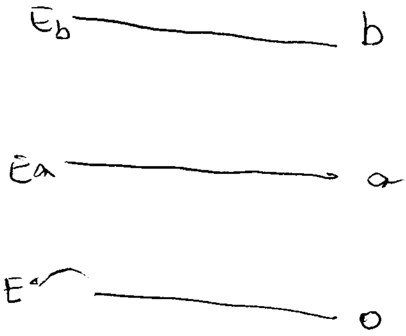
6- Line shapes and widths

Let us consider an atom in an external field of angular frequency ω, and assume that, apart from the gd. state, it supports the energy levels a and b



* Previous results (1st-order perturbation theory):

ω is sharply peaked at $\omega_{ba} = \frac{E_b - E_a}{\hbar}$

So that one-photon absorption from a to b, or one-photon emission from b to a may occur.

Due to the uncertainty relation, however, the spectral lines cannot be infinitely sharp.

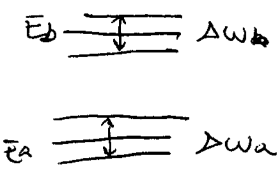
6.(a) Natural linewidth

An atomic level (except the gd state) decays with radiative lifetime τ. Hence, according to the uncertainty principle,

$$\tau \underbrace{\Delta\omega}_{\text{frequency width}} \sim \hbar \Rightarrow \Delta\omega \sim \frac{\hbar}{\tau}$$ is the natural linewidth of the level.

As far as the transition from b to a, or vice-versa, is concerned,

$$\Delta\omega \sim \underbrace{\overbrace{\frac{\hbar}{\tau_a}}^{\Delta\omega_a}}_{\text{natural linewidth of a}} + \underbrace{\overbrace{\frac{\hbar}{\tau_b}}^{\Delta\omega_b}}_{\text{natural linewidth of b}}$$



⊛ Computation of the natural linewidth

• <u>framework</u>: first-order perturbation theory

$$\cdot\ \Psi(\vec{r},t) = \sum_k c_k(t)\, \psi_k(\vec{r}) \exp\left[-\frac{iE_k t}{\hbar}\right]$$

$$= \sum_k \Psi_k(\vec{r},t)$$

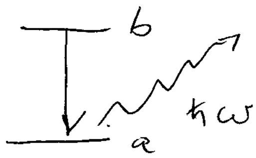
sum over number of levels

$$c_m^{(1)} = \frac{1}{i\hbar} \sum_k \langle \psi_m | H_{int} | \psi_k \rangle e^{-i\omega_{km} t}$$

Let us now consider a two-level atom in a radiation field.

Initial state: $|\psi_b\rangle$ (excited state)

Final state: $|\psi_a\rangle$ (gd. state) + photon of polarization ε_λ, frequency ω and emitted in a direction (θ,ϕ)



In this case:

$$\dot{c}_a(\omega,t) = -\frac{e}{m} A_0(\omega)\, M_{ab}^{1}(\omega) \exp[i(\omega-\omega_{ba})t - i\delta_\omega]\, c_b(t) \quad (*)$$

Previously we assumed that $c_b(t)=1$. Physically, this means we neglected the decay of level b.

we will now assume that

$$c_b(t) = 1 \quad , t < 0$$
$$c_b(t) = \exp[-t/(2\tau_b)] \quad , t \geq 0$$

- $t \geq 0$

$$\Psi_b(\vec{r},t) = c_b(t)\, \psi_b(\vec{r}) \exp(-iE_b t/\hbar) = \psi_b(\vec{r}) \exp\left[-i\left[E_b - \frac{i\hbar}{2\tau_b}\right]\frac{t}{\hbar}\right]$$

- $t < 0$

$$\Psi_b(\vec{r},t) = \psi_b(\vec{r}) \exp[-iE_b t/\hbar] \quad \text{(as before)}.$$

We are not, however, interested in this regime and could even set $\Psi_b(\vec{r},t) = 0$ without loss of generality

(*) Consequences

- In the absence of a radiation field, the state b would be stable.

$\Rightarrow$ $$\phi_b(\vec{r},t) = \psi_b(\vec{r}) \exp[-iE_b t/\hbar]$$

$$i\hbar \frac{\partial}{\partial t} \phi_b(\vec{r},t) = E_b\, \phi_b(\vec{r},t)$$ (stationary state which is an eigenstate of the energy operator)

$\Rightarrow$ The system possesses a well-defined real energy E_b

- If there is a coupling with the external radiation field, then

$$i\hbar \frac{\partial}{\partial t} \Psi_b(\vec{r},t) = \left[E_b - i\frac{\hbar}{2\tau_b}\right] \Psi_b(\vec{r},t)$$

$\Rightarrow$ one may associate a complex energy $\hat{E}_b = E_b - \dfrac{i\hbar}{2\tau_b}$

* Natural Linewidths

Inserting $c_b(t) = \exp[-t/(2\tau_b)]$ in (*)

$$\Rightarrow \dot{c}_a(\omega, t) = -\frac{e}{m} A_0(\omega) M_{ab}^{\lambda}(\omega) \exp[i(\omega - \omega_{ba})t - i\delta\omega] \cdot$$

$$\cdot \exp[-t/(2\tau_b)]$$

$$c_a(\omega, t) = -\frac{e}{m} A_0(\omega) M_{ab}^{\lambda}(\omega) e^{-i\delta\omega} \int_0^t \exp[i(\omega - \omega_{ba})t' - t'/(2\tau_b)]\, dt'$$

$$= -\frac{e}{m} A_0(\omega) M_{ab}^{\lambda}(\omega) e^{-i\delta\omega} \left[\frac{\exp[-i(\omega - \omega_{ba})t - t/(2\tau_b)] - 1}{i(\omega - \omega_{ba}) - 1/(2\tau_b)} \right]$$

The probability that the photon has been emitted is

$$|c_a(\omega, t)|^2 \propto \left| \frac{1}{i(\omega - \omega_{ba}) - (1/(2\tau_b))} \right|^2 = \frac{1}{(\omega - \omega_{ba})^2 + 1/(4\tau_b^2)}$$

$|c_a(\omega, t)|^2$ reaches a maximum at $\omega = \omega_{ba} = \frac{E_b - E_a}{\hbar}$

and decreases to a half maximum when

$$\omega = \omega_{ba} \pm 1/(2\tau_b) = (E_b - E_a \pm \Gamma_b/2)/\hbar$$

where $\Gamma_b = \frac{\hbar}{\tau_b}$ is the natural width of the line

The intensity distribution is of Lorentzian shape. It is proportional to

$$f(\omega) = \frac{\Gamma_b^2/(4\hbar^2)}{(\omega - \omega_{ba})^2 + \Gamma_b^2/(4\hbar^2)}$$

The explicit expression for the lifetime τ_b can be computed by inserting the ~~obtain~~ expression obtained for $c_a(t)$ into the first-order perturbation theory transition amplitude $\dot{c}_b(t)$

Details: Bransden + Joachain, Physics of Atoms and Molecules, p. 218

(4) Please note:

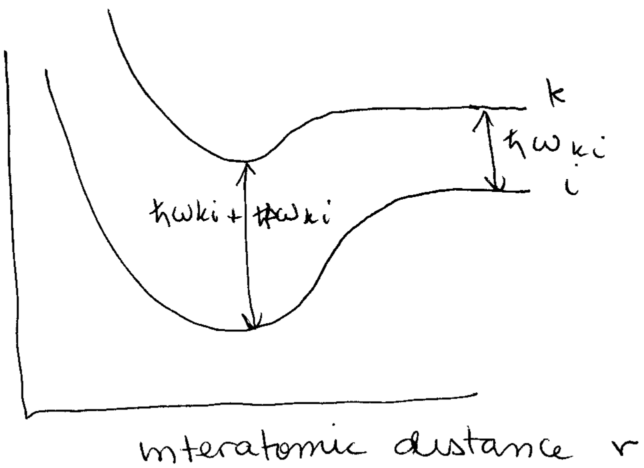
- The natural width of atomic energy levels is very small.
  Example: 2p linewidth: $\Gamma = 4.11 \times 10^{-7}$ eV
- In practice, the experimentally observed spectral lines have much larger widths than the natural linewidths.
  These widths depend on:
  - The pressure of the sample
  - The distributions of the velocities (atoms / molecules in the sample)
  - The resolution of the spectrometer,
  - etc. (this list is non-exhaustive).
- Hence, the width/shape of a spectral line can provide information on the temperature, density and composition existing in the source.

6 (b) - Pressure broadening

- In a real source, an atom will interact / collide with neighboring atoms, electrons or ions
- This interaction will lead to an increase in its linewidth

- The increase in the linewidth is a function of the density of the perturbing species (pressure broadening)

(a) Example (changes in the energy levels of an atom)
Excited atom + single perturber



$$\Delta\omega_{ki} = \frac{\{\Delta V_k(r) - \Delta V_i(r)\}}{\hbar}$$

$$\Delta V_k(r) = \underbrace{C_n^k}_{\text{depends on the excited level involved \& on the perturbing species}} / r^n$$

- $n = 2$: hydrogen and hydrogenic ions in the electric fields produced by other ions / electrons (linear Stark shifts)
- $n = 4$: Stark broadening in Helium and other systems
- $n = 3$: resonance dipole-dipole interaction ⊛
- $n = 6$: Van der Waals dipole-dipole interactions ⊛

⊛ Most significant for line-broadening problems in un-ionized gases

Forces due to chemical bonding / interatomic repulsion have not been included.

(b) Quasi-static / impact approximation

- Since an atom interacts with several perturbers, one must average over the orientations / paths of these perturbers

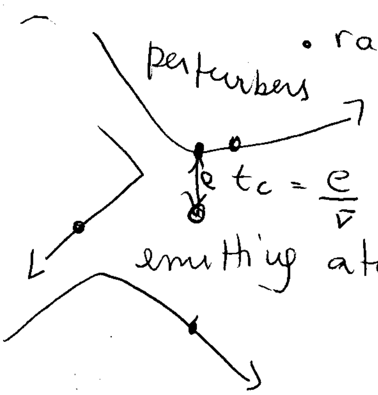
(*) Limiting cases: quasi-static approximation
impact or phase shift approximation
(the averaging can be performed satisfactorily)

- The shape of the line profile at a frequency separation $\Delta\omega = \omega_0 - \omega$ is determined by a wavetrain emitted in the interval $\Delta t \Rightarrow \Delta t \propto \frac{1}{\Delta\omega}$

Let us consider that the atom emits a wavetrain between collisions. Then, $\Delta t = T_c$ → mean time between collisions

- How does T_c compare with the duration of a collision (t_c) ?

Assumption: • perturber moves past the emitting atom in a classical trajectory
• radiating atom perturbed only during the collision



$t_c = \frac{\rho}{\bar{v}}$, with ρ = distance of closest approach
$\bar{v}$ = mean velocity

- Quasi-static approximation

$t_c \gg T_c \Rightarrow$ motion of perturbers can be ignored
$t_c \gg \frac{1}{\Delta\omega} \approx T_c$

Reasonable for high densities and low temperatures

- Impact approximation

$t_c << T_c \Rightarrow$ the phase shift produced by one collision is computed and the result is averaged out over all impact parameters

Impact-approximation theories are appropriate in this case

6.(c) - Doppler broadening

The wavelength of the light emitted by a moving source is shifted by the Doppler effect

Non-relativistic velocities:

$$\lambda = \lambda_0 \left(1 \pm \frac{v}{c}\right)$$

$$\omega = \omega_0 \left(1 \mp \frac{v}{c}\right) \quad (*)$$

Let us assume light is emitted from a gas at absolute temperature T. Hence

$$dN = N_0 \exp\left[-Mv^2/(2k_bT)\right] dv \quad \text{(Maxwell's distributions)}$$

dN: number of atoms with velocities between v and $v + dv$

N_0: Const.

M: atomic mass

k_b: Boltzmann const.

Using $(*) \Rightarrow \mp \frac{v}{c} = \frac{(\omega - \omega_0)}{\omega_0}$

$$v^2 = \frac{(\omega-\omega_0)^2}{\omega_0^2} c^2$$

Intensity of light emitted so that ω is between ω and $\omega + d\omega$

$$I(\omega) = I(\omega_0) \exp\left[-\frac{Mc^2}{2k_bT} \left(\frac{\omega - \omega_0}{\omega_0} \right)^2 \right]$$

Gaussian distribution

Half maximum $\frac{I(\omega_1)}{I(\omega_0)} = \frac{1}{2} \Rightarrow \ln 2 = \frac{Mc^2}{2k_bT} \left(\frac{\omega_1 - \omega_0}{\omega_0} \right)^2$

$$(\omega_1 - \omega_0)^2 = \frac{2k_bT}{Mc^2} \omega_0^2 \ln 2$$

Total Doppler width at half maximum:

$$\Delta\omega_D = 2|\omega_1 - \omega_0| = \frac{2\omega_0}{c} \left[\frac{2k_bT}{M} \ln 2 \right]^{1/2}$$

Please note

- The Doppler width is proportional to the observed frequency $\Rightarrow$ the resolution of experimental studies can be improved by using microwave or radio frequencies
- $\Delta\omega_D \propto \sqrt{T} \Rightarrow$ the Doppler width can be reduced by cooling the source.