PHY208 – atoms and lasers
Lecture 4

Introduction to spectroscopy

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What is spectroscopy ?

Analysis of the energy distribution of a (light) signal

What fraction of the signal is carried by modes with energy between hν and h(ν+dν) ?

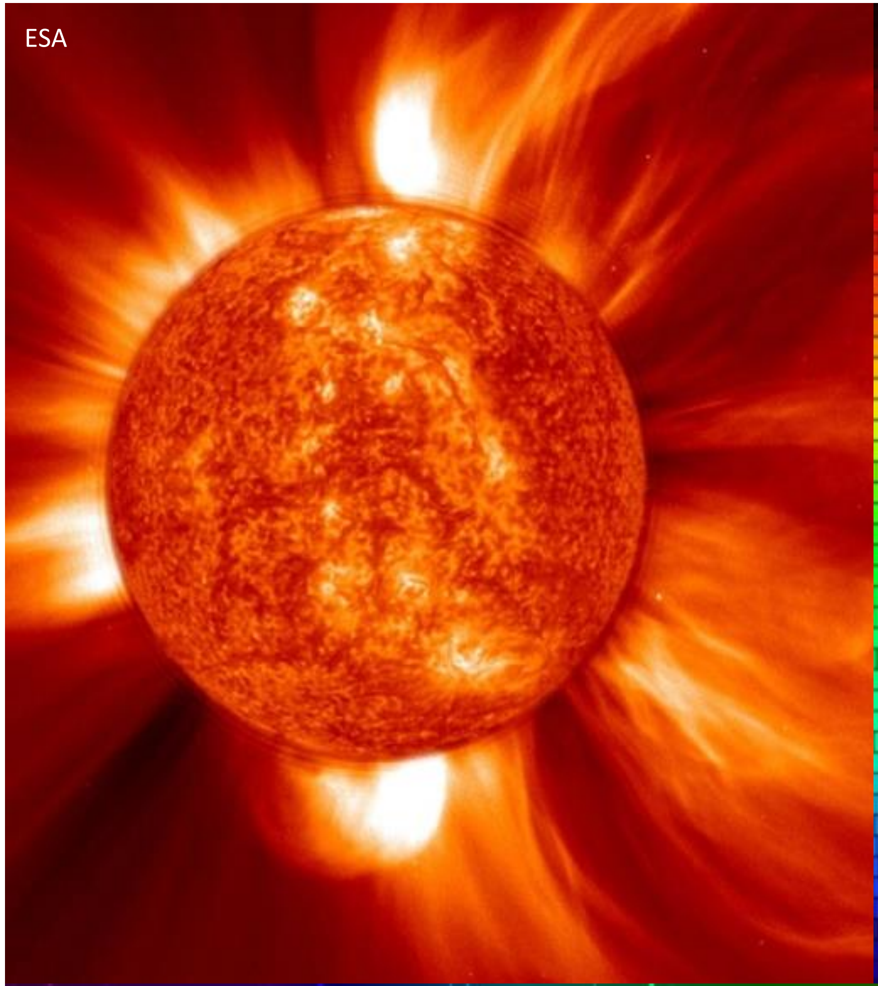
What is the ability of the system under scrutiny to emit (or absorb) light at a given wavelength ?

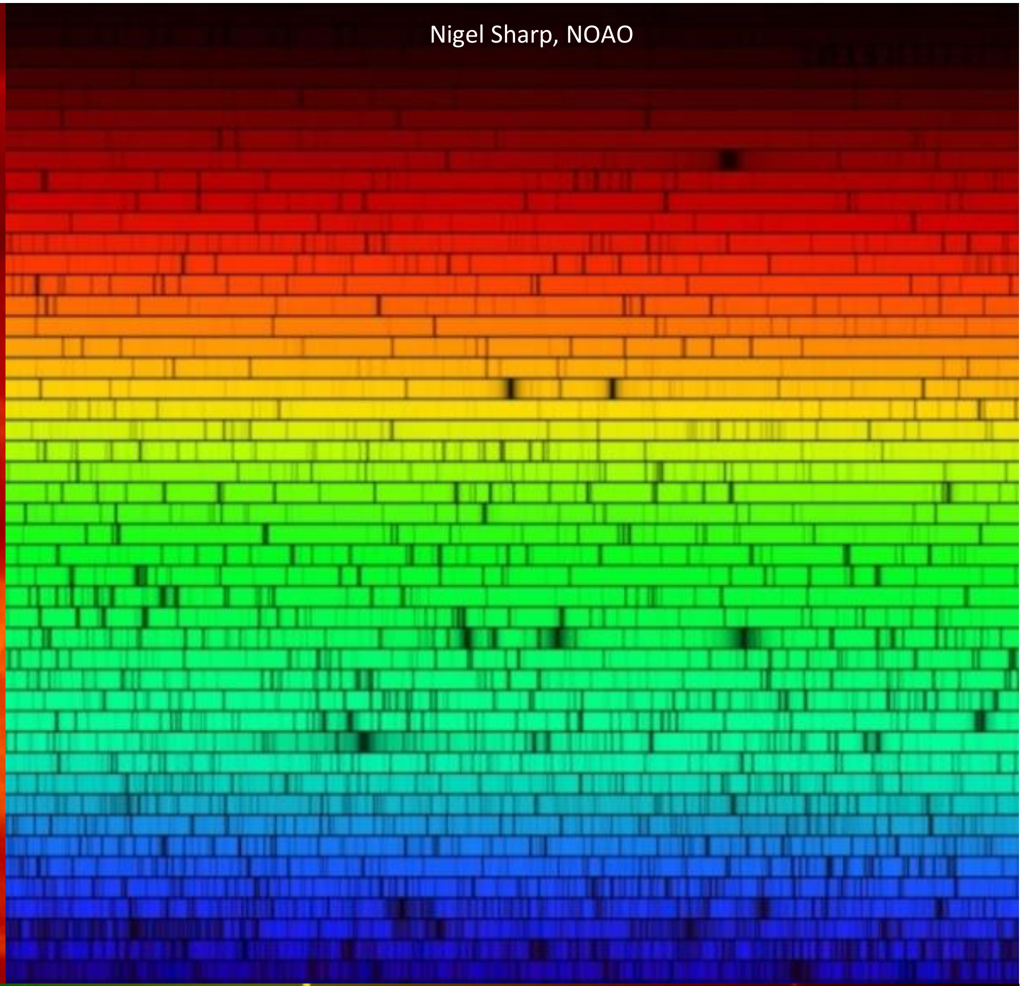
The atomic barcode

Spectral analysis of sunlight

Fraunhofer lines
1814

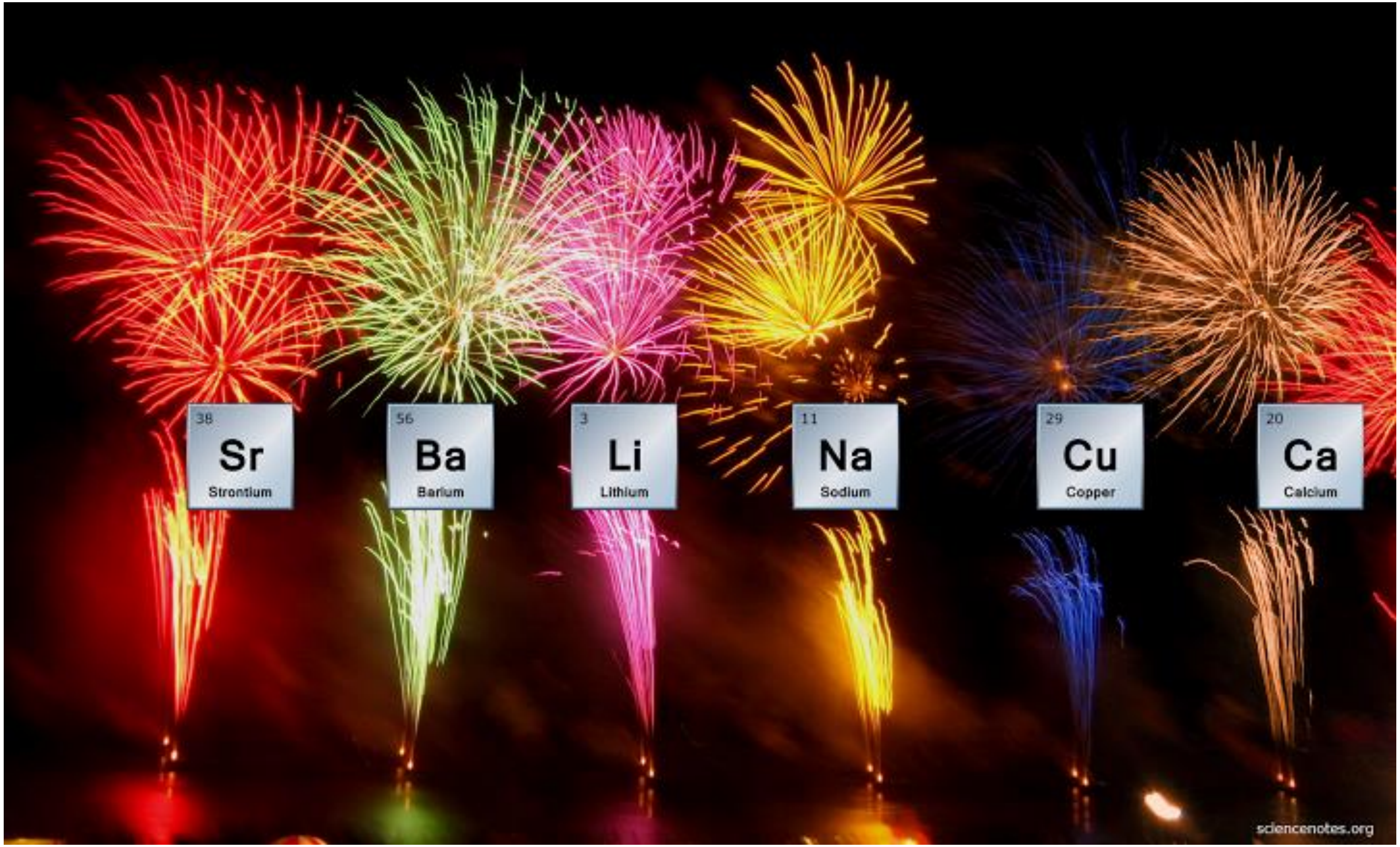
Norman Lockyer
1868



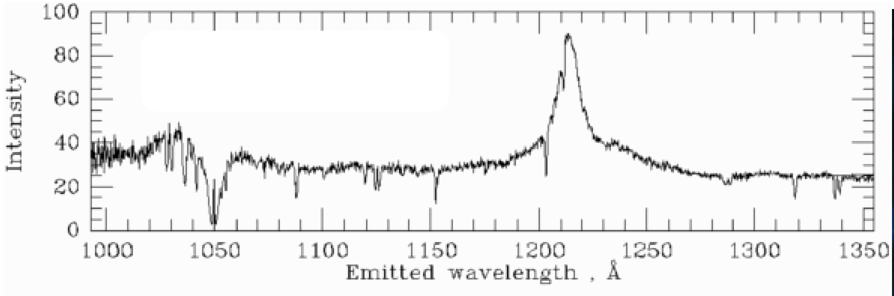


The atomic barcode

Practical applications

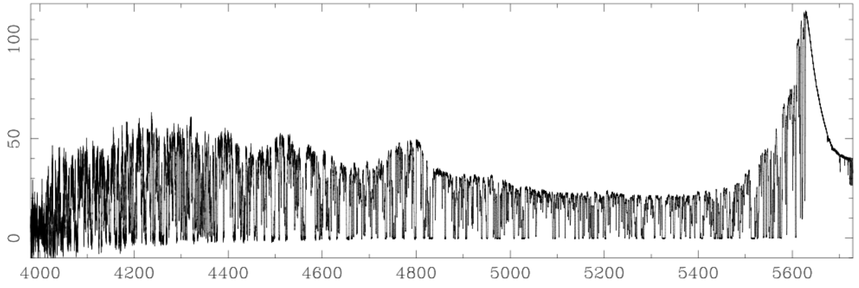


Probing the Universe – Lyman-alpha forest



Spectrum from
nearby star

Spectrum from
a (very) distant quasar



Outline of lecture 4

I. Light emitting transitions

Which light is actually emitted by a sample ?

II. Line width : broadening effects

What is the detailed shape of an atomic line?
How is this shape affected by the environment ?

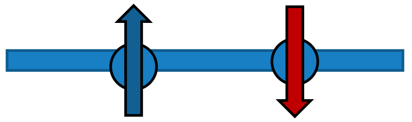
III. Line shift : the Zeeman effect

How does the environnement shifts the emissions ?
How does the emissions probe the environnement ?

Not addressed in this lecture : experimental techniques

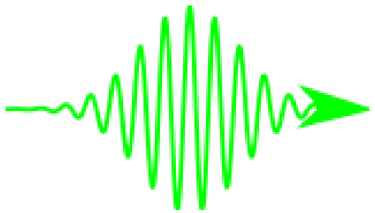
Optical transitions

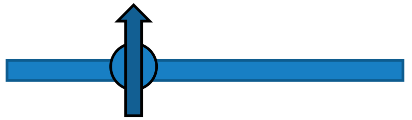
What light is actually emitted ?



What are the atomic states ?

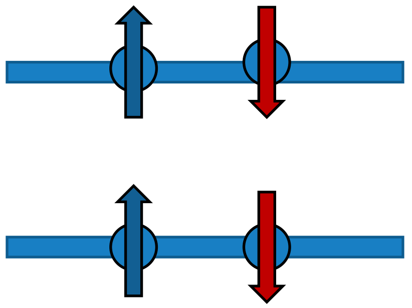
(Transition from one state to another)





How are these states populated ?

(Absorption from an occupied low energy state to an empty high energy state.
Emission from an occupied high energy state to an empty low energy state.)



What light correspond to this transition ?

(No mode, no transition)

Energy states

Internal structure

Attractive Coulomb potential from nucleus

Quantitative treatment in lecture 6

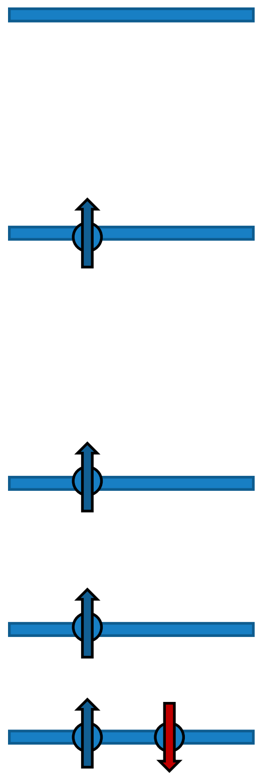
Repulsive interaction from the other electrons

(Interaction due to the spin of the electron)

H_{atom}

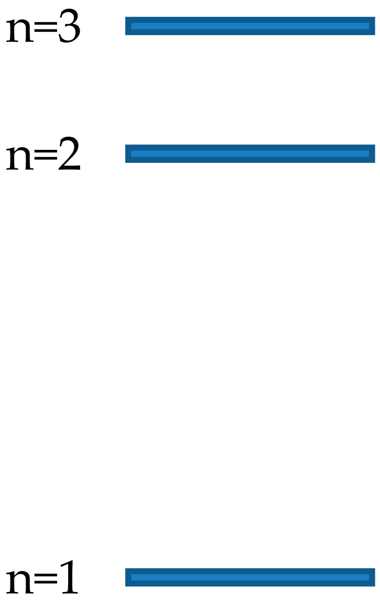
Energy levels
for the atom ‘‘alone’’

(n, L, m, S…)



Example: atomic states for Hydrogen

Results from the most simple Schrodinger model (full derivation in lecture 6)



Energy levels :

$$E_n = -\frac{1}{n^2}\frac{m_e e^4}{2\hbar^2}$$

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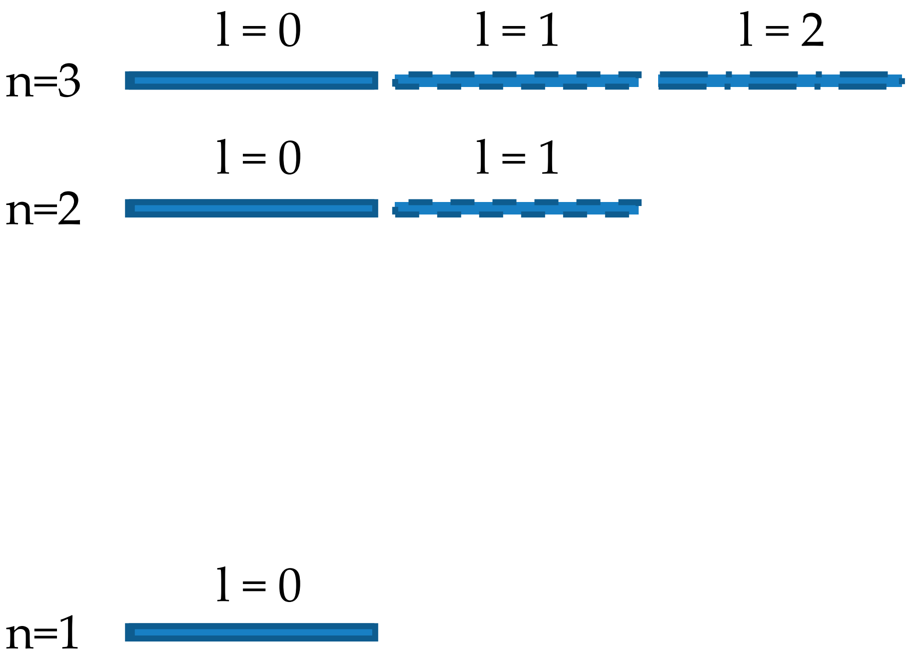

Energy levels : $E_n = -\frac{1}{n^2}\frac{m_e e^4}{2\hbar^2}$

Total angular momentum : $L^2 = l(l+1)\hbar^2$

$l \leq n-1$

Label : S (l=0), P (l=1), D(l=2), f…

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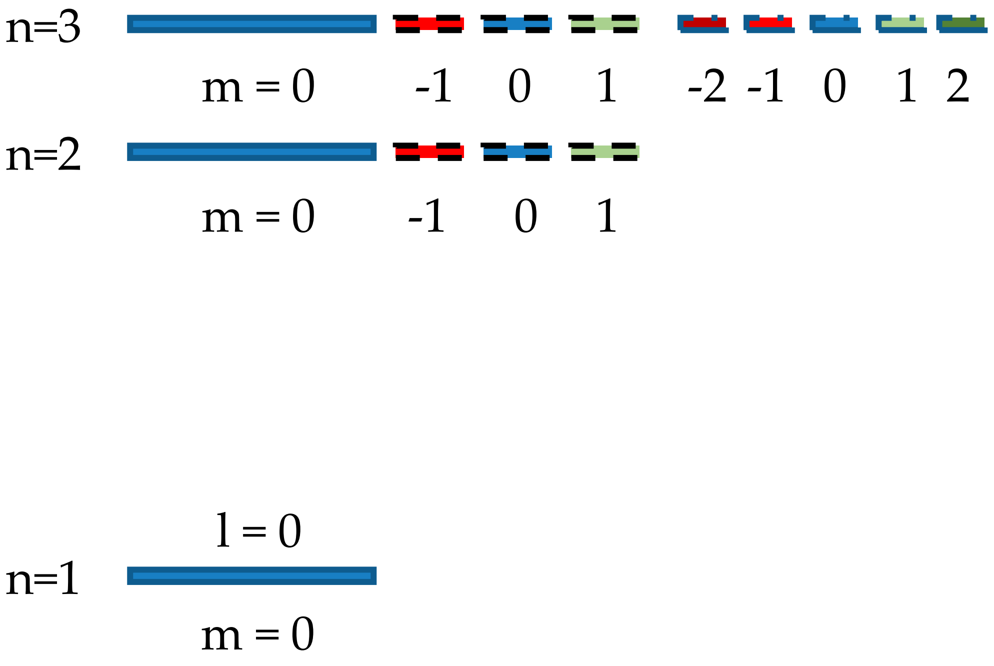

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Total angular momentum : $L^2 = l(l+1)\hbar^2$

$l \leq n-1$

Label : S (l=0), P (l=1), D(l=2), f…

Angular momentum along z : $L_z = m\hbar$

$-l \leq m \leq +l$

Each energy state is degenerated n² times.

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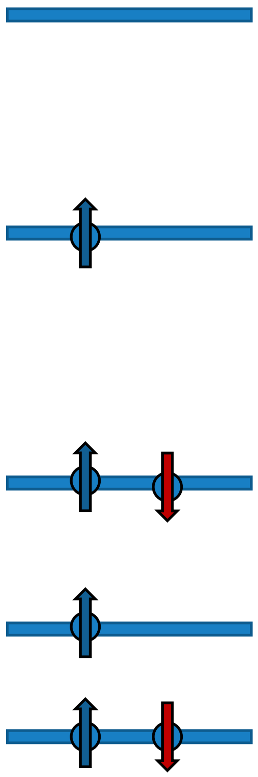


External environment

Magnetic field

Electric field

Light

Interaction with other atoms

$H_{\mathrm{env.}}$

Influence of
external parameters

(**R**, **P**)

Light: allowed and forbidden transitions

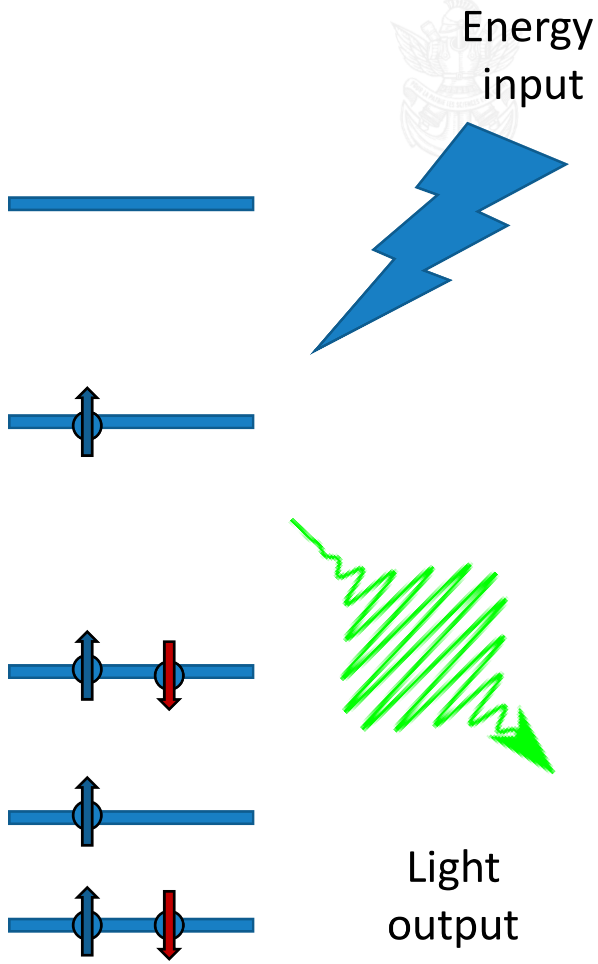
Selection rule : basic conservation *(semi quantum or quantum model)*	*Before* Atom in an excited state 0 photon	*After* Atom in a ground state 1 photon
Energy $\hbar\omega = E_f - E_i$	E_i	$E_f + \hbar\omega$
Angular momentum	$m_i\hbar$	$m_f\hbar + L_{z,\,\text{photon}}$

$$m_f - m_i = 0$$
$$m_f - m_i = \pm 1$$

π polarization → $L_z = 0$
$\sigma_\pm$ polarization → $L_z = \pm\hbar$

Available modes

How many modes satisfy these selection rules ?



Populations: (whatever)-escence

Energy in, photon out.

Incandescence

Energy from thermal agitation $\frac{n(E+dE)}{n(E)} = e^{-\frac{dE}{kT}}$

Photo-luminescence

Energy from light absorption

Fluorescence

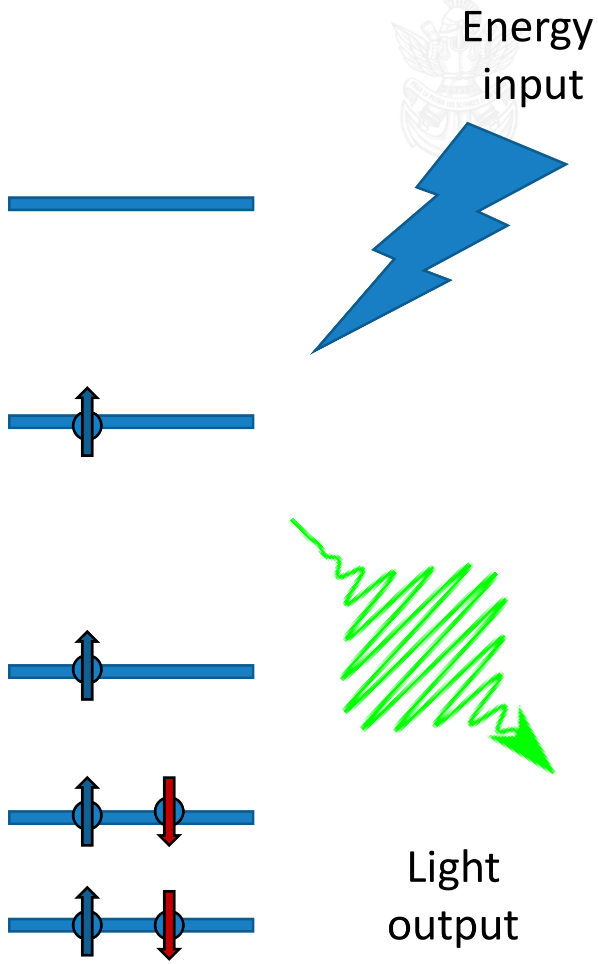
Phosphorescence

Electro-luminescence

Energy from electronic injection

Cathodo-luminescence

Energy from electron beam



(Comment on absorption and emission)

What light is actually emitted ? $\Leftrightarrow$ **What light could be absorbed ?**

2 levels system (Lecture 1) *(semi quantum model)*	Absorption ↔ Stimulated emission $B_{eg} = B_{ge}$	Absorption ↔ Spontaneous emission $\frac{A_{eg}}{B_{ge}} = \frac{8\pi\nu^2}{c^3}$
More generic approach *(classical model)*	*Blackbody*	*Greybody*
Absorptivity $\frac{\#\,\text{absorbed photons}\,@\nu}{\#\,\text{incident photons}\,@\nu}$	$\alpha_{\text{BB}}(\nu) = 1\,\forall\nu$	$\alpha(\nu)$
Emissivity	$\phi_{\text{BB}}(\nu) = \frac{2}{h^2c^2}\frac{(h\nu)^2}{e^{\frac{h\nu}{kT}}-1}$	$\phi(\nu) = \epsilon(\nu) \times \frac{2}{h^2c^2}\frac{(h\nu)^2}{e^{\frac{h\nu}{kT}}-1}$

Kirchhoff law of radiation : $\alpha(\nu) = \epsilon(\nu) \quad \forall\nu$

(Note for the future)

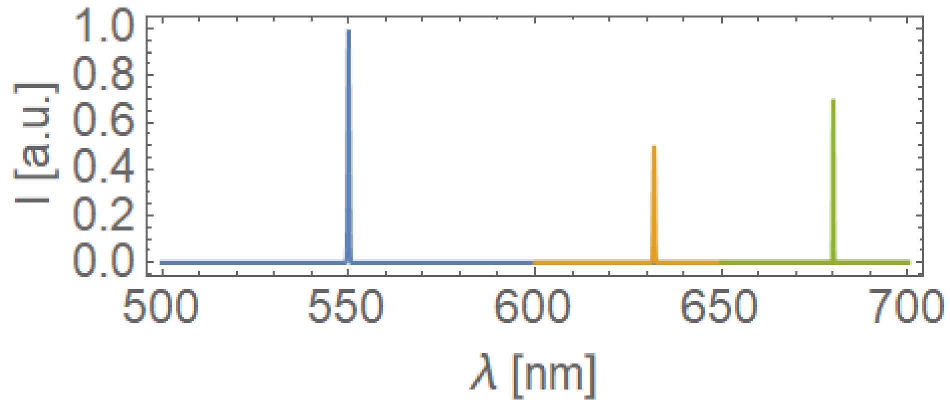
How to calculate quantitatively these rates : Fermi Golden Rule

$$R(h\nu) \propto \sum_{i,j\neq i} |\langle\psi_j| - e\hat{\mathbf{r}}.\mathbf{E}\,|\psi_i\rangle|^2\,\delta\left(E_j - E_i - h\nu\right)\,p_i\left(1 - p_j\right)$$

Full quantum expression for the spontaneous decay rate :

$$\Gamma_{\text{vac}} = \frac{|\langle g|e\hat{\mathbf{r}}|e\rangle|^2 \omega_{eg}^3}{3\pi\epsilon_0\hbar c^3}$$

Outline of lecture 4



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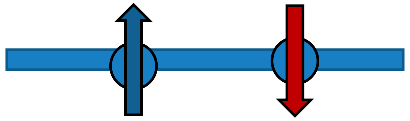
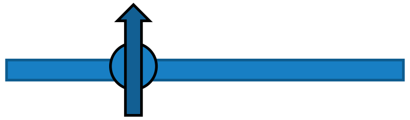
Intrinsic broadening

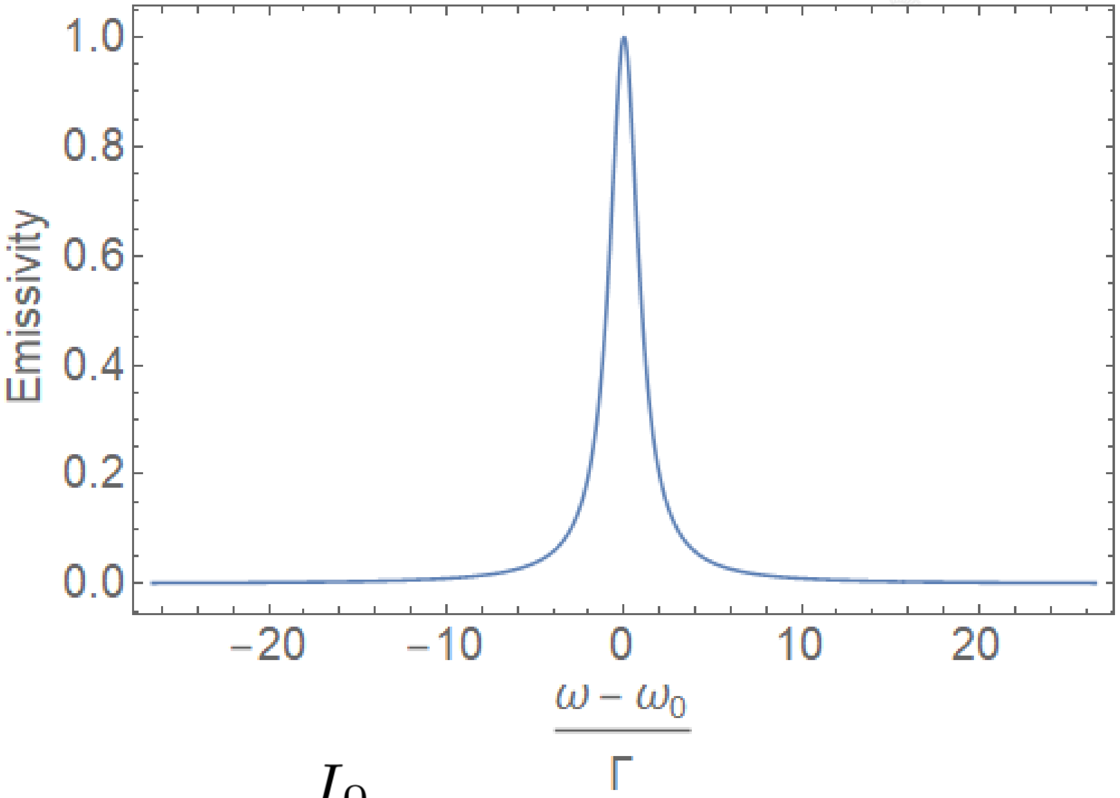
Reminder on Heisenberg inequality



$$\Delta E \Delta t \geq \frac{\hbar}{2}$$



$$\hbar \Delta\omega \geq \frac{\hbar\Gamma}{2}$$

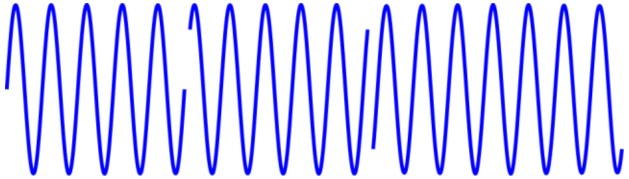


Reminder on Wiener Kitchine theorem

Power spectrum = FT (autocorrelation function)

$$I(\omega) = \frac{1}{2\pi}\frac{2}{\mu_0 c}\int d\tau \langle \mathcal{E}^*(t)\mathcal{E}(t+\tau)\rangle_t \, e^{i\omega\tau} = \frac{I_0}{1+4\left(\frac{\omega-\omega_0}{\Gamma}\right)^2}$$

Wavetrain model



Comment on spontaneous emission

Consider an atom in an energy eigenstate of H_{atom}

$$i\hbar\frac{\partial}{\partial t}\psi = H_{\text{atom}}\psi \Rightarrow \psi(t) = \psi_0 e^{-iEt/\hbar}$$

the atom remains in the eigenstate forever…

What actually causes spontaneous emission ? What gives the decay rate Γ ?

Collision between atoms

Collisionnal broadening

Nature of interactions, density (pressure)…

$$\Gamma_{\text{coll}}$$

But what if the atom is alone ?

Need quantum description for the field.

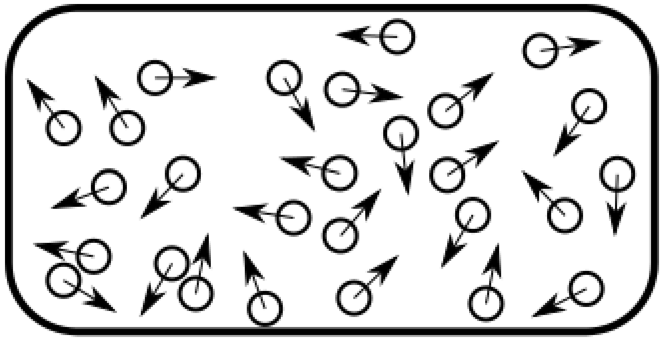
$$\Gamma_{\text{vac}} = \frac{\left|\langle g|\hat{\mathbf{D}}|e\rangle\right|^2 \omega_{eg}^3}{3\pi\epsilon_0\hbar c^3}$$

$$\simeq 1 - 100\,\text{MHz}$$

for an allowed atomic transition

$$\Gamma = \Gamma_{\text{coll}} + \Gamma_{\text{vac}} + \ldots$$

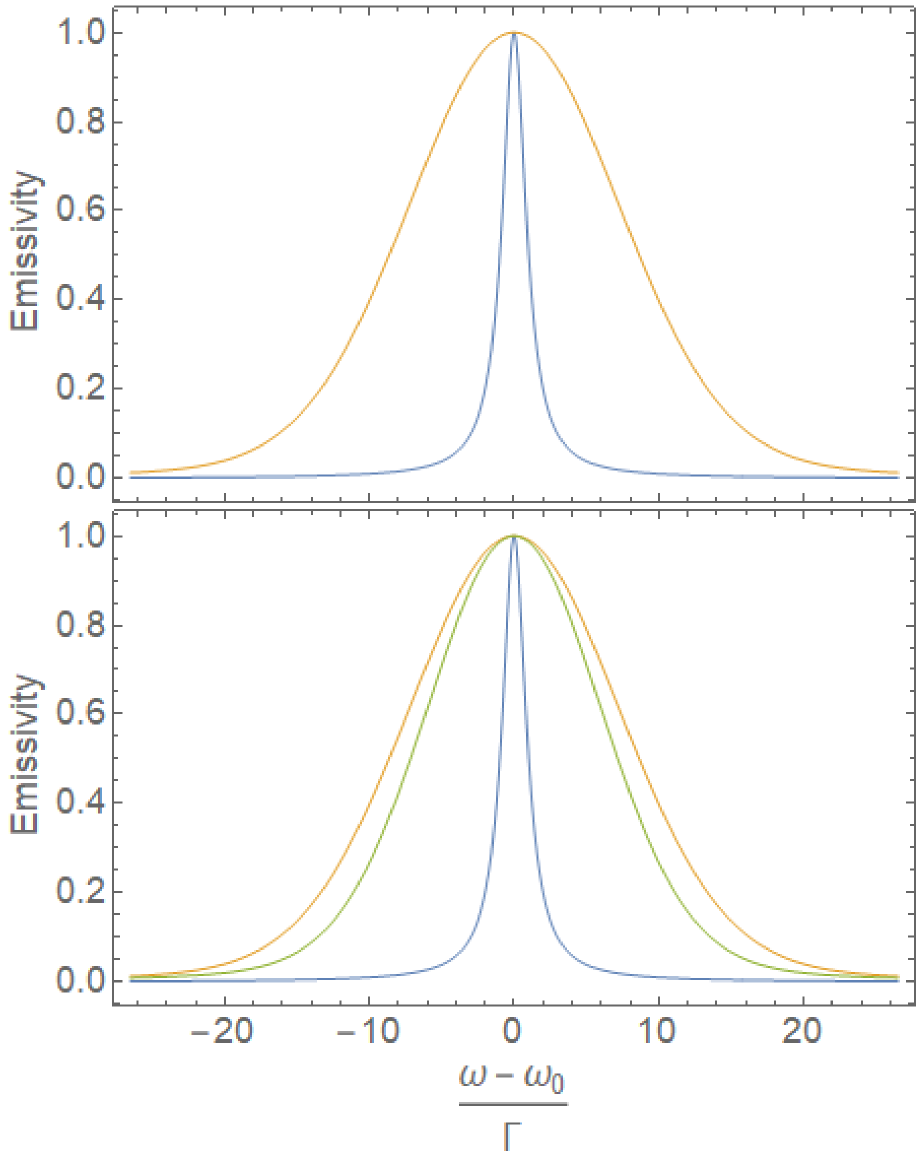
Thermal broadening



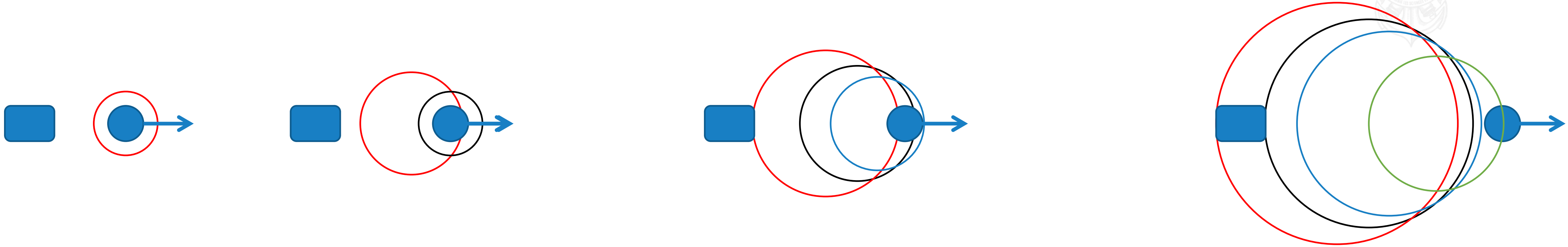
Previous model vs actual result for a bunch of atom…

- Not a Lorentzian shape
- Much broader than Γ
- Depends on the temperature…

Should include the thermal motion of the atoms !



The Doppler effect

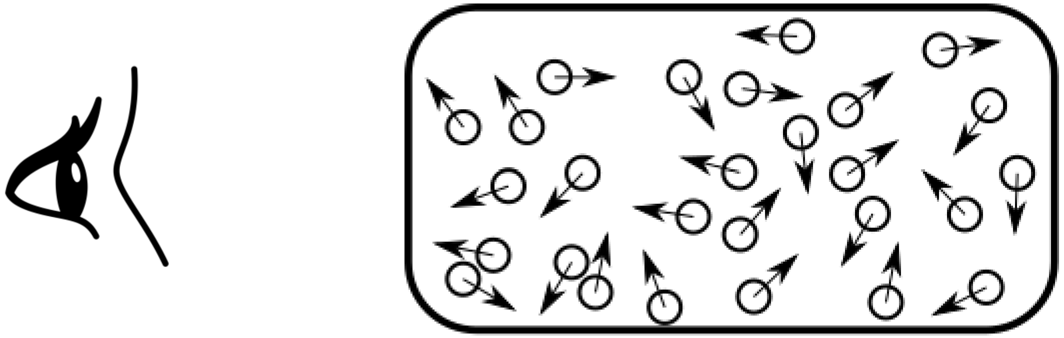


Emission 1	Emission 2	Reception 1	Reception 2
t_1^{em}	t_2^{em}	$t_1^{\mathrm{rec}} = \left(1 + \frac{V}{c}\right) t_1^{\mathrm{em}} + \frac{d_0}{c-V}$	$t_2^{\mathrm{rec}} = \left(1 + \frac{V}{c}\right) t_2^{\mathrm{em}} + \frac{d_0}{c-V}$

Doppler Frequency shift :

$$\omega = \frac{\omega_0}{1+\frac{V}{c}}$$

Doppler broadening

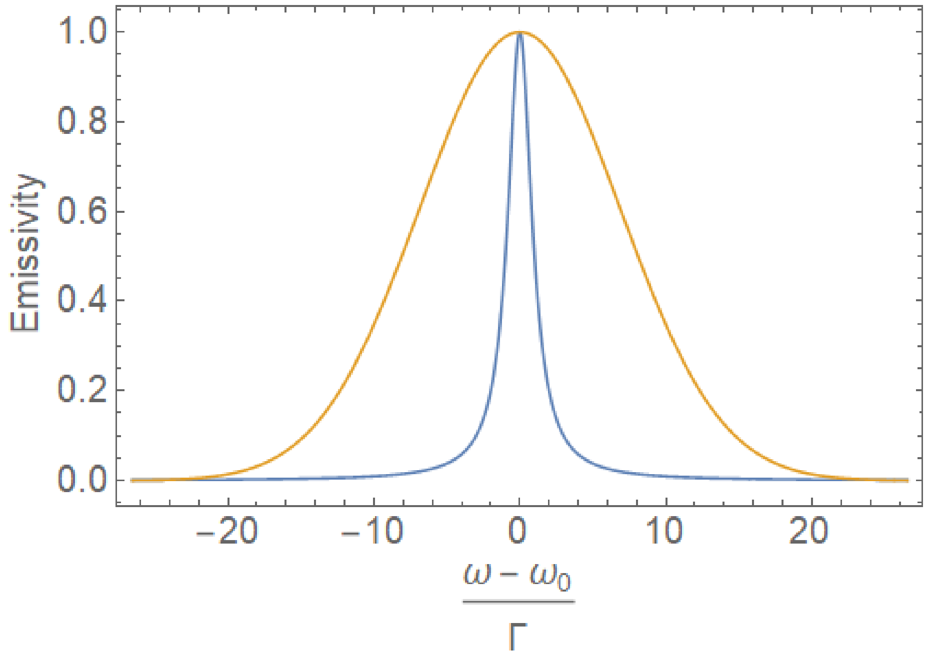


$$I_{\text{tot}}(\omega) = \int dv_x dv_y dv_z \, I_{\text{at}}\left(\omega\left(1+\frac{v_x}{c}\right)\right) \, n_{\text{at}}(\mathbf{v})$$

Thermal distribution $\quad n_{\text{at}}(\mathbf{v}) \propto \exp\left(-\frac{\frac{1}{2}m(v_x^2+v_y^2+v_z^2)}{kT}\right)$

Considering sharp emission profile (atomic emission @ω_0 only) $\quad I_{\text{at}}(\omega) \propto \delta(\omega-\omega_0)$

$$I_{\text{tot}}(\omega) \propto \int dv_x \, \delta\left(v_x - c\frac{\Delta\omega}{\omega}\right) \, n_{\text{at}}(\mathbf{v})$$



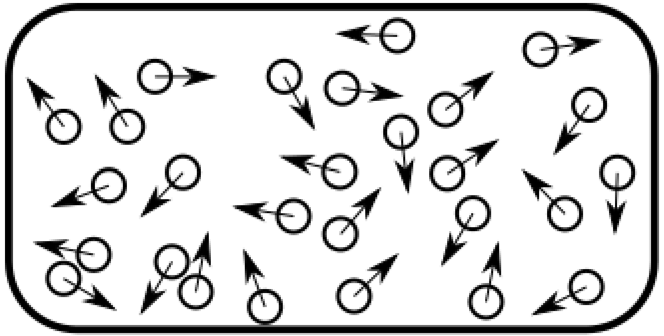
Thermal broadening:

$$I_{\text{tot}} \simeq \frac{I_0}{\sqrt{2\pi\Delta\omega^2}} \exp\left(-\frac{(\omega-\omega_0)^2}{2\Delta\omega^2}\right)$$

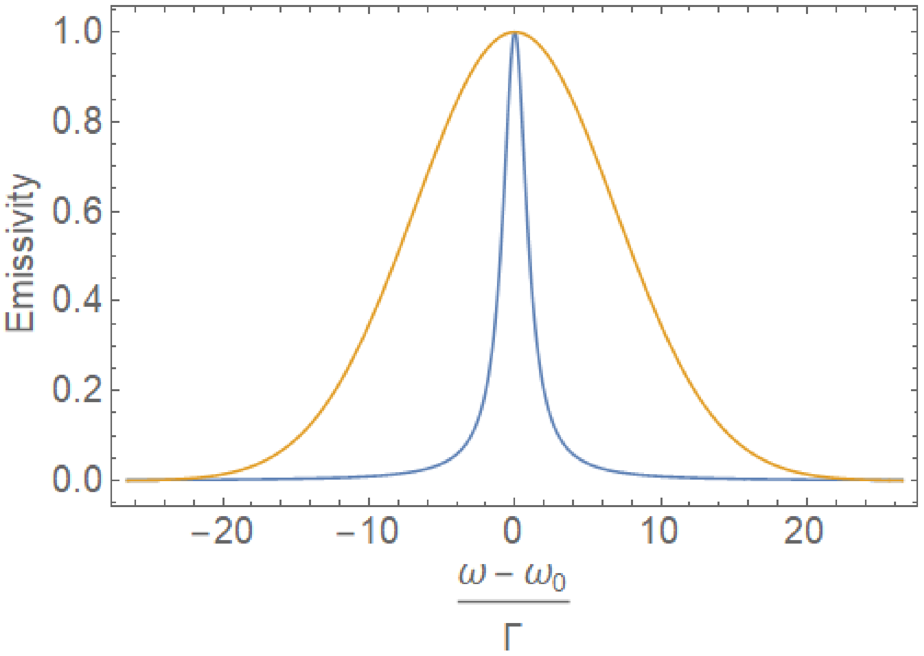
with $\quad \Delta\omega = \omega_0\sqrt{\frac{k_B T}{mc^2}}$

$\simeq 1\,\text{GHz}$

Voigt profile



$$I_{\rm tot}(\omega) = \int dv_x dv_y dv_z\, I_{\rm at}\left(\omega\left(1+\frac{v_x}{c}\right)\right)\, n_{\rm at}\left(\mathbf{v}\right)$$



Considering sharp emission profile (atomic emission @ω_0 only)

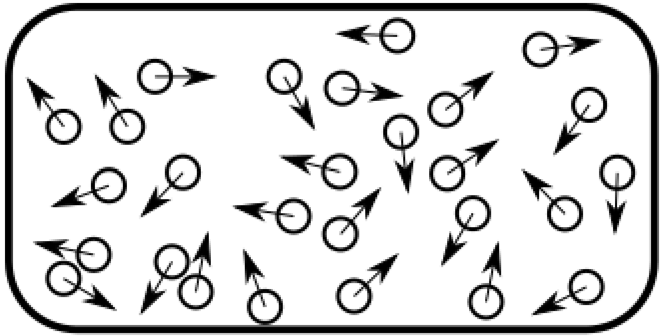
$$I_{\rm tot}(\omega) \propto \exp\left(-\frac{1}{2}\frac{mc^2}{k_B T\omega_0^2}\left(\omega-\omega_0\right)^2\right)$$

Gaussian Doppler profile : $\Delta\omega = \sqrt{\frac{k_B T\omega_0^2}{mc^2}}$

Considering actual Lorentzian emission profile

Voigt profile (no analytical expression)

Voigt profile



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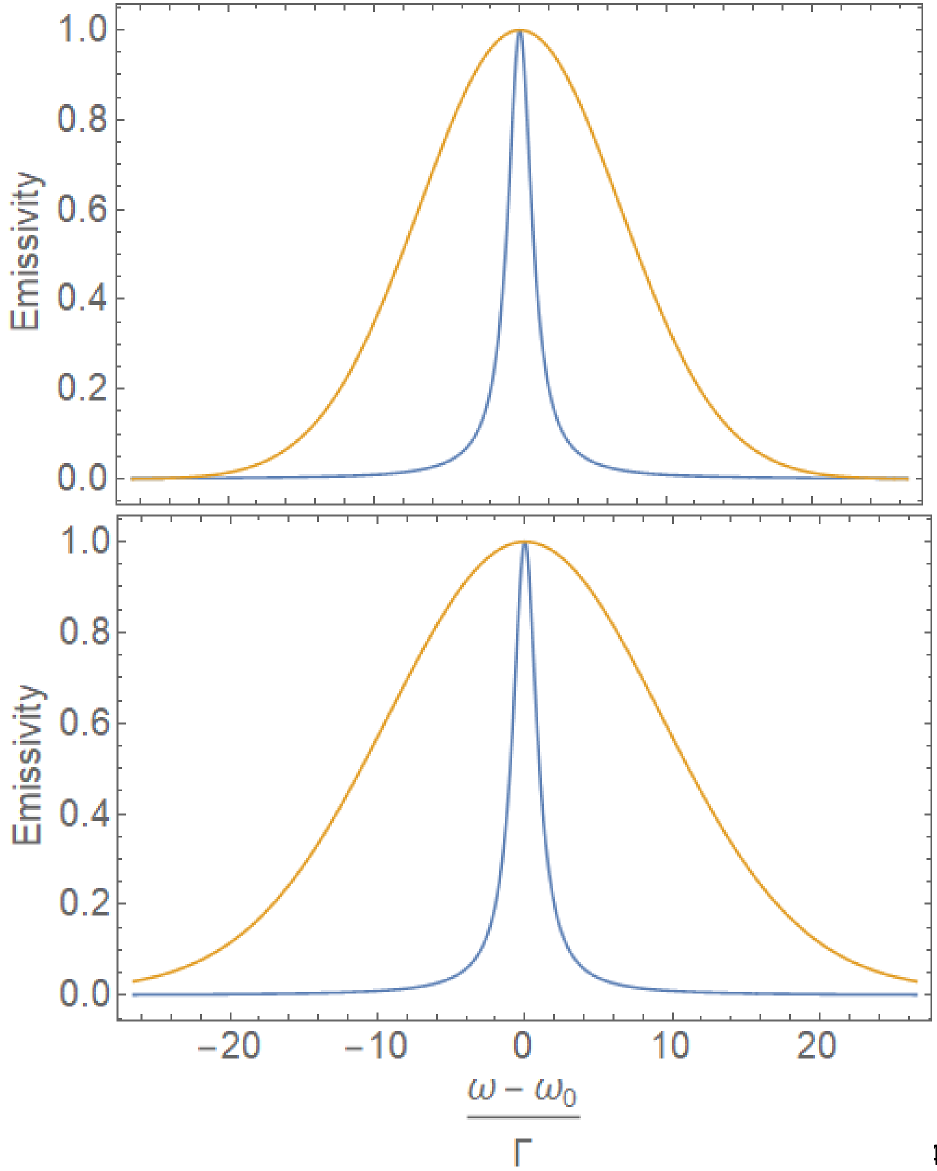

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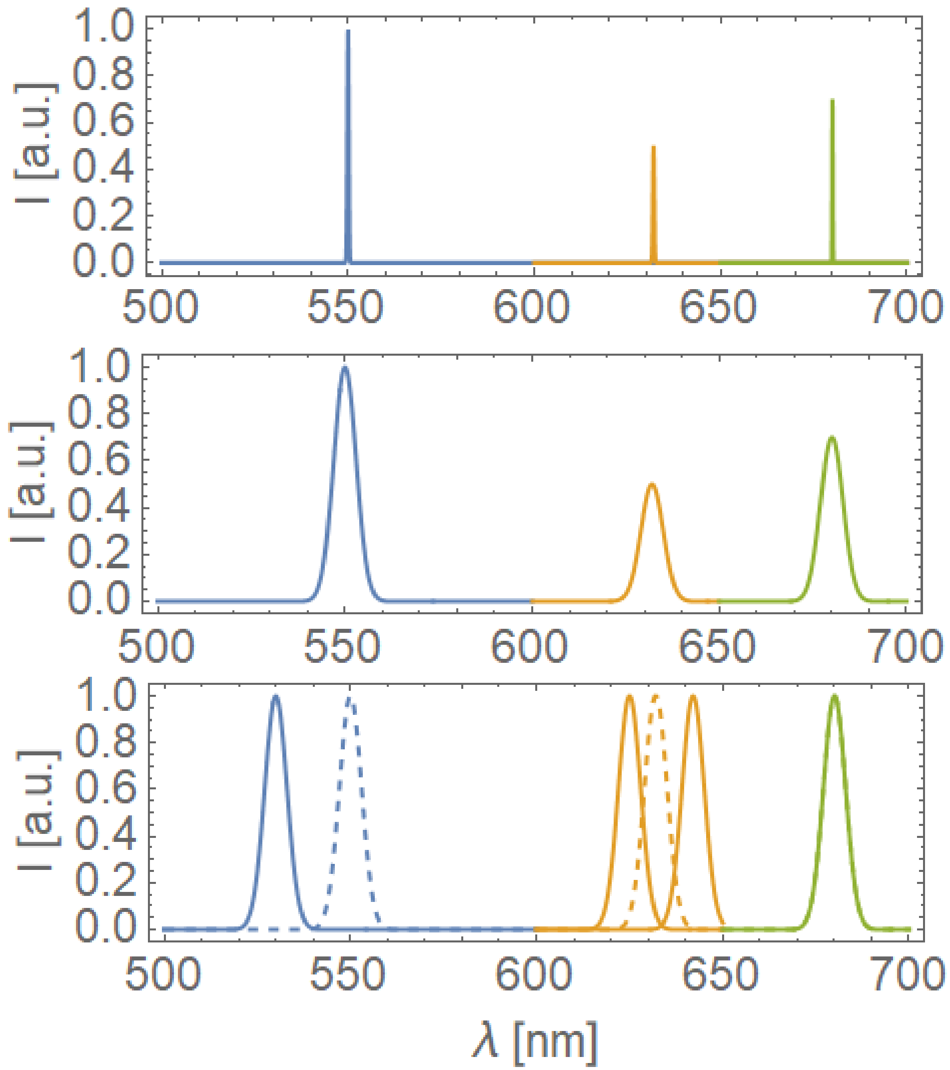
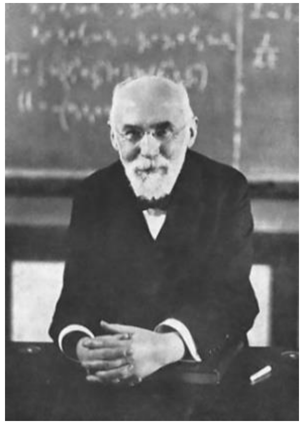
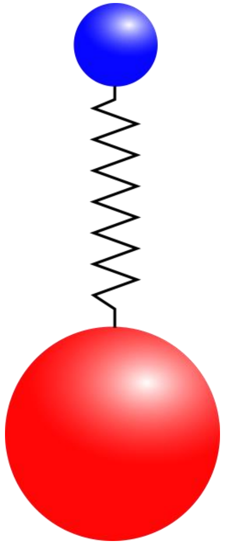


Zeeman effect (classical)



$$m_e \frac{d^2}{dt^2}\mathbf{r} = -m_e\omega_0^2\mathbf{r} - q\mathbf{v}\times\left(B_{\text{ext}}\mathbf{u_z}\right)$$



Motion along z

$$\ddot{z} + m\omega_0^2 z = 0$$

Resonant frequency :

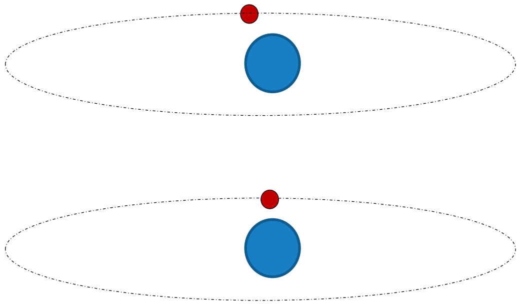
$$\omega_0$$

Motion in the transverse plane

$$\begin{cases} \ddot{x} + \omega_0^2 x + \frac{qB}{m} y = 0 \\ \ddot{y} + \omega_0^2 y - \frac{qB}{m} x = 0 \end{cases}$$

Resonant frequency :

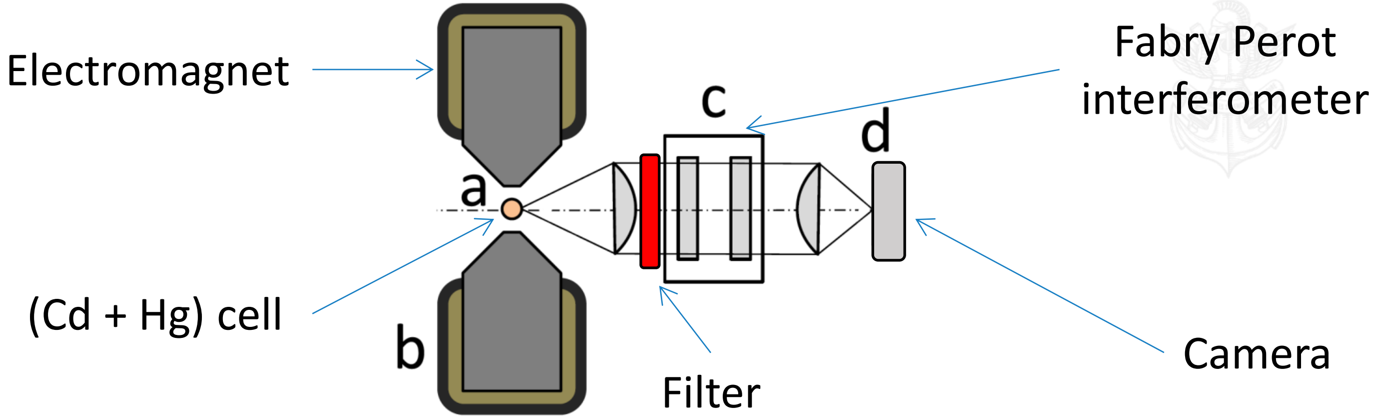
$$\omega_\pm = \omega_0 \pm \frac{qB}{2m}$$



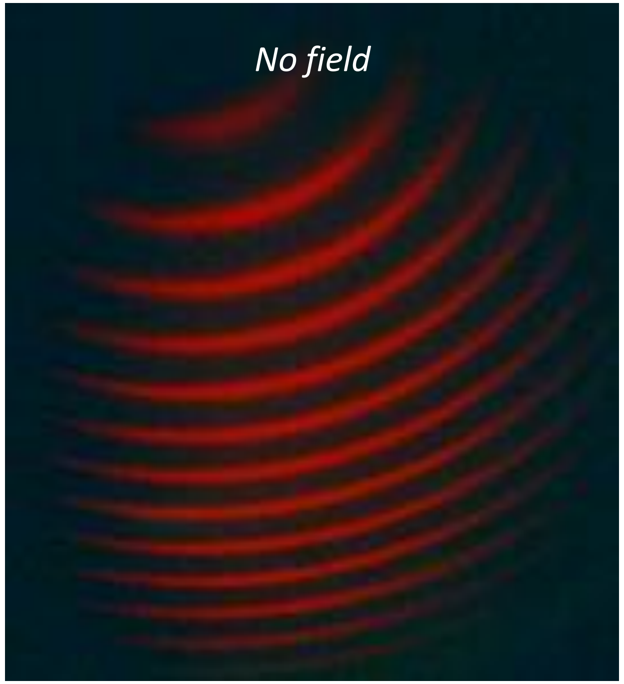
$$\mu_B = \frac{e\hbar}{2m_e} = 14\,\mathrm{GHz/T}$$

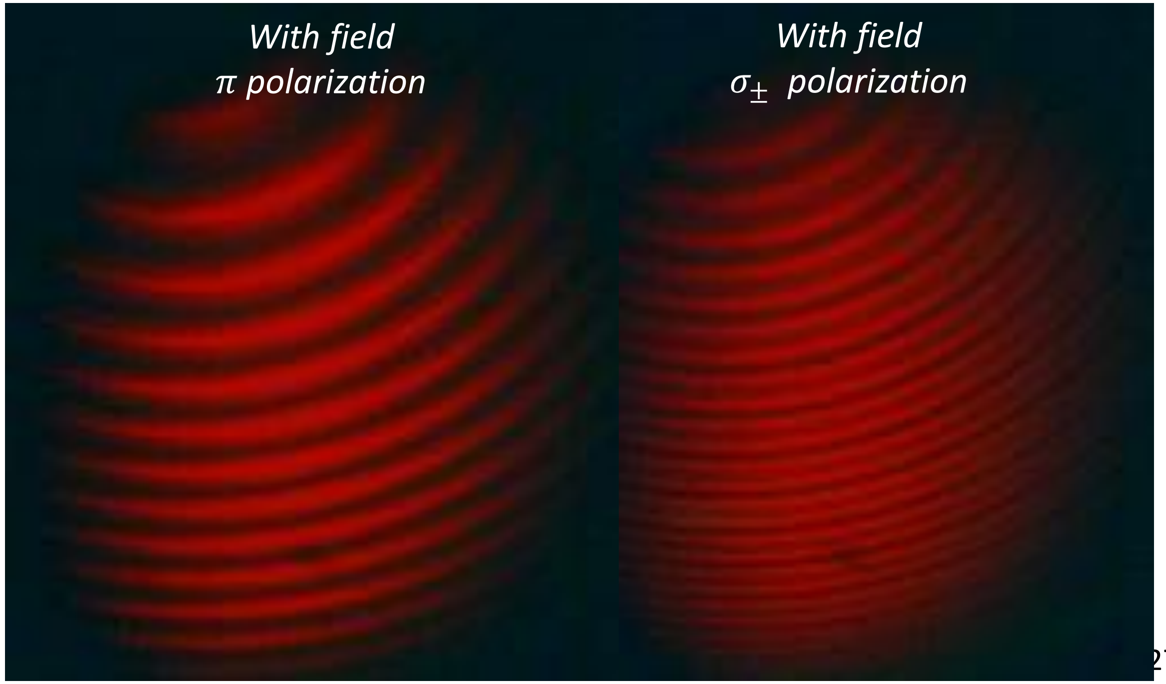
Corresponding to $\sigma_\pm$ polarization

Zeeman effect (classical - continued)



Around 640nm
(Cadmium emission line)

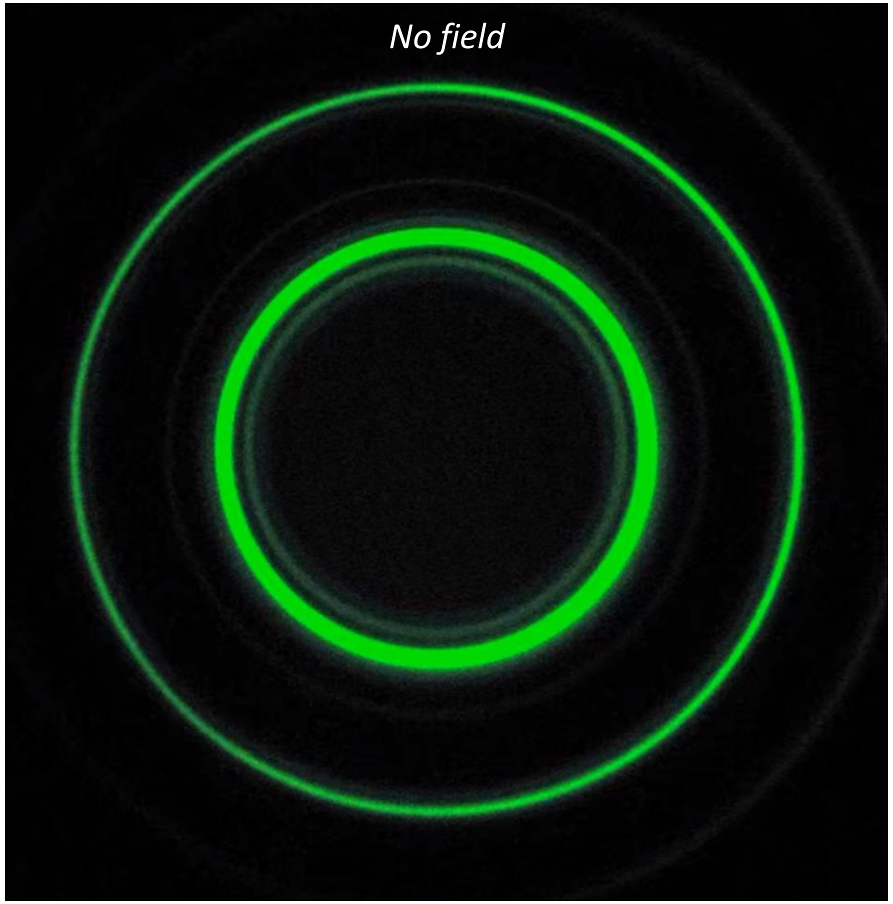


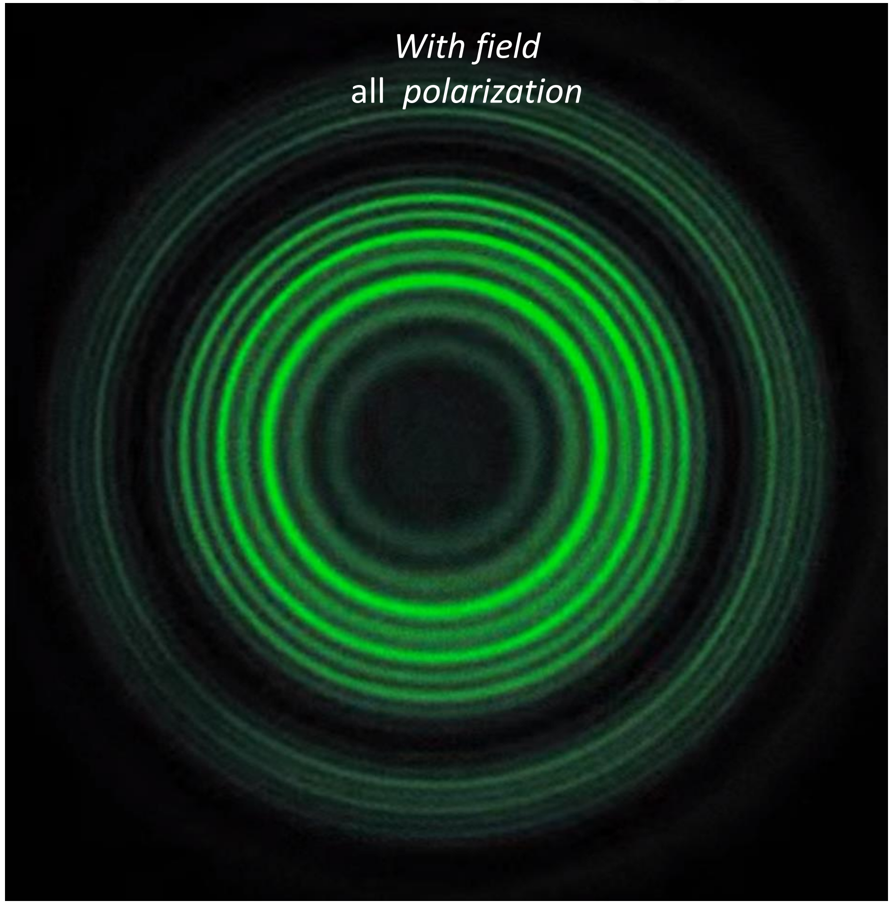


Anomalous Zeeman effect

Let’s try on another transition !

Around 546 nm
(Mercury emission line)



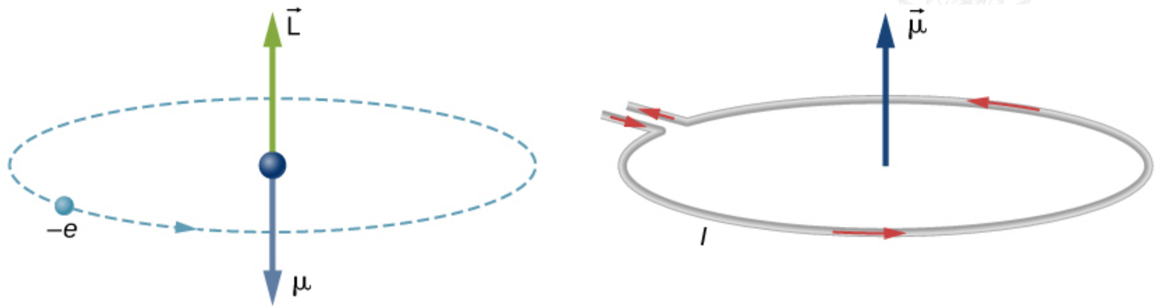


Credit :Dave Gardner University of Scranton

From classical to semi-classical

Atom without mag-field :

$$H_{\text{atom}}$$



How to include the influence of the mag field ?

(reminder from PHY 205)

Elecron orbiting around the proton → electrical current

$$I = \frac{-q}{T} = \frac{-q\,v}{2\pi r}$$

Electrical current → magnetic dipole

$$\boldsymbol{\mathcal{M}} = I\,\mathbf{S} = \frac{-q\,r\,v}{2}\,\mathbf{u_z} = \frac{-q}{2m_e}\,\mathbf{L}$$

Magnetic dipole → magnetic energy

$$E_p = -\boldsymbol{\mathcal{M}}.\mathbf{B} = \frac{q}{2m_e}\,\mathbf{L}.\mathbf{B}$$

Magnetic energy → Zeeman Hamiltonian

$$\hat{V} = \left(g_e \frac{q}{2m_e}\right)\hat{\mathbf{L}}.\mathbf{B}$$

g_e : Landé factor (derivation from full quantum atom)

Toolbox : perturbation theory

$$H_{\text{atom}} + V$$

How does a small change in the Hamiltonian changes the energy levels ?

Without perturbation :

$$\hat{H}_0|\psi_n\rangle = E_n|\psi_n\rangle$$

With perturbation :

$$\left(\hat{H}_0 + \hat{V}\right)|\psi\rangle = E|\psi\rangle$$

1st order development

$$|\psi\rangle = |\psi_n\rangle + |\delta\psi\rangle + \ldots$$
$$E = E_n + \Delta E + \ldots$$

Energy shift :

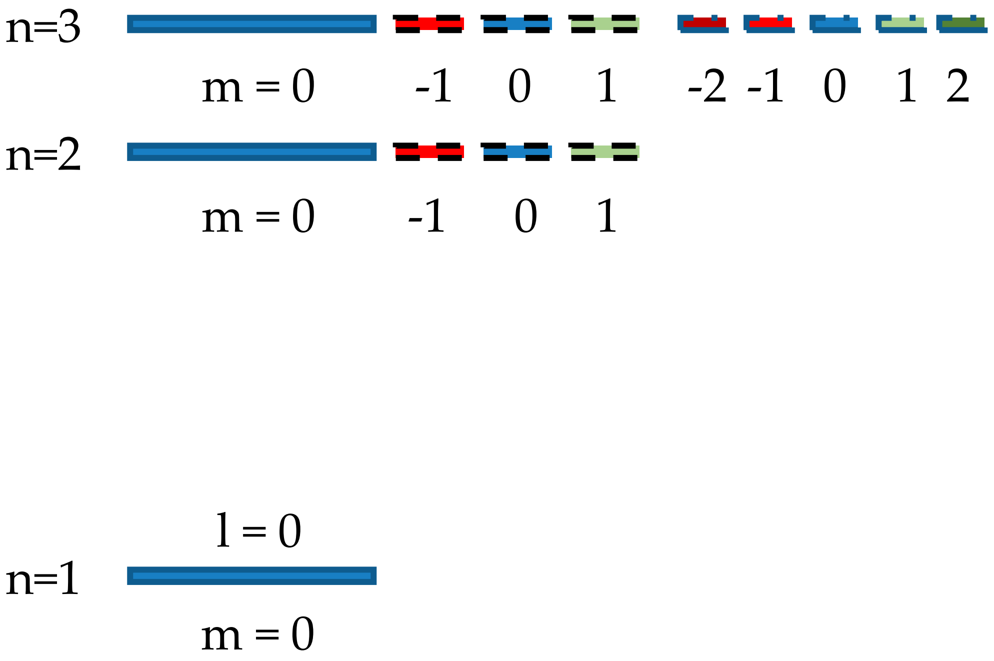
$$\Delta E_n = \langle\psi_n|\hat{V}|\psi_n\rangle$$

For the Zeeman effect :

$$\Delta E_n = \left(\frac{qB}{2m_e}g_e\right)\langle\psi_n|\hat{L_z}|\psi_n\rangle$$

Example: atomic states for Hydrogen

Results from the most simple Schrodinger model (full derivation in lecture 6)



Energy levels : $$E_n = -\frac{1}{n^2}\frac{m_e e^4}{2\hbar^2}$$

Total angular momentum : $$L^2 = l(l+1)\hbar^2$$

$$l \leq n-1$$

Label : S (l=0), P (l=1), D(l=2), f…

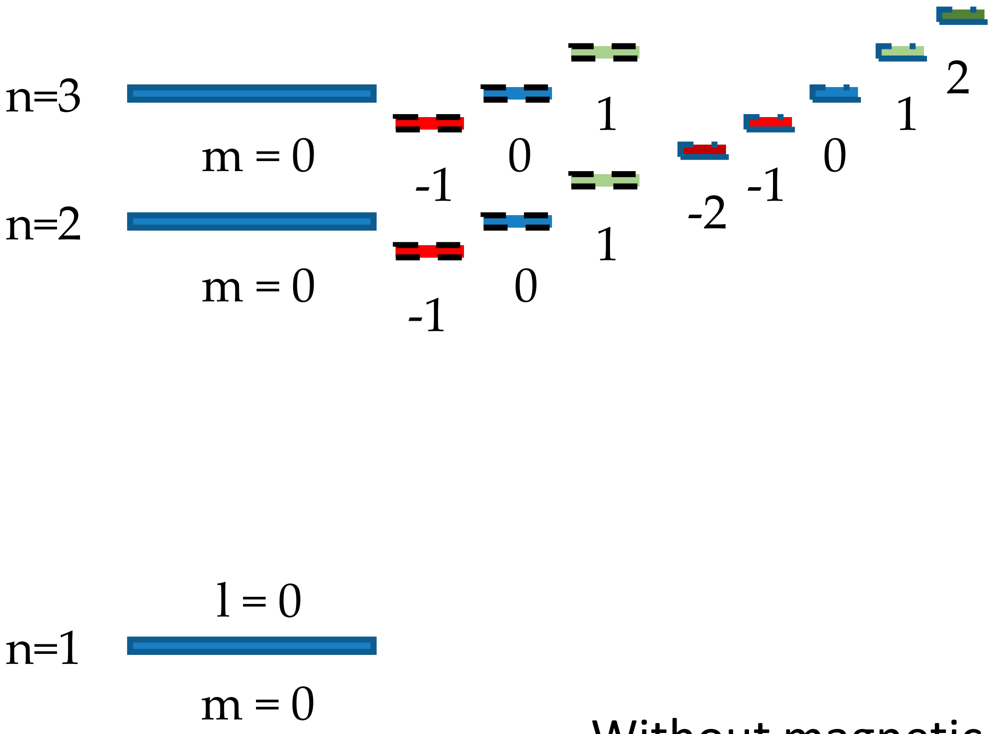
Angular momentum along z : $$L_z = m\hbar$$

$$-l \leq m \leq +l$$

Each energy state is degenerated n² times.

Atomic states

Results from the most simple Schrodinger model (full derivation in lecture 6)



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$l \leq n-1$

Label : S (l=0), P (l=1), D(l=2), f…

Angular momentum along z : $L_z = m\hbar$

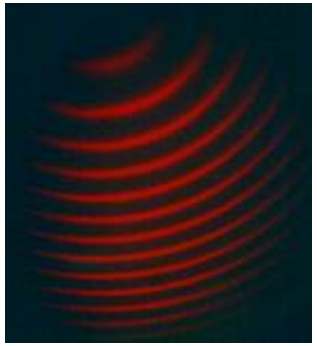
$-l \leq m \leq +l$

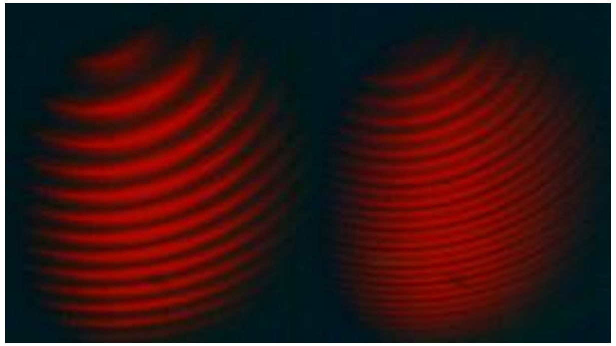
Without magnetic field, each energy state is degenerated n^2 times.

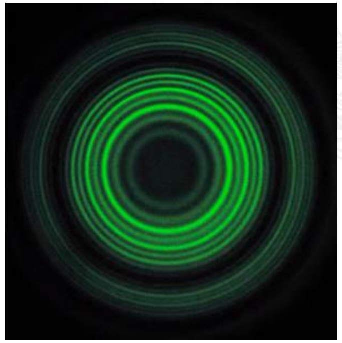
Mag. Field lifts the degeneracy : each energy shifts according to its angular momentum along z

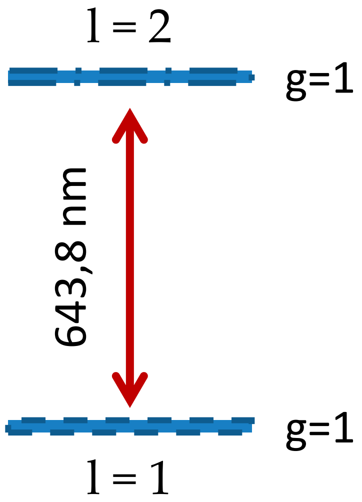
$$\Delta E = \frac{qB}{2m_e} g_e \langle n,l,m|\hat{L}_z|n,l,m\rangle = \frac{qB}{2m_e} g_e m\hbar$$

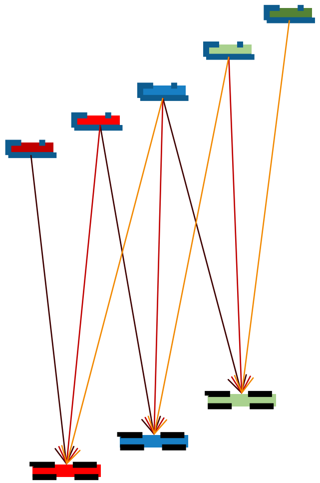
Cd-Hg Zeeman shifts

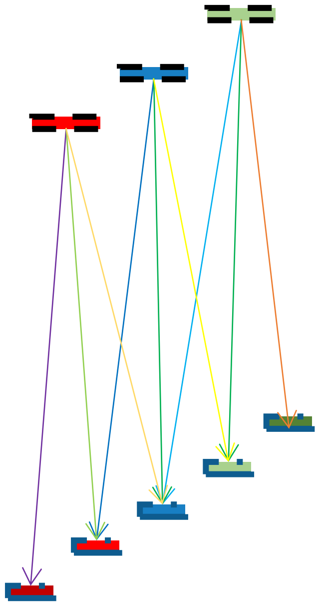




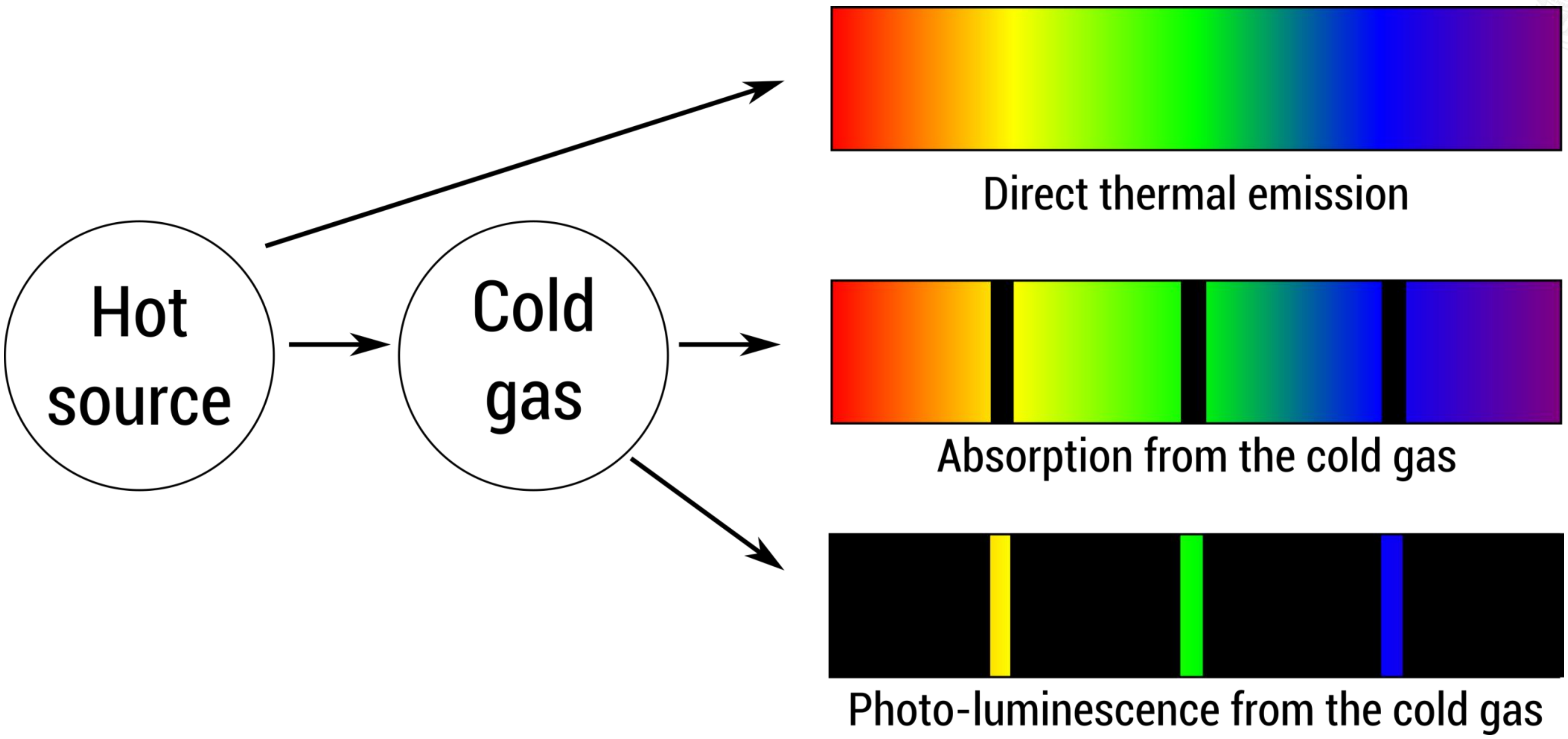








Ex: magnetic sunspot



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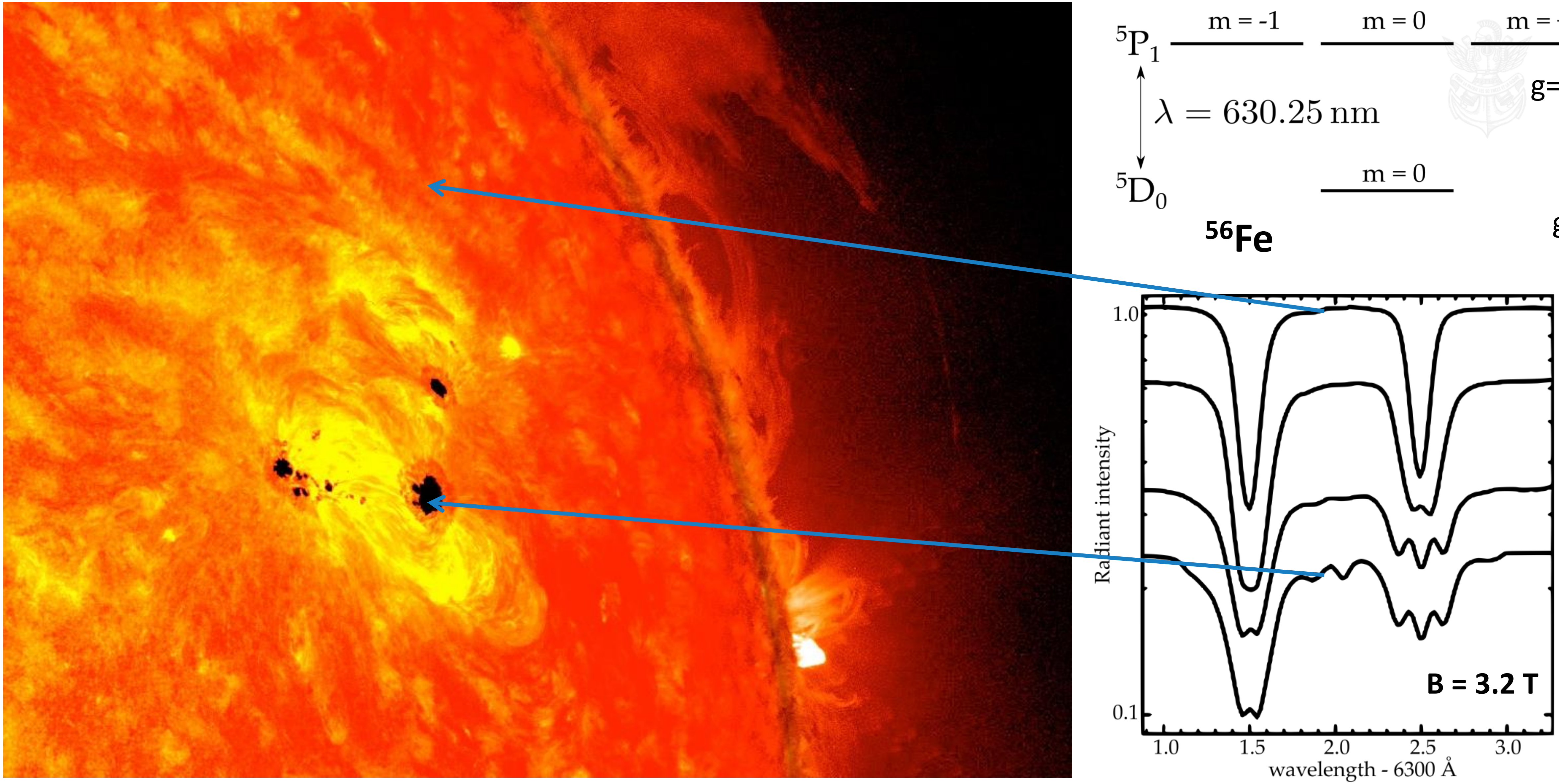
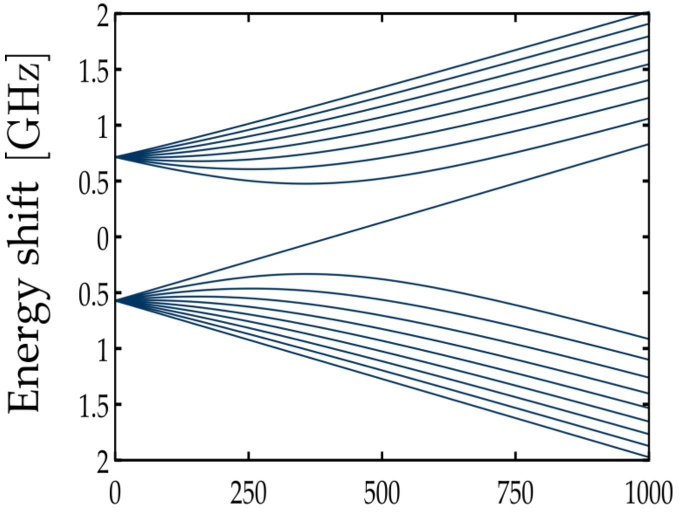
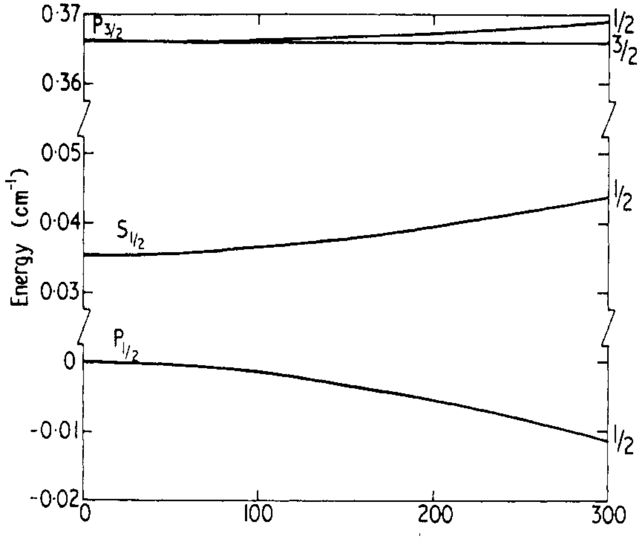


Data : Hinode space telescope

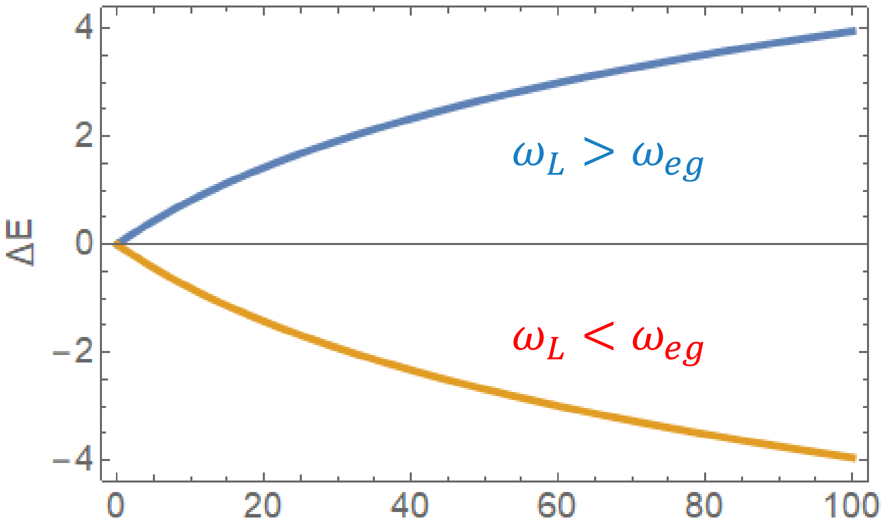
The usual effects



Magnetic field



Electric field



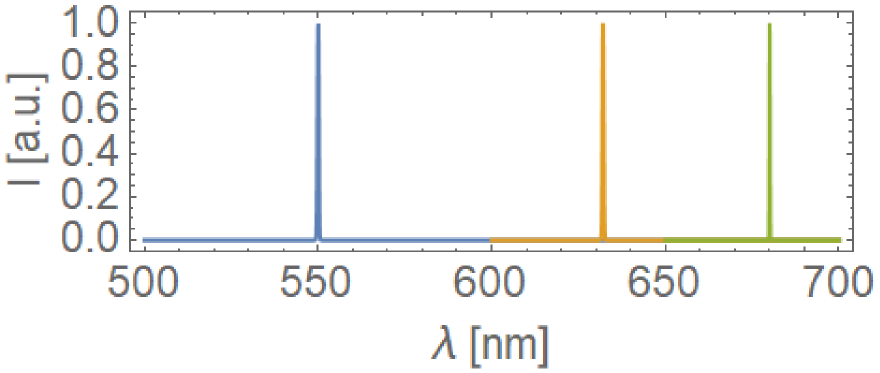
Laser light

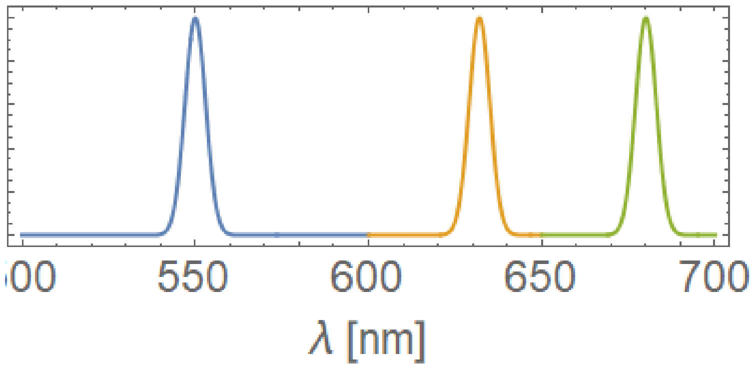
Zeeman shift

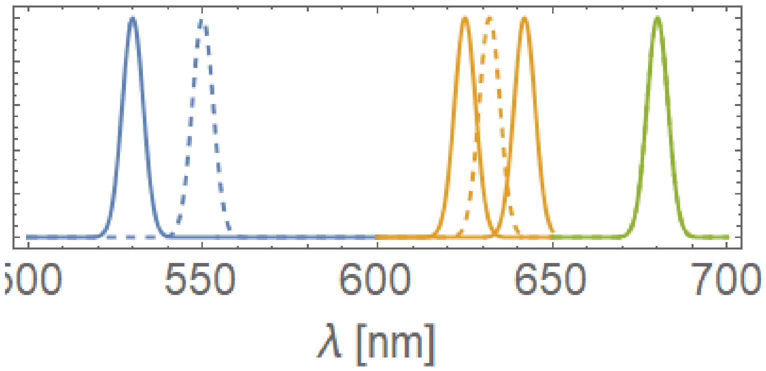
Stark shift

Lamp (or light) shift

Take home message







What light is actually emitted ?

What are the atomic states ?

H_{atom} $H_{\text{env.}}$ Internal vs external degrees of freedom

How are these states populated ?

(whatever)-escence.

What light correspond to this transition ?

Selection rules, available modes

$\Delta E = \hbar\omega$ $\Delta m = 0, \pm 1$

Intrinsic bandwith

Lorentzian profile

Extrinsic bandwith

Doppler gaussian broadening :

$$\Delta\omega = \sqrt{\frac{k_B T \omega_0^2}{mc^2}}$$

Energy shift :
1st order pertrubation theory

$$\Delta E_n = \langle \psi_n | \hat{V} | \psi_n \rangle$$

Zeeman effect :

$$\Delta E = \frac{qB}{2m_e} g_e m$$