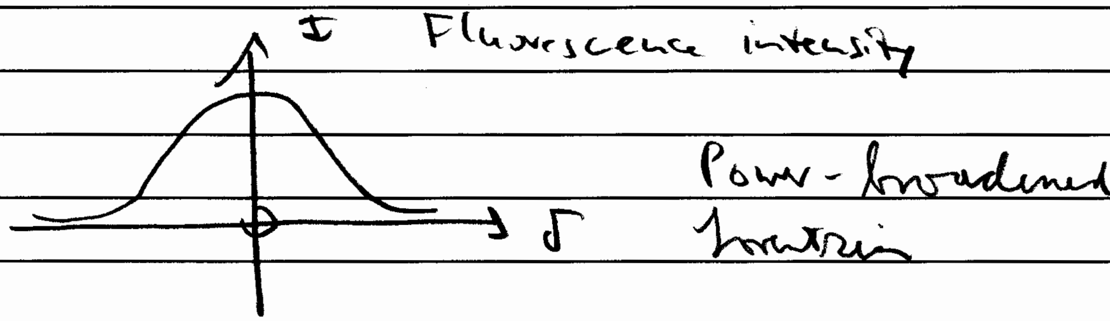
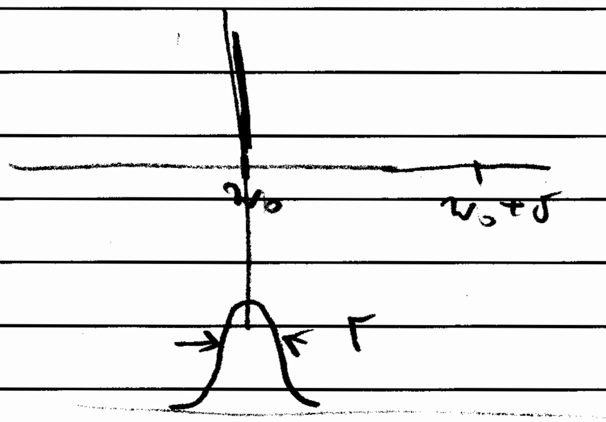
Fluorescence spectrum of an atom

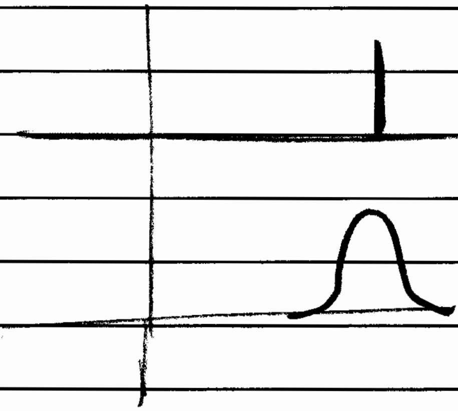
What happens when we excite an atom and scan the frequency



Now: at fixed detuning δ and very low power, what is the spectrum of the emitted light

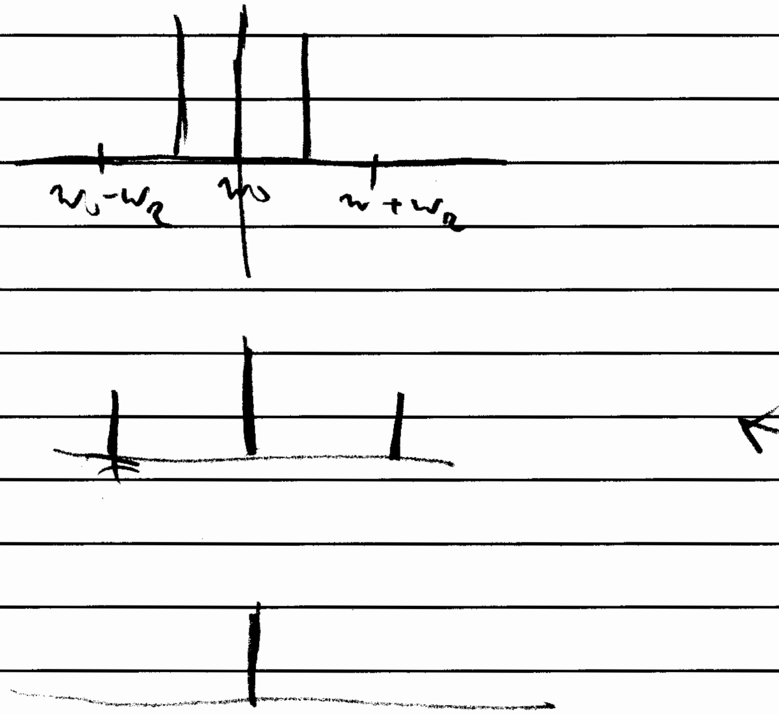
Q:



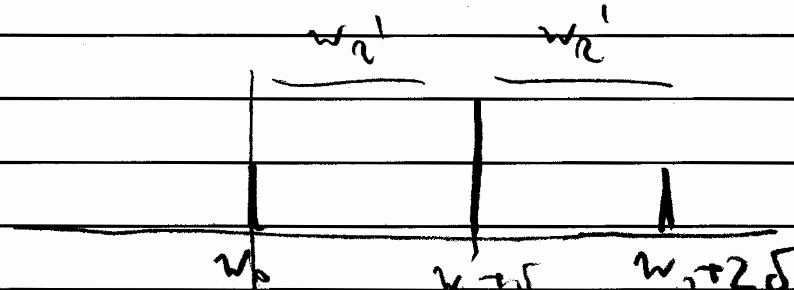


High power, on resonance
Rabi oscillations

Q:



off resonance

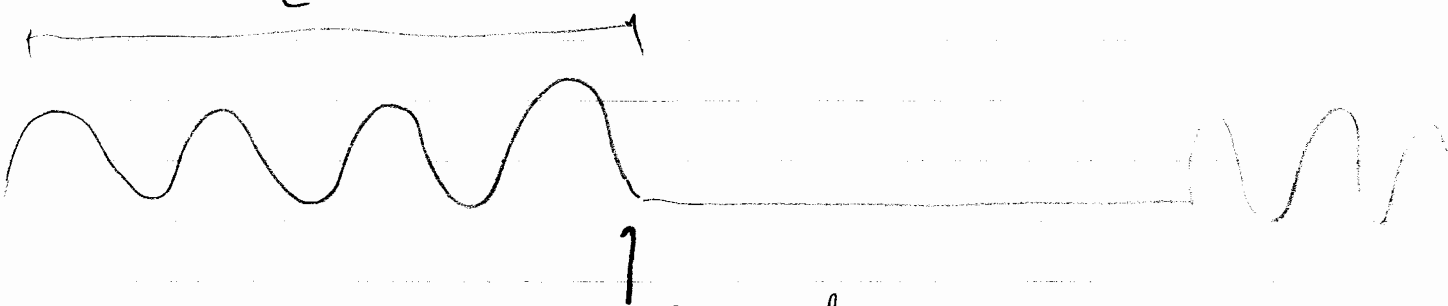


dipole moment oscillates at $\omega_L = \omega_0+\delta$;
excited state population
is modulated at ω_R'
$\Rightarrow$ sidebands

More detailed discussion in 8.422

Pressure broadening

- Excited atom as an oscillator

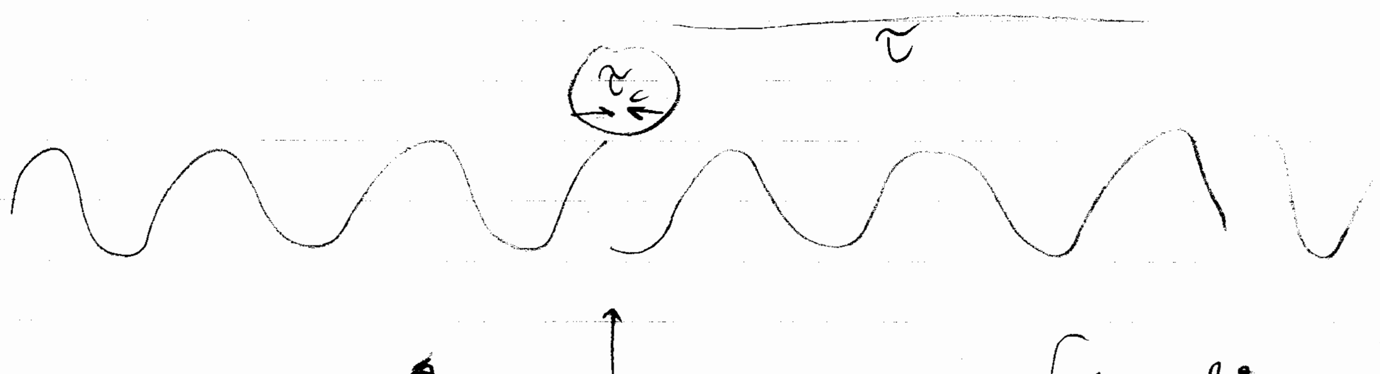


quenching, deexcitation

$$\Gamma_t = \Gamma + ap \qquad (2\pi\tau)^{-1}$$

↑ total width   ↑ pressure

Lorentzian with FWHM Γ_t

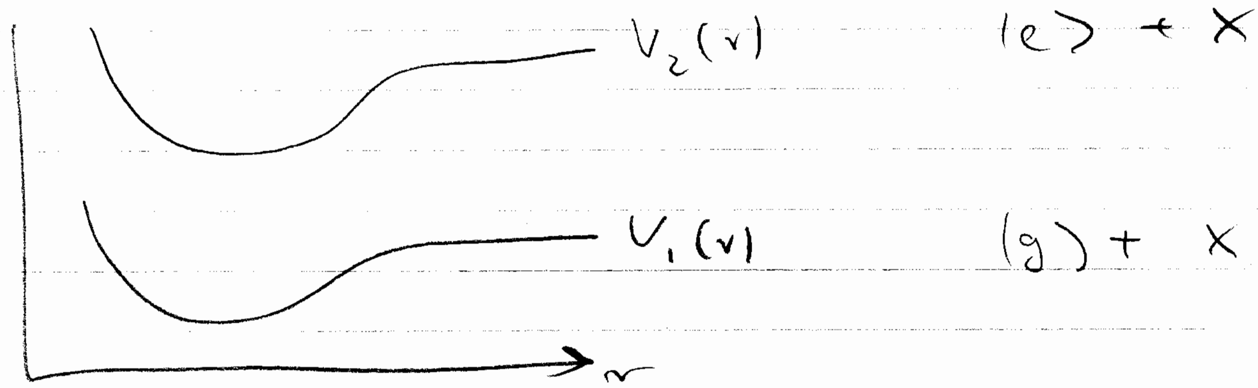
- 

random phase jump [more likely in neutral atom coll than quenching, whereas coll with electrons are more likely to be inelastic]

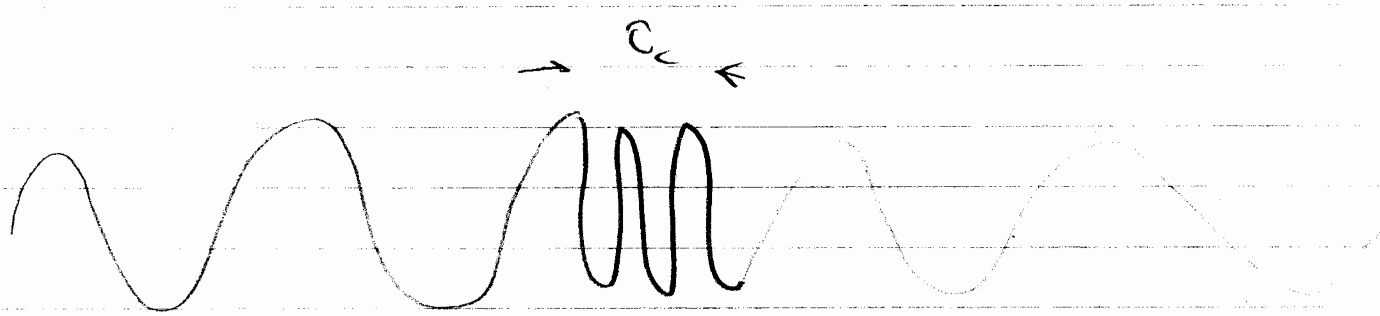
→ same result

Lorentz model (1906), impact approximation $\tau_c \to 0$

How does the phase change come about?



$$\dot{\phi} = \Delta\omega = \frac{1}{\hbar}\left[V_2(r) - V_1(r) \right]$$



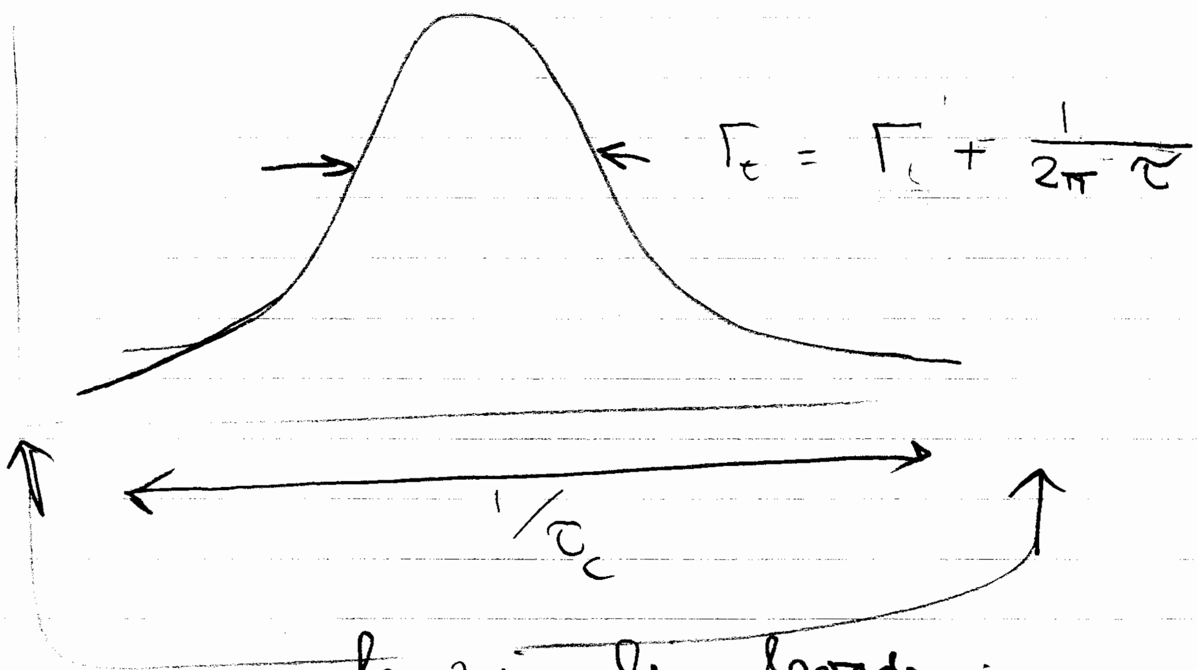
$I(\Delta\omega) \propto \rho_{corr}(r(\Delta\omega))$ ← probability that two atoms are at distance r which produces line shift $\Delta\omega$

e.g. $P(r)\,dr = \frac{4\pi r^2\,dr}{V}$ $\quad V = n^{-1}$

simplest pair correlation function

Which model is correct?

$\Delta\omega$ only becomes resolvable when $\Delta\omega > \tau_c^{-1}$



far wing line broadening:

$\Rightarrow$ information about molecular potentials

What is the time τ between collisions?

Soft and hard collisions?

$\Delta\phi$ small or large

$\Rightarrow$ Weisskopf theory (1933)

page 17a from previous notes

Weisskopf theory (1933)

goes beyond impact approximation

assumption: radiation not disrupted, but change of phase

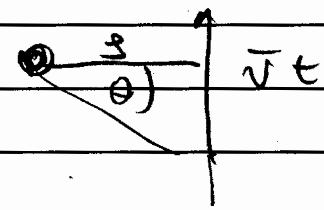
$$\eta(\rho) = \int_{-\infty}^{\infty} \Delta\nu \, dt$$

$\Delta\nu = C_n' / r^n$

$C_n' = C_n^b - C_n^a$

ρ impact parameter

$$= \int_{-\infty}^{\infty} \frac{C_n' \, dt}{(\rho^2 + \bar{v}^2 t^2)^{n/2}}$$



Substitute $\bar{v} t = \rho \tan\theta$

$$\eta(\rho) = \frac{C_n' \, a_n}{\bar{v} \, \rho^{n-1}}$$

a_n: order of unity

Weisskopf's assumption

$\eta(\rho) = 1 \Rightarrow$ wavetrain becomes incoherent

$\Rightarrow$ Weisskopf radius

$$\rho_W = \left(\frac{C_n' a_n}{\bar{v}} \right)^{1/n-1}$$

Rate of decohering collisions $\pi \rho_W^2 n \bar{v}$

$= 1/\tau$ in Lorentz model

explains why cross sections for pressure broadening of 10^{-14} to 10^{-15} cm^2 are much larger than gas kinetic cross sections (10^{-16} cm^2)

Weisskopf theory does not account for line shifts

NOW: What happens in a soft collision (phase shift $\ll 2\pi$)

Lindholm theory (1941)

We obtained earlier

$$W_{ab}(\omega) \propto FT\left[\overbrace{e^{i(\Phi(t')-\Phi(t))}}^{f(\tau)}\right]$$

Lineshape

e.g. $\phi(t') - \phi(t) = k v (t'-t) + \omega(t'-t)$
→ Doppler broadening

<u>Now</u>: Phase change during the collision $\eta(\varsigma)$

$\eta(\varsigma)$ ↑ impact parameter

do ensemble average over random impact parameter

$$f(\tau) = e^{-n\bar{v}(\sigma_r - i\sigma_i)\tau}$$

σ_r → broadening | σ_i → line shift, qm: mean field shift

[See Demtröder, Laser Spectroscopy Handout for details]

result shows: collisions with $\eta(\varsigma) \ll 1$ contribute to the line shift (σ_i) but not to broadening

$\eta(\varsigma) \gtrsim 1$ for $\varsigma < \varsigma_W$ Weisskopf radius

don't contribute to shift

$\sigma_r \simeq \pi \varsigma_W^2$

Some #s : Na D line with argon

Broadening 30 MHz / Torr

Shift −1 MHz / Torr

self broadening 150 MHz / Torr

even at several Torr < Doppler width (≈ 1.2 GHz)