Line Shapes and Broadening

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Books and reviews

- H.R. Griem, Spectral Line Broadening by Plasmas (1974)
- H.-J. Kunze, Introduction to Plasma Spectroscopy (2009)
- I.I Sobelman et al, Excitation of Atoms and Broadening of Spectral Lines (1995)
- I. Hubeny and D. Mihalas, Theory of Stellar Atmospheres (2015)
- N. Konjević, Phys. Rep. 316, 339 (1999)
- M.A. Gigosos, J. Phys. D 47, 343001 (2014)
- S. Alexiou, HEDP 5, 225 (2009)
- E. Stambulchik and Y. Maron, HEDP 6, 9 (2010)

Line broadening

- Instrumental
- Doppler
- Natural
- Collisional (broadening)
  - Stark
  - Van der Waals
  - Resonance

Many-body problem:
QM picture of line broadening is described in terms of a complete QM system of
radiator + all perturbers

Line Profiles

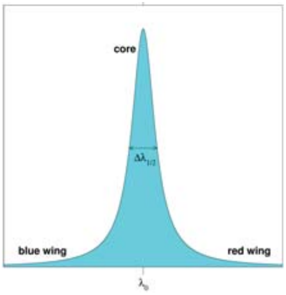
- Units: *frequency* ν, ***wavelength*** λ, ***angular frequency*** ω, *wavenumber* σ

Normalized profile: $\int \varphi(\omega)d\omega = 1$

$\int \varphi(\lambda)d\lambda = 1$

$$\varphi(\lambda) = \frac{2\pi c}{\lambda^2}\varphi(\omega)$$

Full Width at Half Maximum (FWHM): $\Delta\lambda_{1/2}$ or $\Delta\lambda_{FWHM}$
Sometimes HWHM=FWHM/2



Doppler broadening

Doppler shift: $\frac{\Delta\omega}{\omega_0} = -\frac{\Delta\lambda}{\lambda_0} = \frac{v_x}{c}$

Fraction of atoms with $v_x \le v \le v_x + dv_x$:

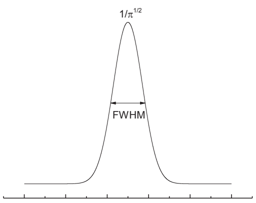
$$\frac{dN(v_x)}{N} = \frac{1}{\sqrt{\pi}v_p}exp\left(-\frac{v_x^2}{v_p^2}\right)dv_x$$

$$v_p = \left(\frac{2kT}{M}\right)^{1/2}$$

$$\varphi_D(\omega) = \frac{1}{\delta\omega_D\sqrt{\pi}}exp\left[-\left(\frac{\omega-\omega_0}{\delta\omega_D}\right)^2\right]$$

$$\delta\omega_D = \omega_0\cdot\left(\frac{2kT}{Mc^2}\right)^{1/2}$$

FWHM = $2\sqrt{ln2}\cdot\delta\omega_D = \omega_0\cdot 7.715\times10^{-5}\sqrt{\frac{T(eV)}{M(u)}}$



Doppler (Gauss) profile

peak x FWHM ~ 0.94

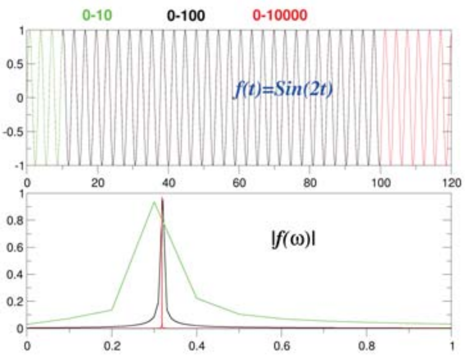
$$\delta\omega = \sqrt{\delta\omega_1^2 + \delta\omega_2^2}$$

Essence of the lineshape theory

- Fourier transform relation between time and frequency (classical picture)
  - If a physical quantity evolves with time as *f(t)*, then its energy spectrum is:

$$I(\omega) \propto \left|\int_0^\infty f(t)e^{-i\omega t}dt\right|^2$$

Fourier of an interrupted sine

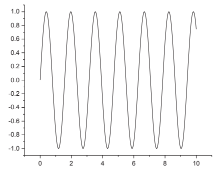


Three sine functions

Three profiles

Classical atomic oscillator

$$f(t) = f_0\exp(i\omega_0 t)$$



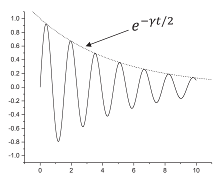
$$I(\omega) = f_0^2\delta(\omega-\omega_0)$$

Energy spectrum:

$$I(\omega) = \left|\int_0^\infty f(t)e^{-i\omega t}dt\right|^2$$

Radiator loses energy:

$$f(t) = f_0\exp(i\omega_0 t - \gamma t/2)$$



Lorentz profile:

$$I(\omega) = \frac{f_0^2}{\pi}\frac{\gamma/2}{(\omega-\omega_0)^2+(\gamma/2)^2}$$

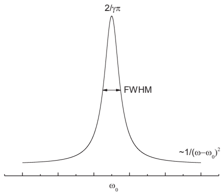
natural broadening

Lorentz profile

Lorentz, Cauchy, dispersion, Breit-Wigner…

$$\varphi_L(\omega) = \frac{1}{\pi}\frac{\gamma/2}{(\omega-\omega_0)^2 + (\gamma/2)^2}$$

FWHM = γ

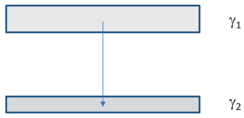


Lorentz profile

peak x FWHM ~ 0.64

Natural Broadening: QM

- Quantum mechanics gives the same result as classical theory although it is the finite width of the discrete energy levels rather than decay of the wave train
  - $\Delta E \cdot \Delta t \geq \hbar/2$
  - $\gamma\tau = \hbar$ ($\gamma = 2\Delta E$, $\tau = 1/\Sigma A$)



$\gamma = \gamma_1 + \gamma_2$

$$\delta\omega = \gamma;\ \frac{\delta\lambda}{\lambda} = \frac{\delta\omega}{\omega} = \frac{\lambda}{2\pi c}\gamma = \frac{\lambda}{2\pi c}\hbar\Sigma A$$

Weisskopf & Wigner

Generally, natural broadening is negligible compared to Doppler
But: sum over A's includes autoionization (if present)

Gauss+Lorentz? Voigt!

Convolution of G and L: Voigt profile

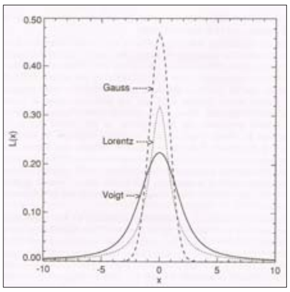
$$\varphi_V(\omega) = \int_{-\infty}^{+\infty} \varphi_D(\omega - x)\varphi_L(x)dx$$

$$= \frac{\gamma}{2\pi^{3/2}\delta\omega_D^2}\int_{-\infty}^{+\infty}\frac{exp(-x^2)}{\left(\frac{\omega}{\omega_D} - x\right)^2 + a^2}dx$$

$$a = \frac{\gamma/2}{\delta\omega_D}$$

$$H(a,v) \equiv \frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{exp(-x^2)}{(v-x)^2 + a^2}dx$$

$$H(a,v) \approx e^{-v^2} + a/(\pi^{1/2}v^2)$$



Griem, Principles of Plasma Spectroscopy

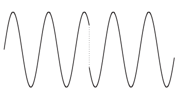
At 1%: $\delta\lambda_V^{FWHM} \approx \left[\left(\frac{\delta\lambda_L}{2}\right)^2 + \delta\lambda_G^2\right]^{1/2} + \frac{\delta\lambda_L}{2}$

Collisional (pressure) broadening

- Interaction of the atom(-ic oscillator) with other plasma particles
- Electric fields are most important and therefore "Stark broadening"
- Van der Waals: two dipole moments (neutrals); short-range interaction

Pressure broadening: classical approach

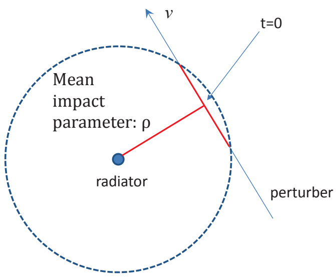
- **Impact theory**
  - Oscillator
  - Emitted wavetrain is interrupted
    - Instantaneous phase shift
    - Transition to another level
  - Oscillator "starts" and "stops"
  - Duration of collision is small compared to the mean time between collisions
- **Quasi-static theory**
  - Atom is embedded in plasma of motionless (slowly moving) charged perturbers
  - The field fluctuates
    - Spectral line position shifts
    - Final shape is obtained from the distribution of microfields



Impact Approximation

Weisskopf theory:

- Atom is unperturbed between collisions (τ_c)
- Perturber is a classical particle
- Perturber moves with a constant velocity, straight line, velocity v, impact parameter ρ
- No transitions are produced by the perturber (phase shifts only)
- Interaction between atom and perturber is described by: $\Delta\omega(t) = \frac{C_p}{r(t)^p}$ where $r(t) = (\rho^2 + v^2t^2)^{1/2}$



Lorentz: $I(\omega) = \frac{1/\pi\tau_c}{(\omega-\omega_0)^2 + \left(\frac{1}{\tau_c}\right)^2}$

$$\Gamma = 2\pi N\bar{v}\left(\frac{C_p\psi_p}{\bar{v}}\right)^{2/(p-1)}$$

1. Some arbitrary choice of parameters
2. No small phase shifts
3. No line shift

Impact (cont'd)

Lindholm-Foley approximation:

$$f(t) = exp\left[i\omega_0 t + i\int_{-\infty}^{t}\Delta\omega(t')dt'\right] \equiv e^{i[\omega t + \eta(t)]}$$

$$I(\omega) = \frac{N\bar{v}\sigma_R/\pi}{(\omega - \omega_0 - N\bar{v}\sigma_I)^2 + (N\bar{v}\sigma_R)^2}$$

$$\sigma_R \equiv 2\pi\int_0^{\infty}[1 - \cos\eta(\rho)]\,\rho\,d\rho;\quad \sigma_I \equiv 2\pi\int_0^{\infty}\sin\eta(\rho)\,\rho\,d\rho;$$

Width: $\Gamma = 2N\bar{v}\sigma_R$

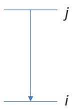
Shift: $\Delta\omega_0 = N\bar{v}\sigma_I$

Problems with the classical impact approximation

- Time of interest $\tau = 1/\Delta\omega$ becomes smaller than the collision time $\tau_c = \rho/v$ for large $\Delta\omega$: problem at large displacements!
- Low densities preferred
- Collisions overlap at $\rho \rightarrow \infty$ (τ_c exceeds the mean time between collisions)
- Classical impact theory is adiabatic

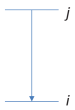
Impact Approximation: quantum

M. Baranger, 1958:



$$\Delta\omega = n_e \int_0^\infty v f_e(v) \left(\sum_{i' \neq i} \sigma_{ii'}(v) + \sum_{j' \neq j} \sigma_{jj'}(v) \right) dv +$$
$$n_e \int_0^\infty v f_e(v) \left(\int \left| f_i(\theta, v) - f_j(\theta, v) \right|^2 d\Omega \right) dv$$

Impact Approximation: FWHM



electron density EEDF inelastic cross sections

$$\Delta\omega = n_e \int_0^\infty v f_e(v) \left(\sum_{i' \neq i} \sigma_{ii'}(v) + \sum_{j' \neq j} \sigma_{jj'}(v) \right) dv +$$
$$n_e \int_0^\infty v f_e(v) \left(\int \left| f_i(\theta, v) - f_j(\theta, v) \right|^2 d\Omega \right) dv$$

elastic amplitudes

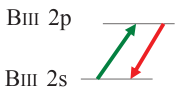
M. Baranger, 1958

$$\Delta\omega \propto \frac{n_e}{T_e^x}, 0.2 < x < 0.5$$

Example: problems in isolated lines

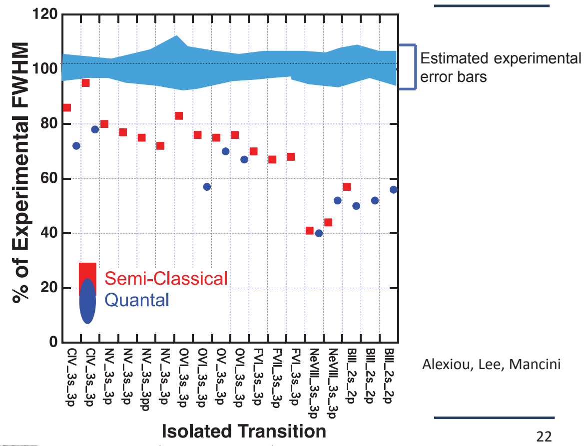
Alexiou, Lee, Mancini

- **Isolated** ion lines, which are purely e[-] impact broadened, show factor of ~2 discrepancies between theory and experiment.
  - Techniques used to resolve this issue are:
  - –sophisticated semiclassical calculations
  - –fully quantum mechanical (close coupling) calculations, different formulations
  - –population effects
  - ***However, there has been no resolution yet***



$|2s\rangle$ *via a collision* $\rightarrow$ $|2p\rangle$ *via a collision* $\rightarrow$ $|2s\rangle$

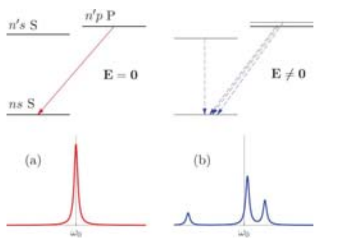
Comparison between theory and experiment for isolated lines

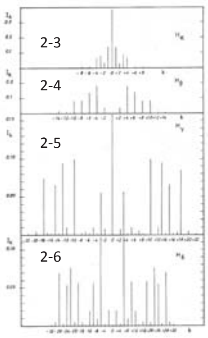


Alexiou, Lee, Mancini

Stark effect

From: MA Gigosos (2014)

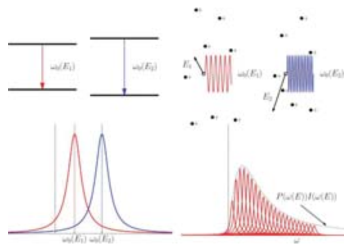




Linear for H, quadratic for others (weak field)

Quasi-static approximation

- Electric field (*by the ions*) is considered (almost) constant at the radiator during emission
- Plasma microfield splits and shifts level via Stark effect
- E is not constant but has some distribution ⇒ components smeared ⇒ line profile



From: MA Gigosos (2014)

Nearest Neighbor Approximation

- Only nearest neighbor is important
- No interaction between the perturbers
- Not really a “statistical” model

$$W(r)dr$$
$$\Delta\omega = \frac{C_p}{r^p}$$
$$I(\Delta\omega)d\omega \propto W(r)\left[\frac{dr}{d(\Delta\omega)}\right] d(\Delta\omega)$$
$$W(r)dr = \left[1 - \int_0^r W(x)dx\right](4\pi r^2 N)dr$$
$$W(r) = 4\pi r^2 N exp\left(-\frac{4}{3}\pi r^3 N\right)$$

Simple…and wrong!

Holtsmark model (1919)

- Ensemble of perturbers; statistically independent; interaction isotropic
- No interaction between perturbers
- Calculation steps
  - Probability of finding the nearest ion at distance r: P(r)
  - Probability of the emitter being subjected to filed F: P(F)
  - Shift of levels calculated for each field, result convolved

Normal field strength (Stark):

$$F_0 = 2.603 e N^{2/3}$$

$$\beta = \frac{F}{F_0}, \quad \int_0^\infty H(\beta) d\beta = 1$$

$$H(\beta) = \frac{2}{\pi}\beta \int_0^\infty x \cdot \sin(\beta x) \cdot e^{-x^{3/2}} dx$$

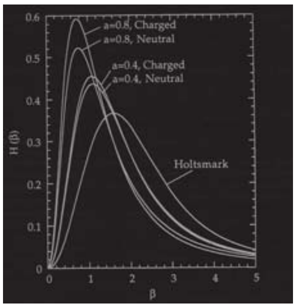
Wings: $\sim(\Delta\omega)^{-5/2}$

How good is Holtsmark?..

Holtsmark vs Hooper
(ion-ion correlations,
Debye shielding)

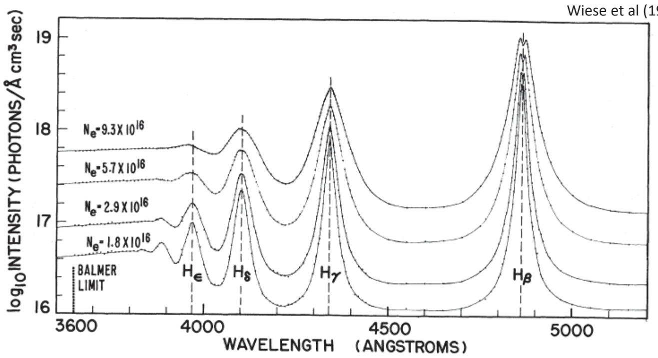
$$a = \frac{R_0}{\rho_D}$$

$$R_0 = \sqrt[3]{\frac{3}{4\pi N}}$$



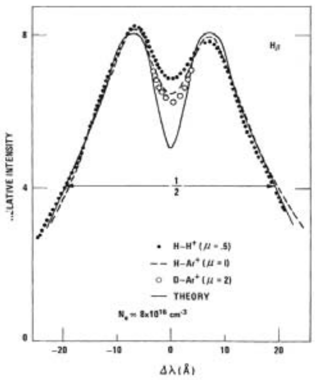
Inglis-Teller effect

Wiese et al (1972)



$$\lg n_z[cm^{-3}] \approx 23.12 + 4.5\,lgZ\ - 1.5\,lgz\ - 7.5\,lgn_{max}$$

WKH (1975)



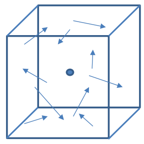
N_e = 8x10^{16} cm^{-3}

Quasi-static theory works quite well for hydrogen but ion dynamics is important (sometimes electrons are important too)

Modern computer simulations

$$i\hbar\frac{d}{dt}U(t) = H(t)U(t) = (H_0 + q\boldsymbol{E}(t)\cdot\boldsymbol{R})U(t)$$

$$\boldsymbol{D}(t) = U^{+}(t)\boldsymbol{D}(0)U(t)$$



$$\Phi(t) = Tr[\boldsymbol{D}(0)\cdot\boldsymbol{D}(t)\hat{\rho}]$$

$$I(\Delta\omega) = \frac{1}{\pi}\mathcal{R}\int_0^{\infty} e^{i\Delta\omega t}\langle\Phi(t)\rangle dt$$

Modern computer simulations

Evolution operator — Unperturbed Hamiltonian — electric microfield

$$i\hbar\frac{d}{dt}U(t) = H(t)U(t) = (H_0 + q\boldsymbol{E}(t)\cdot\boldsymbol{R})U(t)$$

Dipole interaction

Dipole moment operator

$$\boldsymbol{D}(t) = U^{+}(t)\boldsymbol{D}(0)U(t)$$

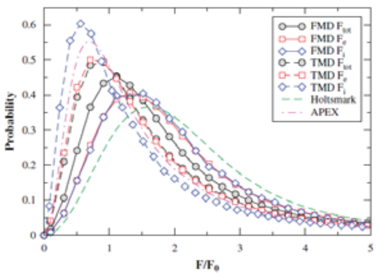
Autocorrelation function — Density matrix

$$\Phi(t) = Tr[\boldsymbol{D}(0)\cdot\boldsymbol{D}(t)\hat{\rho}]$$

Final spectrum

$$I(\Delta\omega) = \frac{1}{\pi}\mathcal{R}\int_0^{\infty} e^{i\Delta\omega t}\langle\Phi(t)\rangle dt$$

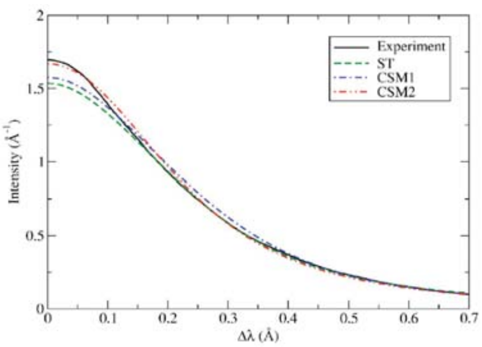
Modern CS



Stambulchik et al (HEDP, 2007)

- Trivial MD
  - Electrons and protons move along straight lines
- Full MD
  - All perturbers interact
- 200 e and 200 p; a cube with mirror walls

Exp vs theory (CSM)



H_9

$n_e = 1.2\times10^{13}\ cm^3$

$T_e = 0.16\ eV$

Stambulchik et al, 2007

Where's good data?

- Hydrogen atoms
  - Griem (1974)
- Non-hydrogenic ions
  - Griem (1974)
  - Modified semiclassical approach, Dimitrijevic and Konjevic (1980)

- NIST Atomic Spectral Line Broadening Bibliographic Database
  - http://physics.nist.gov/cgi-bin/ASBib1/LineBroadBib.cgi
- Stark-B Database
  - http://stark-b.obspm.fr/