Lectures October 4th and 10th 2007

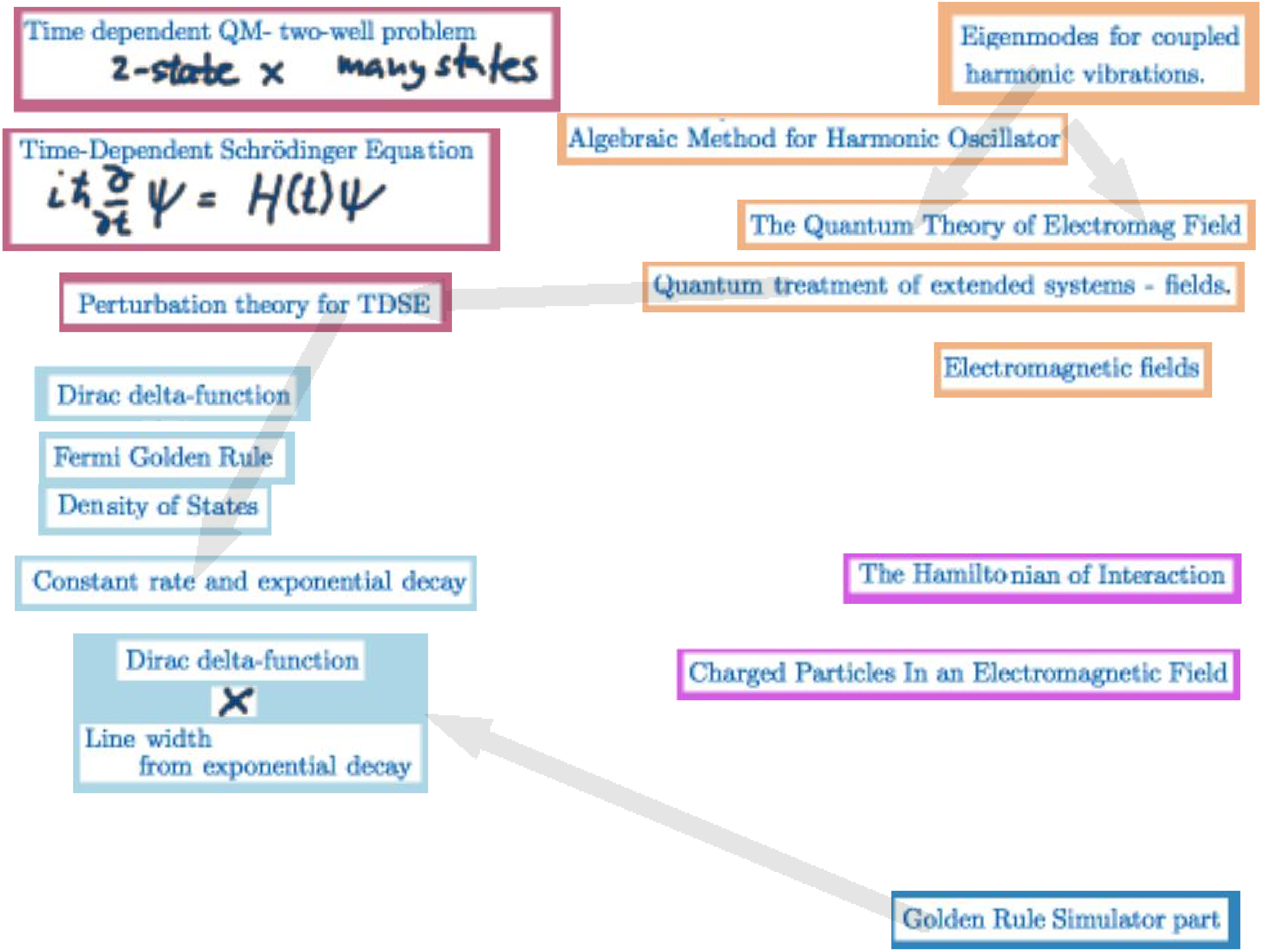
(extra material)

The following 2 slides are
(in ODP - OpenOffice Impress)
a test of designing a presentation of
our very complex topic

(The links from the PDFtalk were copied
and made to lots of small color-coded boxes)

There are 2 such slides - the second will be extended later

Folows: Line profiles Gaussian? – No, Lorentzian – and more



Time dependent QM- two-well problem
2-state x many states
Time-Dependent Schrödinger Equation
$i\hbar \frac{\partial}{\partial t} \psi = H(t)\psi$
Perturbation theory for TDSE
Dirac delta-function
Fermi Golden Rule
Density of States
Constant rate and exponential decay
Dirac delta-function
x
Line width from exponential decay
Eigenmodes for coupled harmonic vibrations.
Algebraic Method for Harmonic Oscillator
The Quantum Theory of Electromag Field
Quantum treatment of extended systems - fields.
Electromagnetic fields
The Hamiltonian of Interaction
Charged Particles In an Electromagnetic Field
Golden Rule Simulator part

Time dependent QM- two-well problem

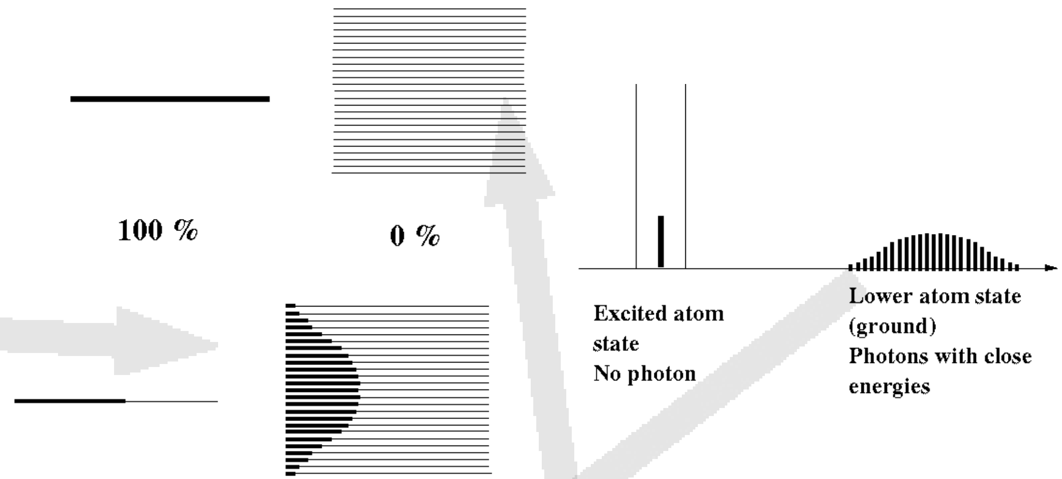
2-state × many states

Golden Rule Simulator part

Time-Dependent Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \psi = H(t)\psi$$

$$i \frac{\mathrm{d}}{\mathrm{d}t} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ . \\ \alpha_n \end{bmatrix} = \begin{bmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ . \\ \alpha_n \end{bmatrix}$$



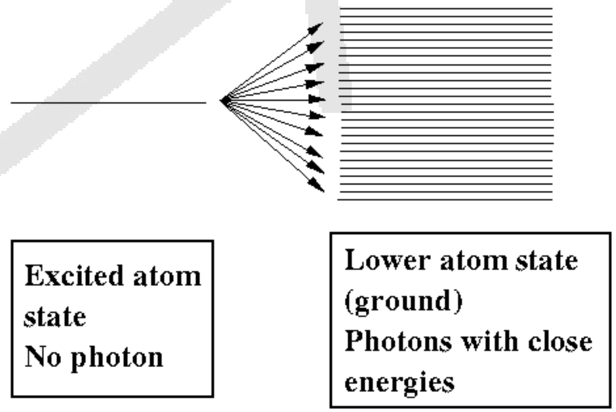
Perturbation theory for TDSE

Dirac delta-function

Fermi Golden Rule

Density of States

$$\frac{dP_i}{dt} = -w$$



Constant rate and exponential decay

$$\frac{dP_i}{dt} = -wP_i$$

Dirac delta-function

×

Line width from exponential decay

The rest of the slides:

Background information

about line shapes, broadening

Lorentz shape Lorentz profile

Line Broadening:
Doppler broadening – Gaussian profile

Voigt profiles (convolution of Lorentz by Gaussian)

(from 2001 talks)

Lorentzian Lineshape

Pressure broadening results from collisions between molecules in a gas. It is the most important source of broadening when pressures are high. The simplest treatment of pressure broadening produces a Lorentzian lineshape centered at the transition frequency ν_0 and given by the functional form

$$\phi(\nu) = \frac{1}{\pi} \frac{\alpha_L}{(\nu - \nu_0)^2 + {\alpha_L}^2}$$

where α_L is the Lorentzian half-width.

$$\begin{aligned} F(\omega) &\approx \tfrac{1}{2} f_0 [\tfrac{1}{2}\gamma - i(\omega - \omega_0)]^{-1} \\ |F(\omega)|^2 &= \frac{{f_0}^2}{\gamma^2} \frac{\frac{1}{4}\gamma^2}{(\omega - \omega_0)^2 + \frac{1}{4}\gamma^2} \\ &= \frac{{f_0}^2}{\gamma^2} \frac{\gamma^2}{4(\omega - \omega_0)^2 + \gamma^2}. \end{aligned}$$

If $f(t)$ is the radiated field, the curve $|F(\omega)|^2$ is known as the Lorentzian lineshape. Collision shortens the duration of emission, widening the peak.

Doppler Lineshape

The broadening of a spectral line as a result of the thermal motion of a gas. Doppler line-broadening results from the random motion of radiating molecules, and is therefore dependent on temperature. The Doppler lineshape takes the form of a Gaussian,

$$\phi(\nu) = \frac{1}{\alpha_D}\sqrt{\frac{\ln 2}{\pi}}\, e^{-(\ln 2)(\nu-\nu_0)^2/\alpha_D{}^2},$$

where the Doppler half-width is given by

$$\alpha_D \equiv \frac{\nu_0}{c}\sqrt{\frac{2\ln 2 RT}{M}} = 1.131 \times 10^{-8}\sqrt{\frac{T}{M}}\,\nu_0$$

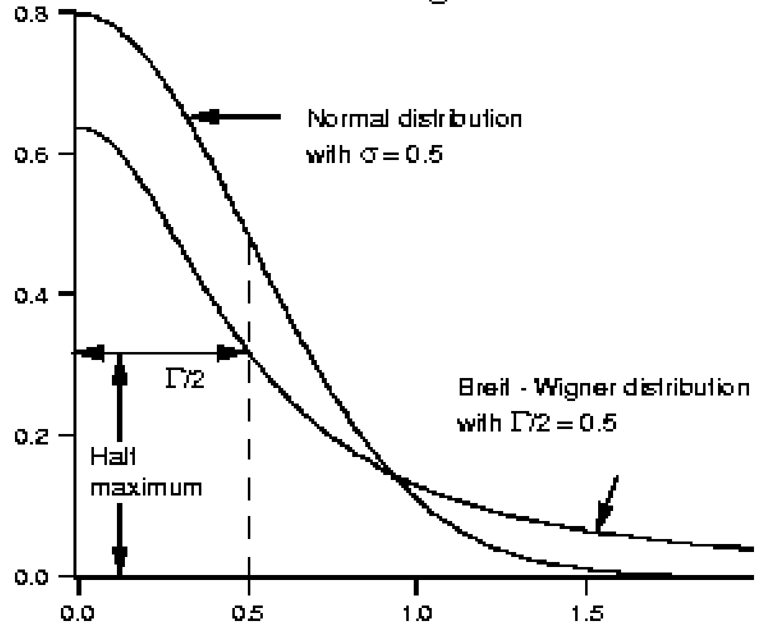
(Townes and Schawlow 1975, pp. 337-338). In (0), R is the universal gas constant, T is the thermal temperature, M is the mean molar mass (in kg), and c is the speed of light.

Breit-Wigner Distribution (also known as Lorentz Distribution)

The Breit-Wigner (also known as Lorentz) distribution is a generalized form originally introduced ([Breit36], [Breit59]) to describe the cross-section of resonant nuclear scattering in the form

$$\sigma(E) = \frac{\Gamma}{(2\pi)[(E-E_0)^2 + (\Gamma/2)^2]} \ ,$$

The equation follows from that of a harmonic oscillator with damping, and a periodic force. A normal (Gaussian) distribution decreases much faster in the tails than the Breit-Wigner curve.



The distribution is fully defined by E_0, the position of its maximum (about which the distribution is symmetric), and by Γ , the full width at half maximum (FWHM), as obviously

$$\sigma(E_0) = 2\sigma(E_0 \pm \Gamma/2) \ .$$

Γ and the lifetime τ of a resonant state are related to each other by Heisenberg's uncertainty principle ($\Gamma\tau = h/2\pi$).

After Rudolf K. Bock, 7 April 1998 http://rkb.home.cern.ch/rkb/AN16pp/AN16pp.html

Voigt Lineshape

The Voigt profile is the spectral line shape which results from a superposition of independent Lorentzian and Doppler line broadening mechanisms (e.g., Armstrong 1967). It is given by the expression

$$\phi(\nu) = \frac{1}{\alpha_D}\sqrt{\frac{\ln 2}{\pi}}K(x, y),$$

where $K(x, y)$ is the "Voigt function"

$$K(x, y) \equiv \frac{y}{\pi}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{y^2 + (x - t)^2}\,dt.$$

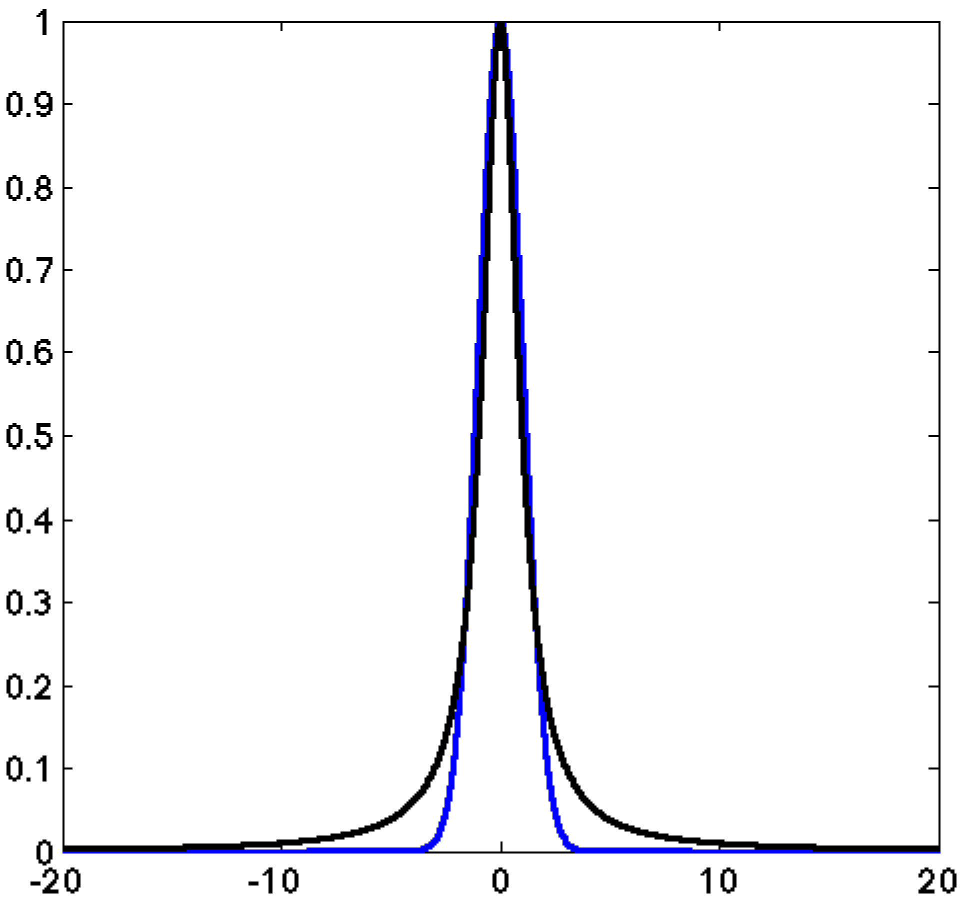
In (2),

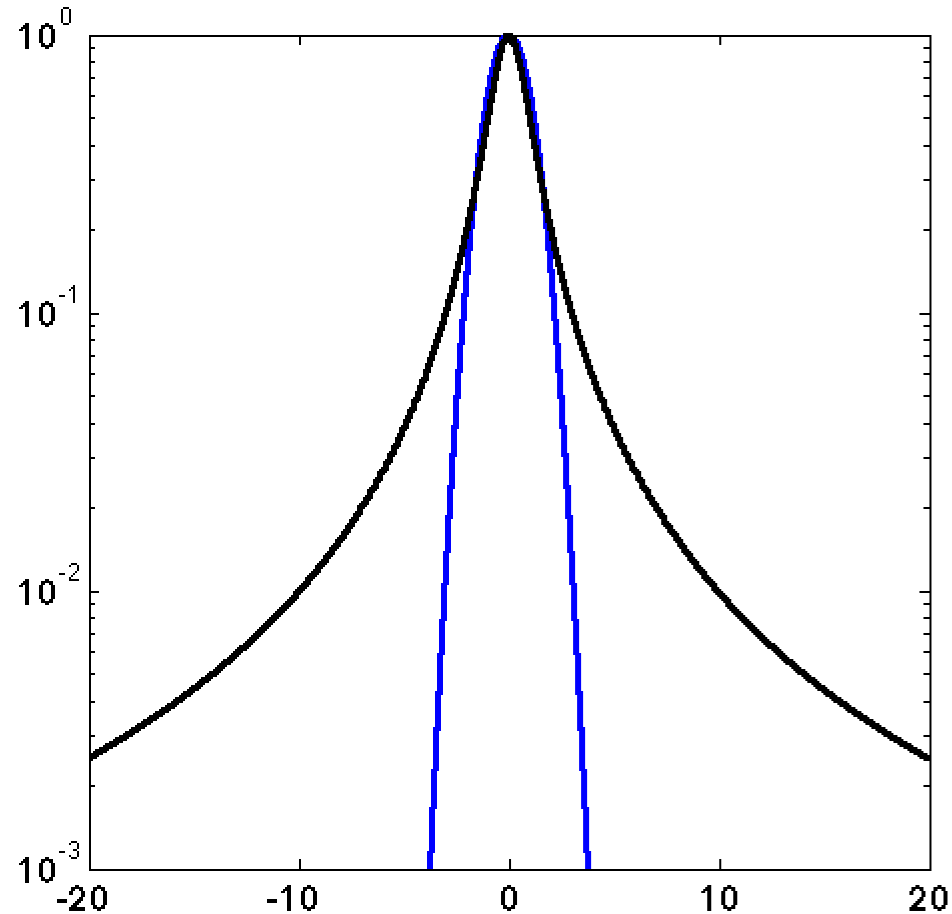
$$y \equiv \frac{\alpha_L}{\alpha_D}\sqrt{\ln 2}$$

is the ratio of Lorentz to Doppler widths and

$$x \equiv \frac{\nu - \nu_0}{\alpha_D}\sqrt{\ln 2}$$

is the frequency scale in units of Doppler lineshape half-width α_D .

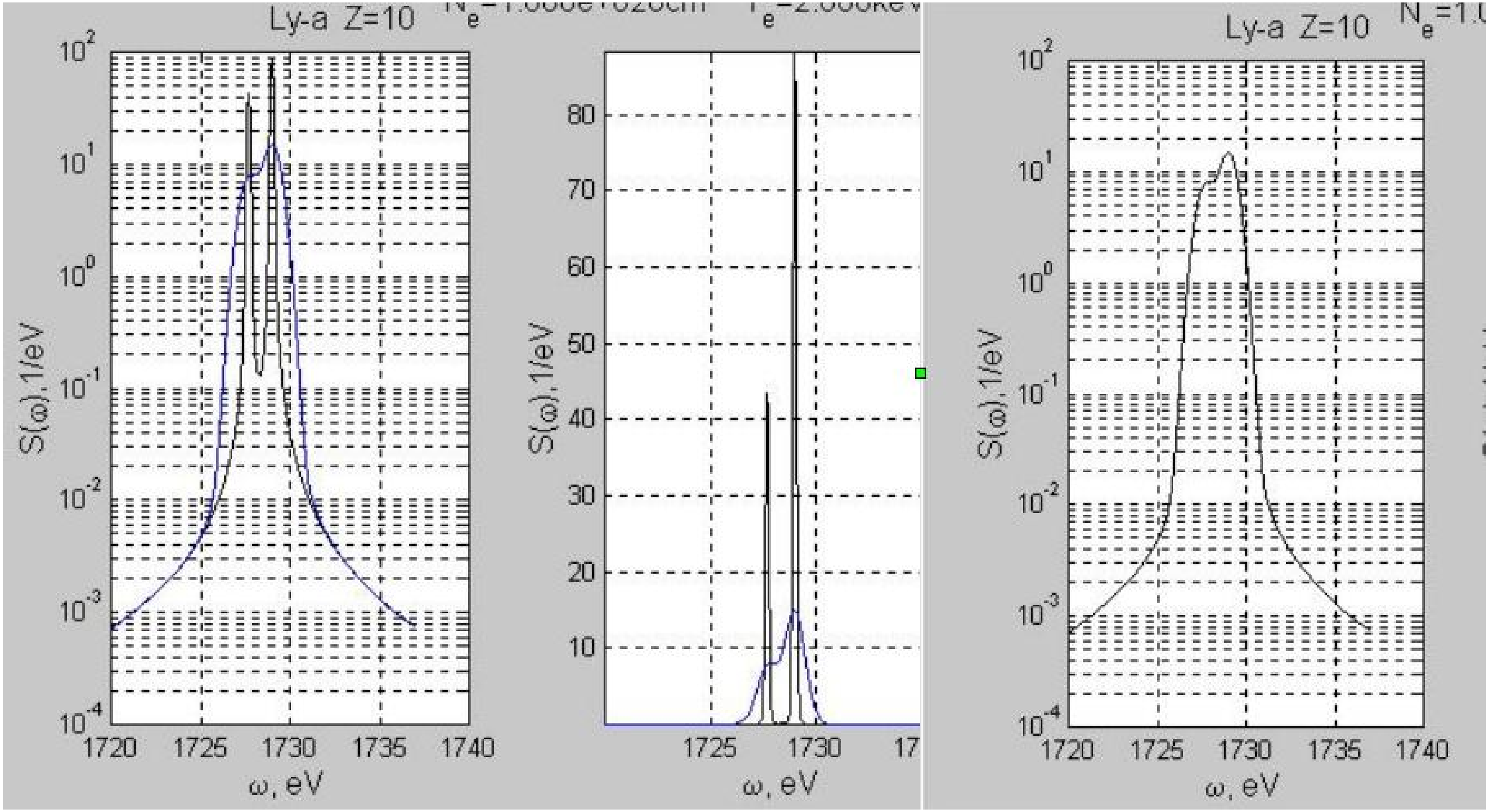




Matlab code

```
x=-20:0.01:20;
gaushalf=1; lorhalf=1;
%
 gaus=exp(-(x/gaushalf*0.7).^2);
 lorentz=1./((x/lorhalf).^2+1);
%
```

```
%
figure(1)
c=plot(x,gaus,'b-',x,lorentz,'k-');set(c,'linewidth',2)
set(gca,'fontsize',18)
set(gcf,'color','white')
figure(2)
d=semilogy(x,gaus,'b-',x,lorentz,'k-');set(gca,'ylim', [0.001 1  ]);;set(d,'linewidth',2)
set(gca,'fontsize',18)
set(gcf,'color','white')
```



Voigt profiles, comparisons of 2 Lorentz lines and their broadened versions. (Dopler broadening in plasmas.

High frequency; very high temperature
(from our theoretical work)