PH585
AMO

Lecture #6

①

Line shapes and widths

In spectroscopy, valuable info about atomic states is provided by line intensities, shapes, and widths.

Intensities are determined by $|M_{ba}|^2$, or, in electric dipole approx., $|\vec{r}_{ba}|^2$

Introduce dimensionless $f_{ka} = \dfrac{2\omega_{ka} m}{3\hbar} |\vec{r}_{ka}|^2$

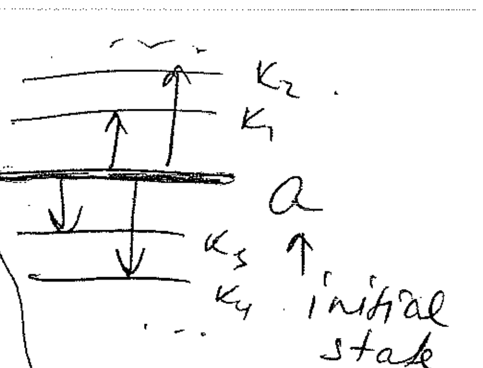
f_{ka} – oscillator strength

such that

$$\sum_k f_{ka} = 1$$

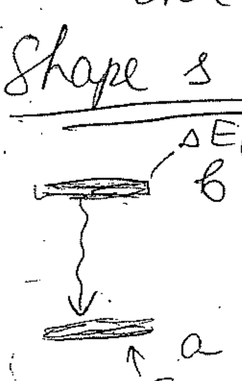
Thomas-Reiche-Kuhn rule

sum of the probabilities to end up at a level k (for all possible k's)



measure of relative intensities of various transitions

Shape & width



unless a is a ground state ($\tau_a = \infty$)

uncertainty principle:

$$\underbrace{\Delta x}_{c\Delta t} \underbrace{\Delta p}_{\hbar \frac{\Delta \omega}{c}} \geq \frac{\hbar}{2} \Rightarrow \Delta E \Delta t \geq \frac{\hbar}{2} \Rightarrow$$

If population of a level is unstable (i.e. decays by spont. emission) $\Rightarrow$ there is a spread ΔE

Lifetime $\tau_b = \dfrac{1}{\sum_k W^s_{kb}}$ ← all possible pathways

level b

So, instead of a stationary state $\Phi_b(\vec{r},t) = \varphi_b(\vec{r}) e^{-\frac{iE_b}{\hbar}}$

we have $\Psi_b(\vec{r},t) = \psi_b(\vec{r})\, e^{-\frac{i}{\hbar}E_b t}\, e^{-t/2\tau_b}$

(so that $P_b \sim e^{-t/\tau_b}$)

(probability to find a particle at a level b)

back to Lectures #3, 4 ⇒

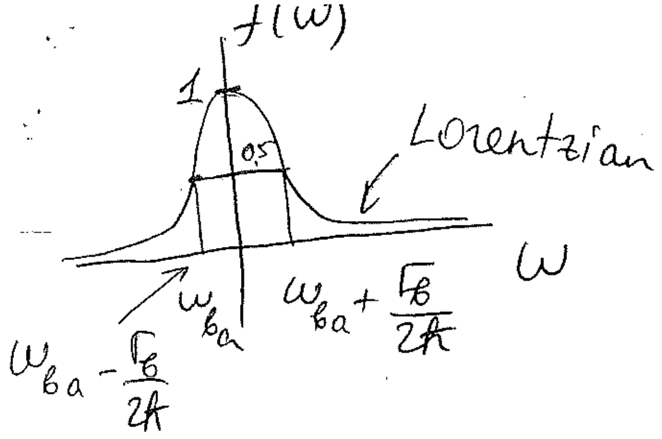
$$C_a^{(1)}(t) = -\frac{e}{2m} A_0(\omega) \overline{M}_{ab}(\omega) e^{-i\delta_\omega} \int_0^t e^{i(\omega-\omega_{ba})t' - \frac{t'}{2\tau_b}} dt'$$

$b \to a \Leftrightarrow$ emission, "monochromatic"

$$= -\frac{e}{2m} A_0(\omega) \overline{M}_{ab}(\omega) e^{-i\delta_\omega} \frac{e^{i(\omega-\omega_{ba})t - \frac{t}{2\tau_b}} - 1}{i(\omega-\omega_{ba}) - \frac{1}{2\tau_b}}$$

Probability of emission at $t \gg \tau_b$ ⇒

$$P \sim |C_a^{(1)}|^2 \sim \frac{1}{(\omega-\omega_{ba})^2 + \frac{1}{4\tau_b^2}}$$



Introduce $\Gamma_b = \frac{\hbar}{\tau_b}$

natural width of the line

Then, $P \sim \frac{1}{(\omega-\omega_{ba})^2 + \frac{\Gamma_b^2}{4\hbar^2}} \cdot \frac{\Gamma_b^2/4\hbar^2}{\Gamma_b^2/4\hbar^2} = \frac{1}{\Gamma_b^2/4\hbar^2} f(\omega)$

So, $W^s_{ab} = \frac{\Gamma_b}{\hbar}$

What about absorption?

from before;

$$\sigma_{ba}(\omega) = \frac{\hbar\omega_{ba}}{I(\omega_{ba})} W_{ba}\, \delta(\omega-\omega_{ba})$$

cross-section

Now: replace $\delta(\omega-\omega_{ba})$ with $a(\omega)$

$$a(\omega) = \frac{1}{\pi} \frac{\Gamma_b/2\hbar}{(\omega-\omega_{ba})^2 + \frac{\Gamma_b^2}{4\hbar^2}} \qquad \left(a(\omega) \xrightarrow[\Gamma_b \to 0]{} \delta(\omega-\omega_{ba})\right)$$

$$\lim_{\varepsilon\to 0} \frac{\varepsilon}{\pi(x^2+\varepsilon^2)} = \delta(x)$$

$\varepsilon = \frac{\Gamma_b}{2\hbar}$, $x = \omega-\omega_{ba}$

$\Rightarrow$ check $\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{\varepsilon\, dx}{x^2+\varepsilon^2} = \frac{\cancel{\varepsilon}\,\cancel{\varepsilon}}{\pi \cancel{\varepsilon^2}} \underbrace{\int_{-\infty}^{+\infty} \frac{d\left(\frac{x}{\varepsilon}\right)}{\frac{x^2}{\varepsilon^2}+1}}_{\pi} = 1 = \int_{-\infty}^{+\infty} \delta(x)\,dx$

<u>Note:</u> if a is not a ground state $\Rightarrow$ need $\Gamma = \hbar\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right)$

Natural width is <u>very small</u> $\Rightarrow$

<u>Example</u> (H)-atom $2p \to 1s \Rightarrow \tau = 1{,}6\,ns \Rightarrow$

$$\Gamma_{2p} = \frac{\hbar}{1{,}6\,ns} = \frac{1{,}05 \cdot 10^{-34}\,J\cdot s}{1{,}6 \cdot 10^{-9}\,s} = 0{,}66 \cdot 10^{-25}\,J \simeq$$

$$= 0{,}41 \cdot 10^{-6}\,eV$$

$$\hbar\omega_{\underset{2p}{b}\underset{1s}{a}} = -\frac{E_I}{\cancel{\hbar}}\cancel{\hbar}\left(\frac{1}{2^2} - 1\right) = \frac{3}{4} \cdot 13{,}6\,eV = 10{,}2\,eV$$

$$\frac{\Gamma_{2p}}{\hbar\omega_{2p\to 1s}} \sim \frac{4{,}1 \cdot 10^{-7}}{10{,}2} \sim \underline{\underline{4 \cdot 10^{-8}}}$$

What if we have He^+ instead of (H)? $\Rightarrow$

$$\tau_{He^+} = 2^{-4}\,\tau_H \; ; \; \hbar\omega_{ba} = +\underset{4}{Z^2}\,\underset{13{,}6\,eV}{E_I} \cdot \frac{3}{4} = 3 \cdot 13{,}6\,eV$$

HW: $\tau(Z) = Z^{-4}\,\tau(Z=1)$

$$\frac{\Gamma_{2p}}{\hbar\omega_{2p\to 1s}} = \frac{2^4\,\underbrace{0{,}41 \cdot 10^{-6}\,eV}}{4\,\frac{3}{4} \cdot 13{,}6\,eV} = 4 \cdot 4 \cdot 10^{-8} = \underline{\underline{1{,}6 \cdot 10^{-7}}}$$

$= 4 \cdot 10^{-8} \leftarrow$ (H)

Line broadening

In most cases, line width is larger than natural width $\Rightarrow$ broadening

Pressure broadening

$\Rightarrow$ if level de-populates not just by spontaneous emission, but by other mech. such as collisions

$$\tilde{\tau}_b = \frac{1}{W_{tot}} \Leftarrow$$

$$\tilde{\Gamma} = \hbar \left(\frac{1}{\tilde{\tau}_a} + \frac{1}{\tilde{\tau}_b} \right)$$

$$W_c = n v \sigma$$

n – number density of atoms; v – relative velocity of pairs of atoms; σ – collision cross-section

$n, v\ (t^0) \Longleftrightarrow$

n (pressure)

Result of collisions $\Rightarrow$ still Lorentzian, but broadened $\Rightarrow$ by measuring line width $\Rightarrow$ get info about physical conditions in stellar atmosphere

homogeneous broadening

Doppler broadening

due to motion of atoms $\Rightarrow$ $\lambda = \lambda_0 \left(1 \pm \frac{v}{c}\right)$

λ – wavelength emitted by a moving source; λ_0 – for stationary source; $+$ – receding source; $-$ – approaching source

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

1st-order Doppler effect

$$dN = N_0 e^{-Mv^2/2k_BT} dv \Rightarrow$$

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

atomic mass

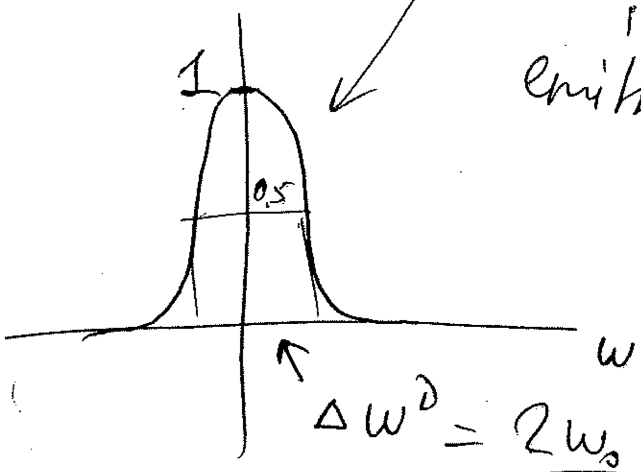
$$I(\omega) = I(\omega_0) e^{-\frac{Mc^2}{2k_BT}\left(\frac{\omega-\omega_0}{\omega_0}\right)^2}$$

intensity emitted at $[\omega, \omega+d\omega]$

Gaussian

⇑

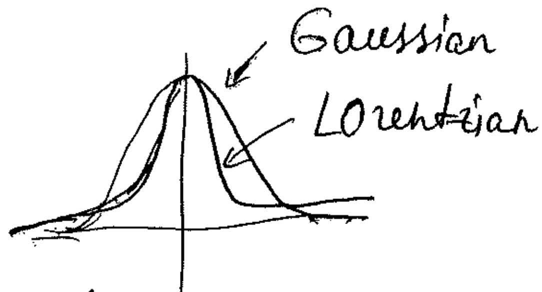
inhomogeneous broadening



$$\Delta\omega^D = \frac{2\omega_0}{c}\left[\frac{2k_BT}{M}\log 2\right]^{1/2} \Rightarrow \text{as } T\uparrow,\ \omega_0\uparrow,\ M\downarrow \quad \Delta\omega^D\uparrow$$

HW!

<u>Note:</u>



If both Lorentzian and Gaussian are present ⇒ <u>Voigt profile</u>

Can eliminate Doppler broadening → level crossing spectroscopy
→ saturation spectroscopy