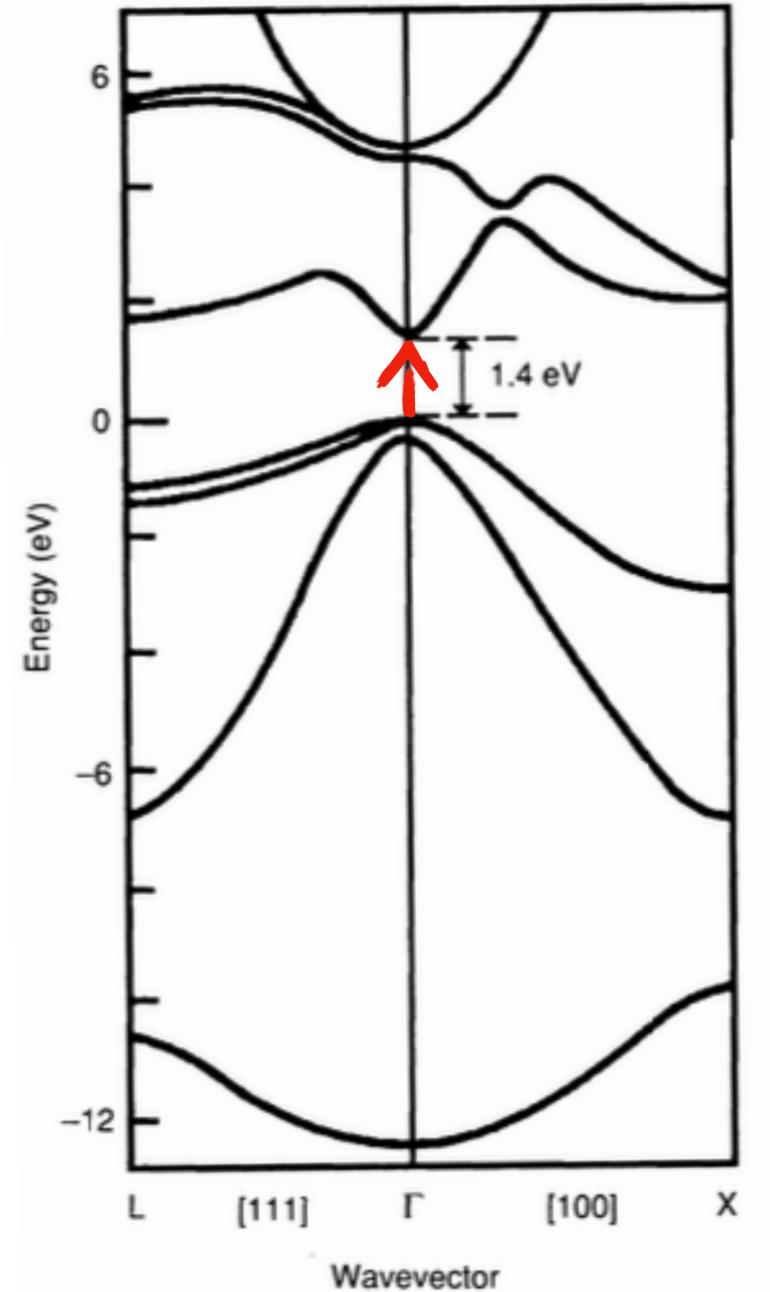
When atoms are arranged in a crystal, the discrete energy levels split into many separate levels forming continuous energy bands.

Optical excitation can promote electrons from the valence band into the conduction band, from which the system can decay radiatively through luminescence.

Luminescence spectra provide insights into the electronic structure.



Silicon

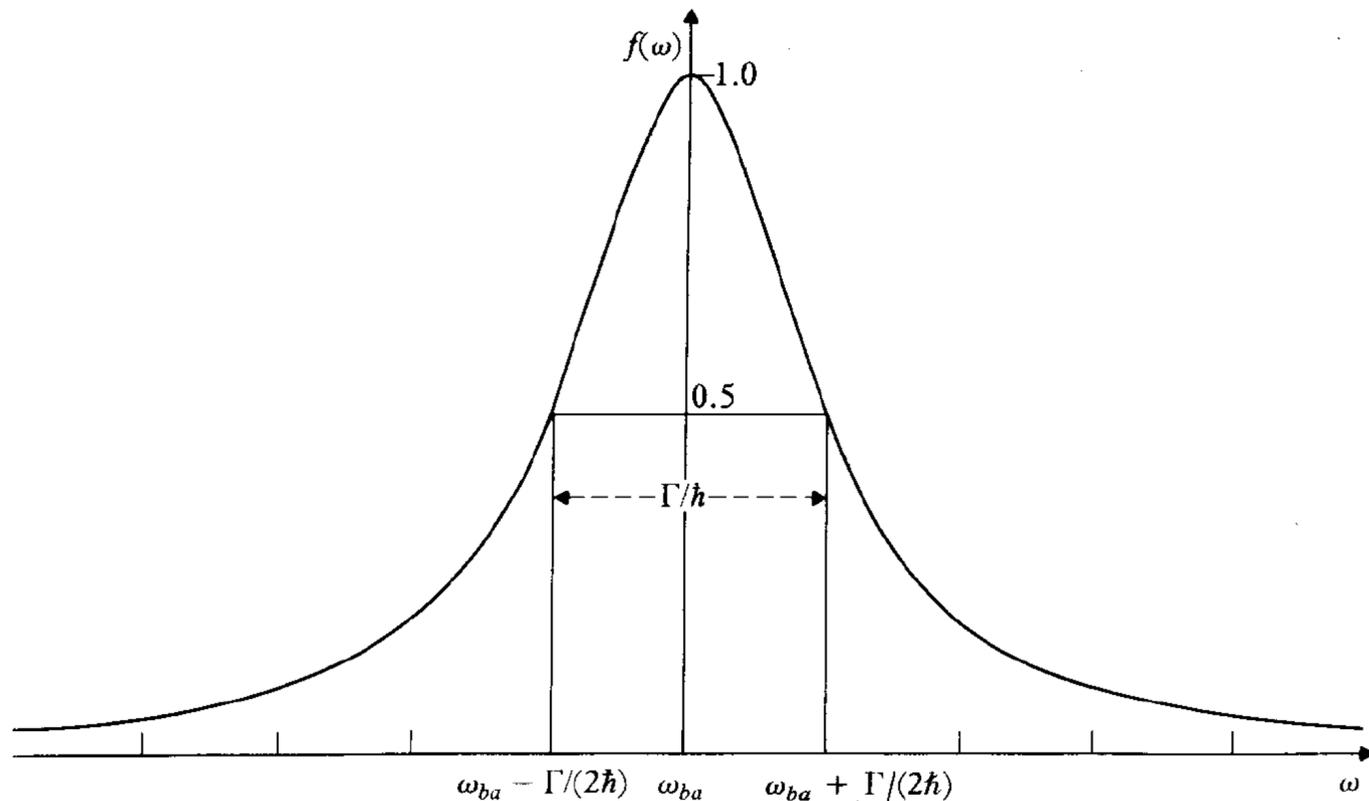


GaAs

[...whiteboard...]

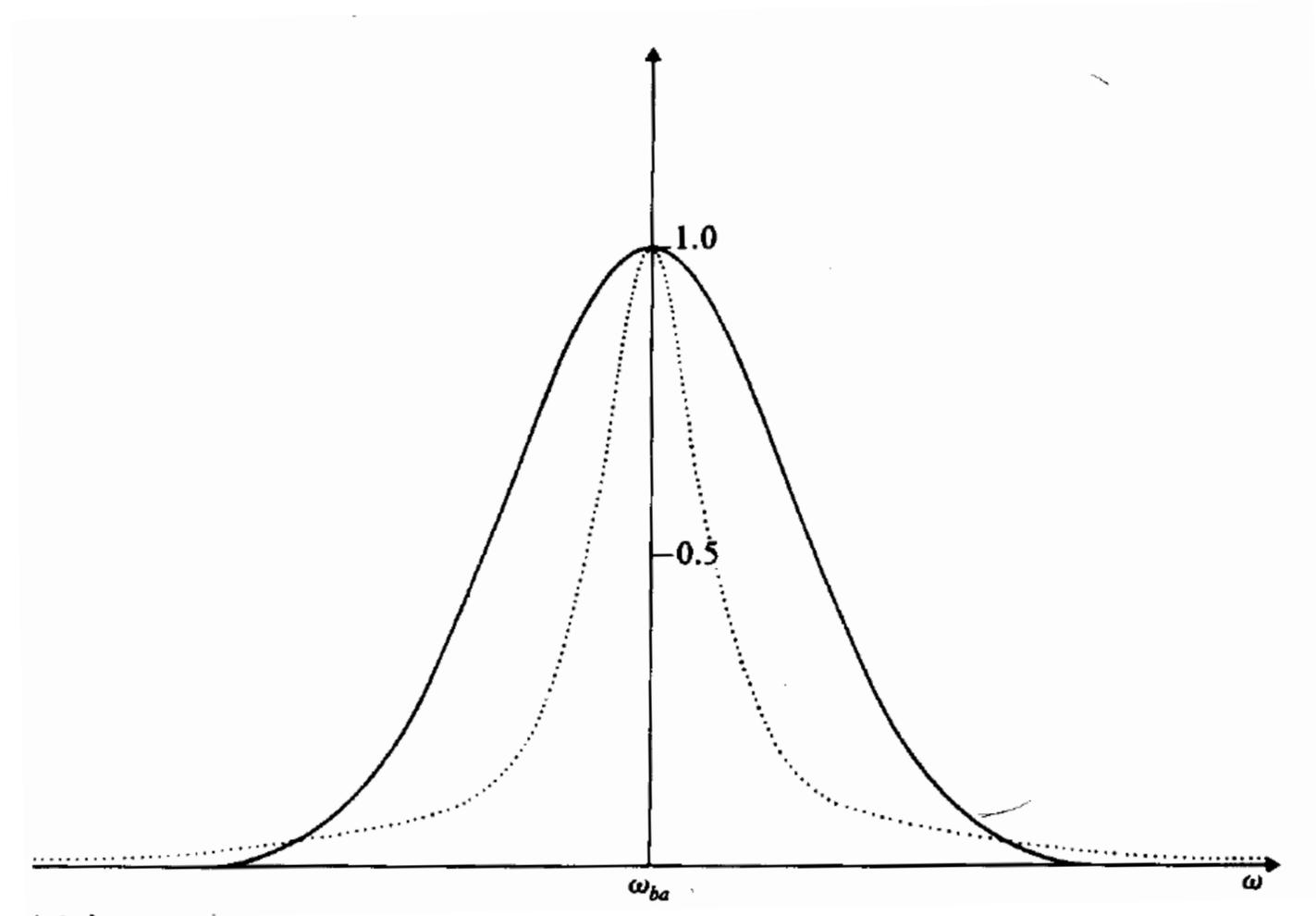
(see Brandsen & Joachain pp. 156-168, Section 4.1-4.3)

# Atomic line widths and shapes



Intrinsic broadening ( $\Gamma_{\text{nat}} \sim 1/\tau$ )

Lorentzian (homogeneous)



Doppler broadening ( $\Gamma_D \sim \sqrt{T}$ )

Gaussian (inhomogeneous)