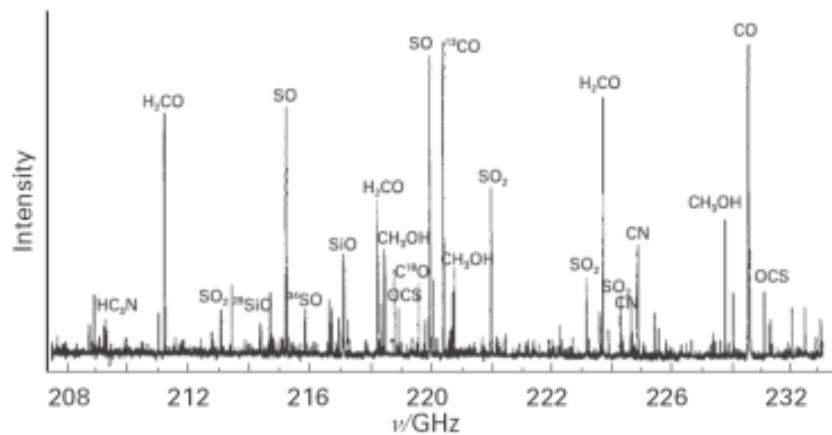




Atomic Structure & Radiative Transitions



Atomic processes

Radiation can be emitted or absorbed when electrons make transitions between different states:

Bound-bound: electron moves between two bound states (orbitals) in an atom or ion. Photon is emitted or absorbed.

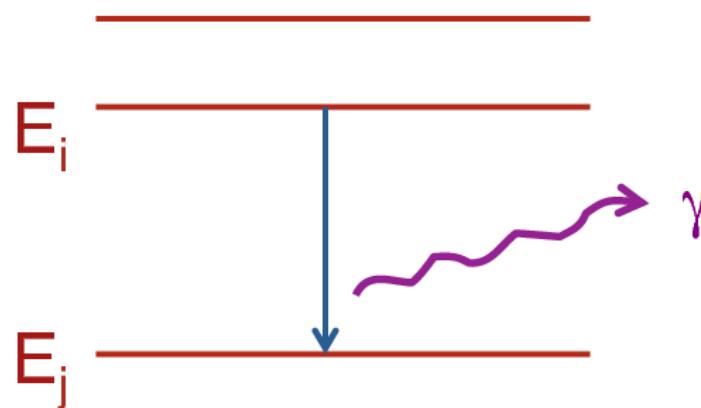
Bound-free:

- Bound -> unbound: **ionization**
- Unbound -> bound: **recombination**

Free-free: free electron gains energy by absorbing a photon as it passes near an ion, or loses energy by emitting a photon. Called **bremsstrahlung**.

Bound-bound transitions

Transitions between two atomic energy levels:



Energy of the emitted / absorbed photon is the difference between the energies of the two levels:

$$h\nu = |E_i - E_j|$$

How to calculate the energy levels

To calculate the energy level, we solve the Schrödinger eq:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi.$$

For a time independent H =Hamiltonian the energy levels are the eigenvalues of the system:

$$H\psi(\vec{r}) = E\psi(\vec{r}).$$

For a system on N electrons around a charge Ze :

$$H = -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - Ze^2 \sum_j \frac{1}{r_j} + \sum_{i>j} \frac{e^2}{r_{ij}},$$

electron kinetic
energy

nucleus-electron
interaction

electron-electron
interaction

A one electron atom

Solutions of $H\psi = E\psi$

$$\psi(r, \theta, \phi) = \frac{1}{r} R_{nl}(r) Y_{lm}(\theta, \phi),$$

where the quantum numbers take the following values

Principle quantum number $n = 1, 2, 3, \dots$

Orbital angular momentum $l = 0, 1, 2, 3, \dots, n - 1$

Z-projection of "l" $m = -l, -l + 1, \dots, l - 1, l$

Electrons with the same ``n'' have same energy: degeneracy!

The levels $l = 0, 1, 2, 3, \dots$ are called: s,p,d,f, + alphabetic order

Remember the meaning of spherical harmonics

$$Y_{l,m}(\theta, \phi)$$

n specifies the energy
l the total ang. momentum
m the orientation of each sub-shell

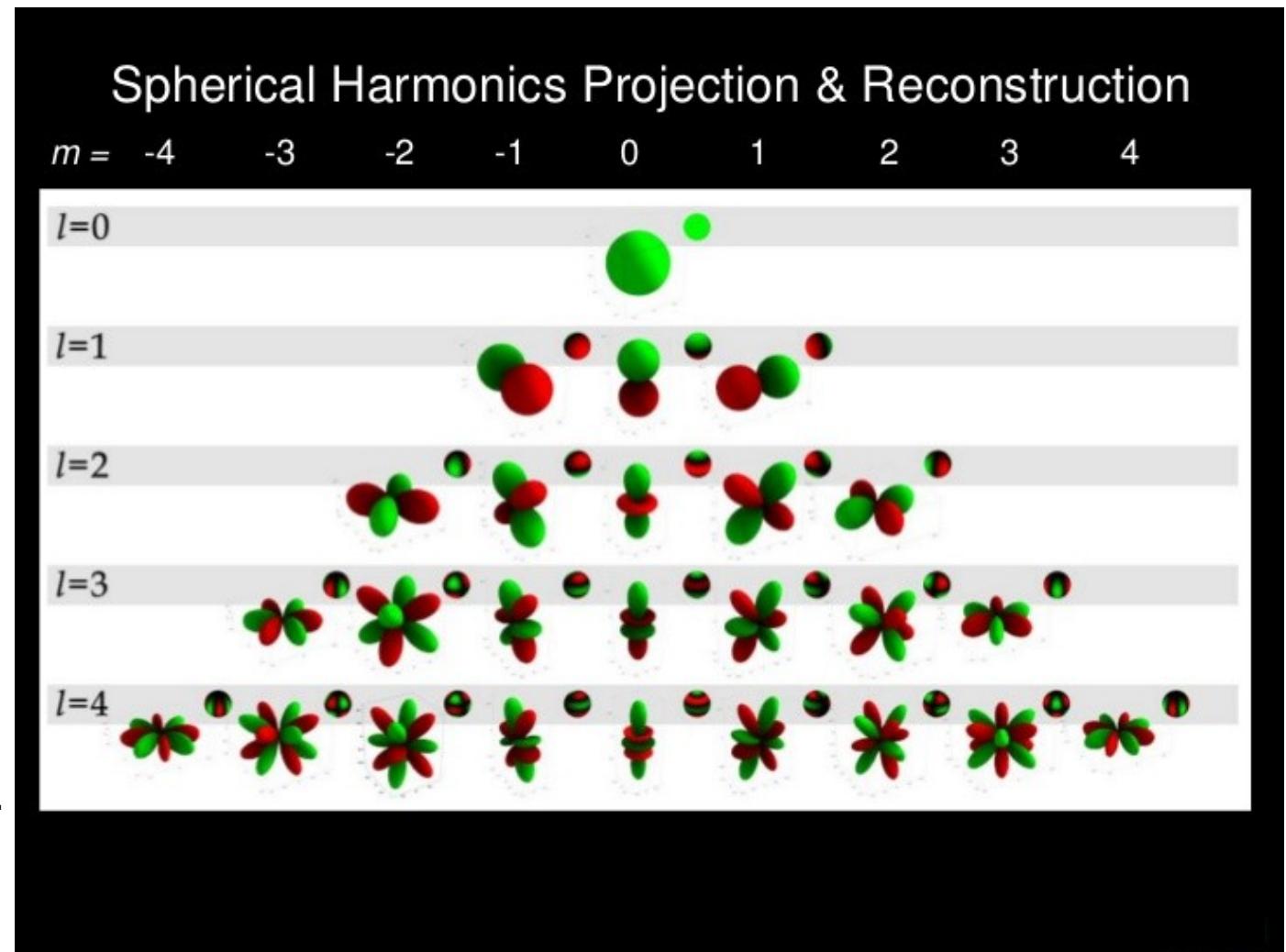
Each sub-shell can accommodate 2 electrons.

So $l=0 \rightarrow 2 e^-$

$l=1 \rightarrow 6 e^-$

$l=2 \rightarrow 10 e^-$

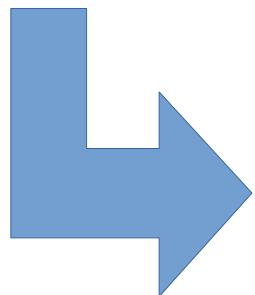
and so on...



In Short:

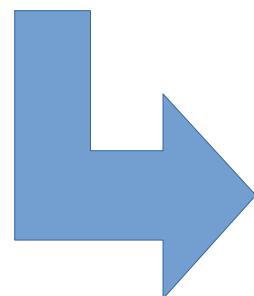
Schroedinger Equation

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



Applied to

Hydrogen Atom



Yields
Three

$$H = -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - Ze^2 \sum_j \frac{1}{r_j} + \sum_{i>j} \frac{e^2}{r_{ij}}$$

Quantum Numbers

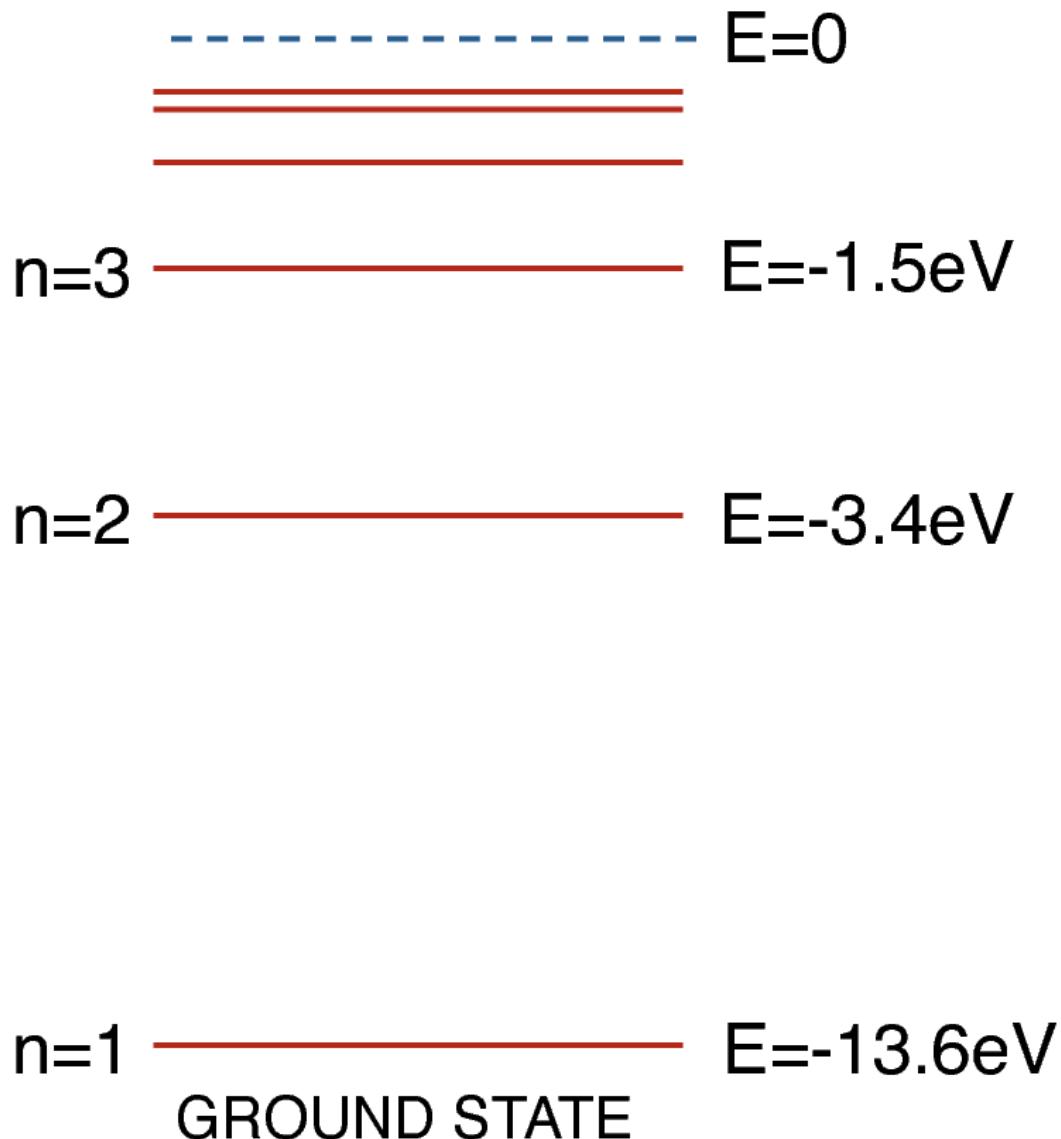
$$\Psi(r, \theta, \phi) = R(r) P(\theta) F(\phi)$$

n ↓
principal quantum number

ℓ ↓
Orbital quantum number

m_ℓ ↓
Magnetic quantum number

Hydrogen energy levels



Energy levels are labeled by n - the *principal quantum number*.

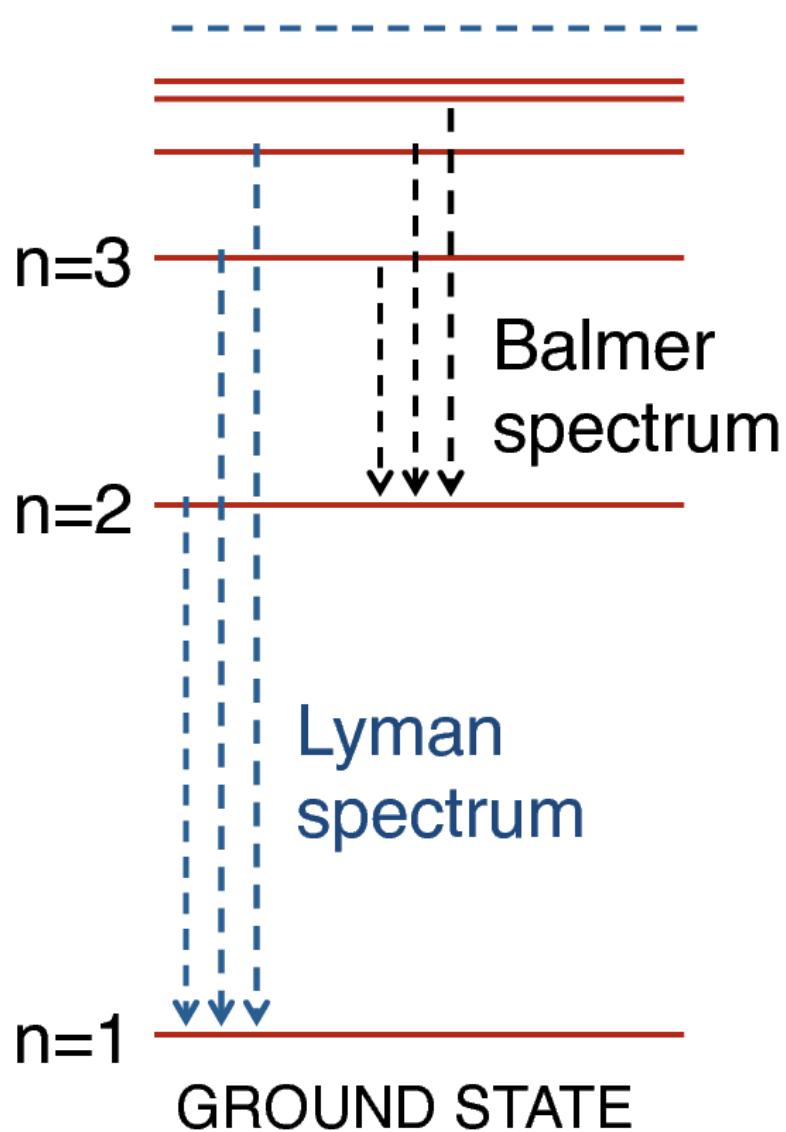
Lowest level, n=1, is the ground state.

$$E_n = -\frac{R}{n^2}$$

where R=13.6 eV is a Constant .

quantum states are degenerate : same E different orbital angular momentum.

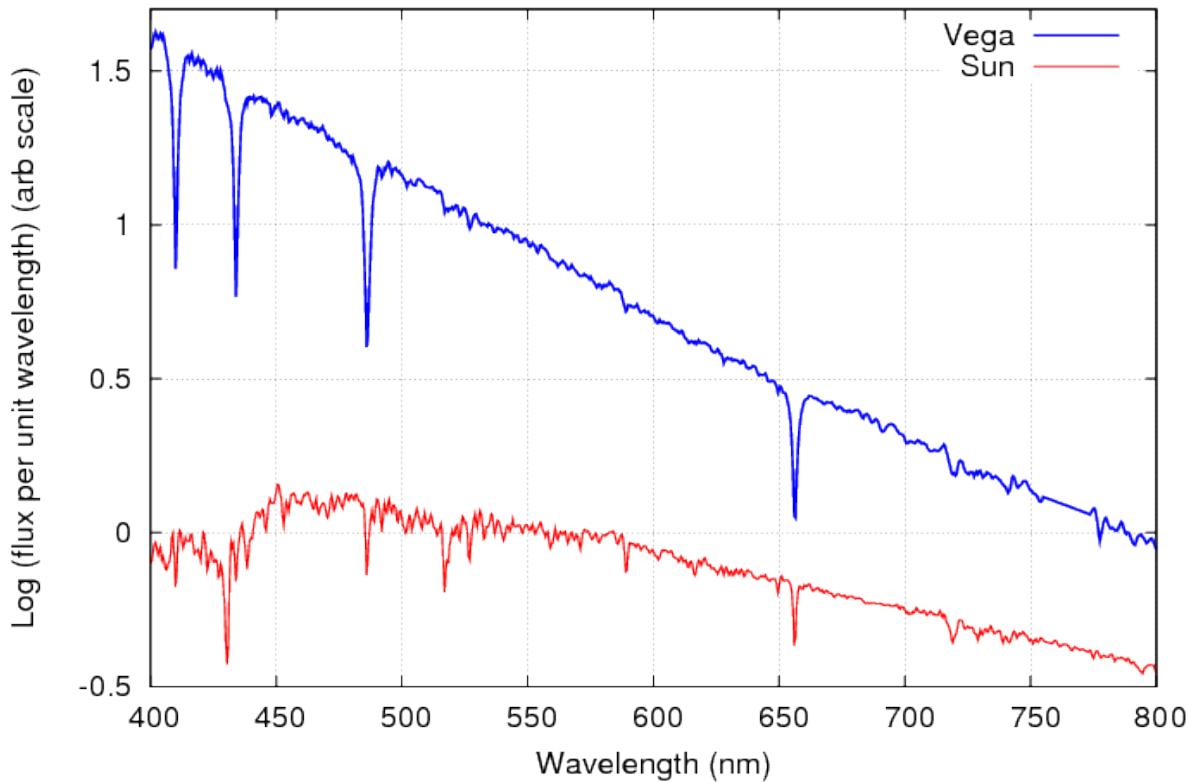
Hydrogen spectrum



Terminology:

- Transitions involving $n=1, 2, 3, 4$ are part of the *Lyman*, *Balmer*, *Paschen*, *Brackett* series.
- Different transitions are labeled with Greek letters - e.g. the Lyman α line arises from the $n=2$ to $n=1$ transition.
- Balmer series includes H α , H β etc.

Spectra of two stars



Balmer series is seen very prominently in many stars as absorption lines.

Some emission lines (especially Haplha) are also seen in accretion disks and in stellar winds.

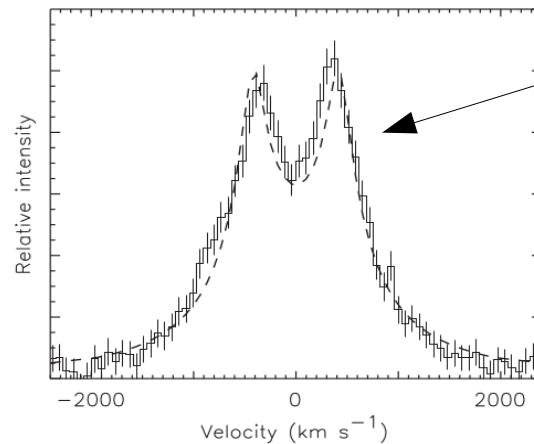
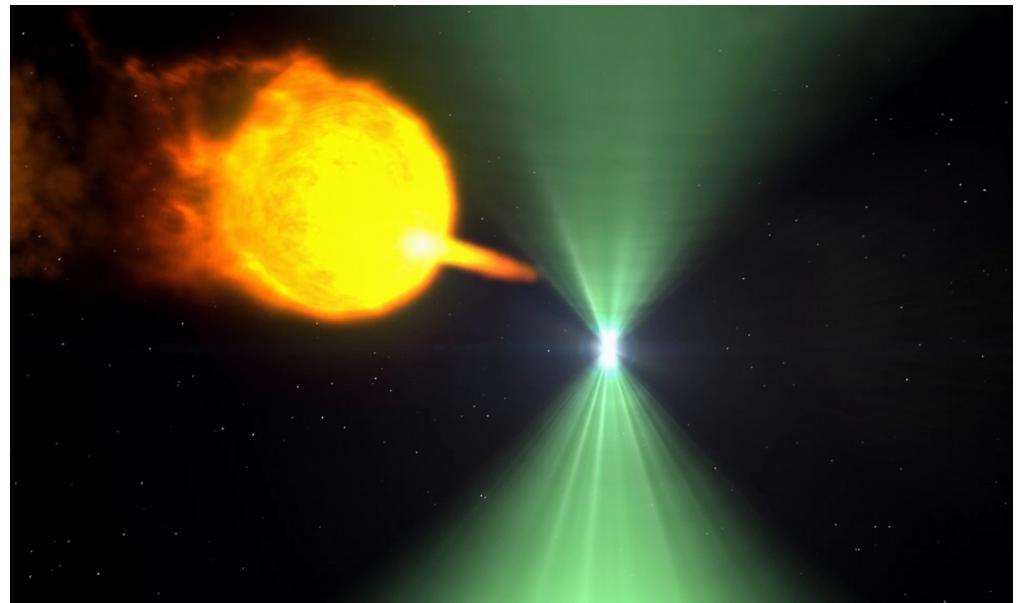
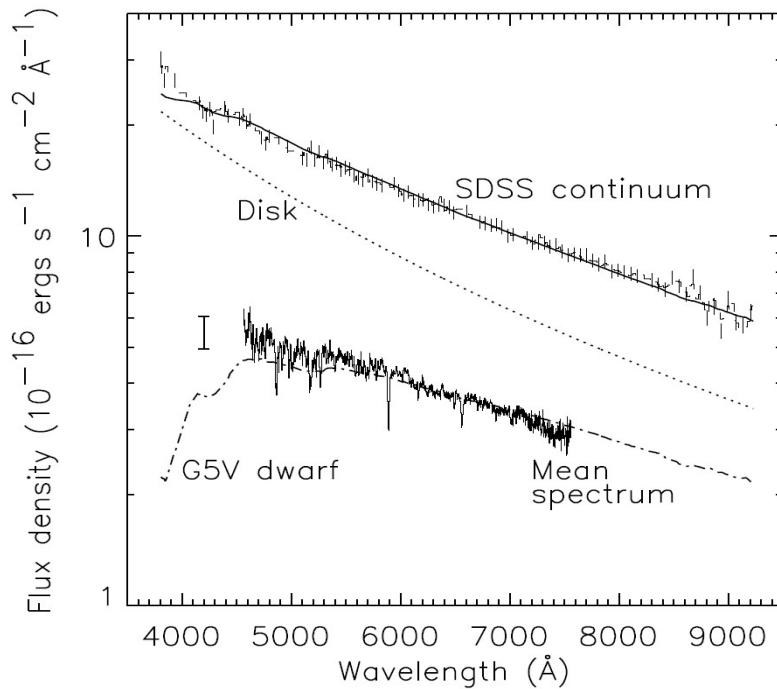
Transitional Millisecond Pulsars

PSR J1023+0038

1.69 ms spin period

4.8 hr orbital period

0.2 Msun companion



Halpha emission line with “double horn” Doppler shift due to motion in the accretion disk

Hydrogen spectrum

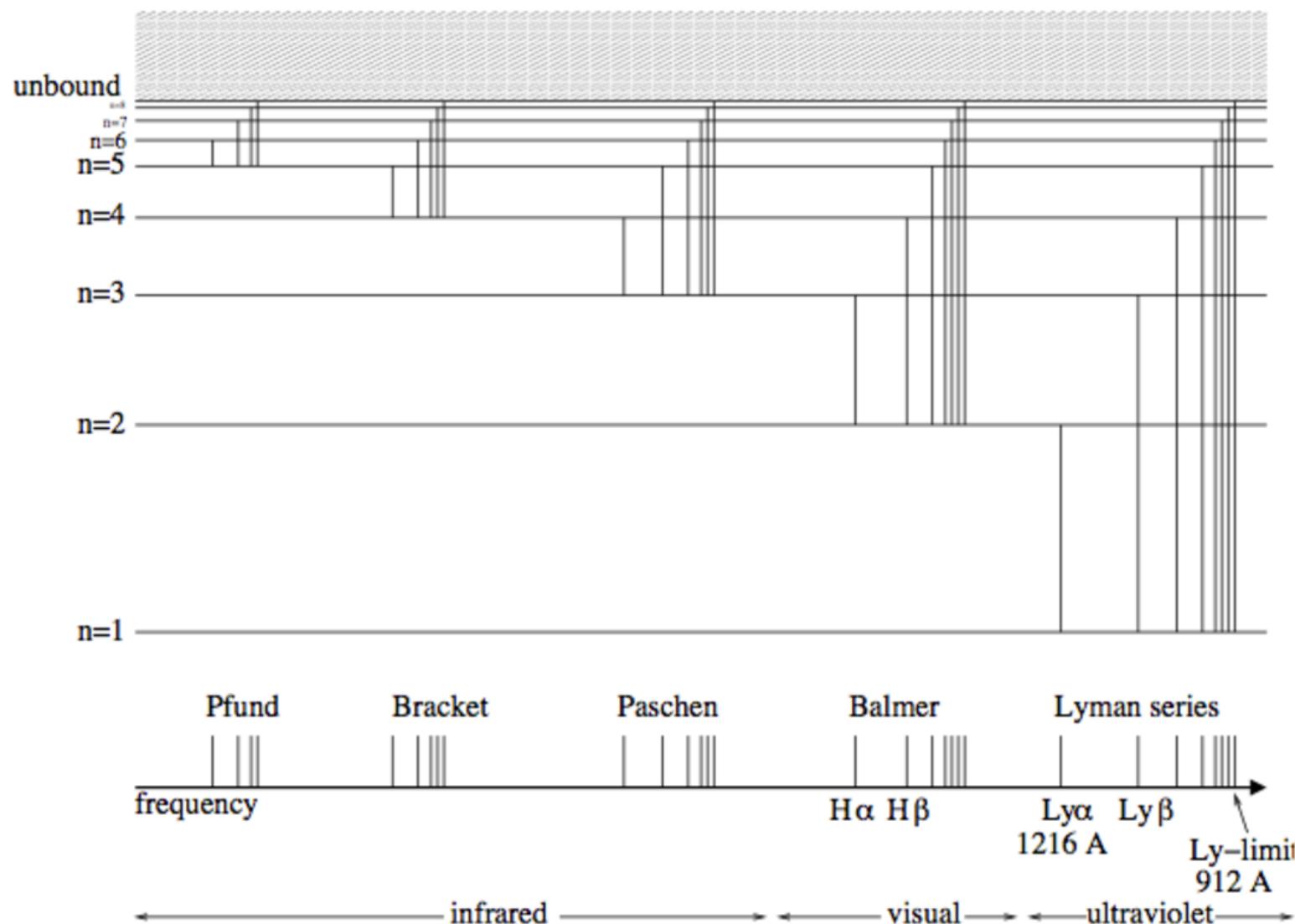


Figure 8.1: Schematic overview of the energy levels and spectral lines of the hydrogen atom.

Atomic Transitions without fine/hyper-fine structure

Ignoring fine and hyper-fine structure, a transition $n \rightarrow n'$
Produces a photon with wavelength λ :

Rydberg formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

Where Rydberg constant $R_H = 109,677.583 \text{ cm}^{-1}$

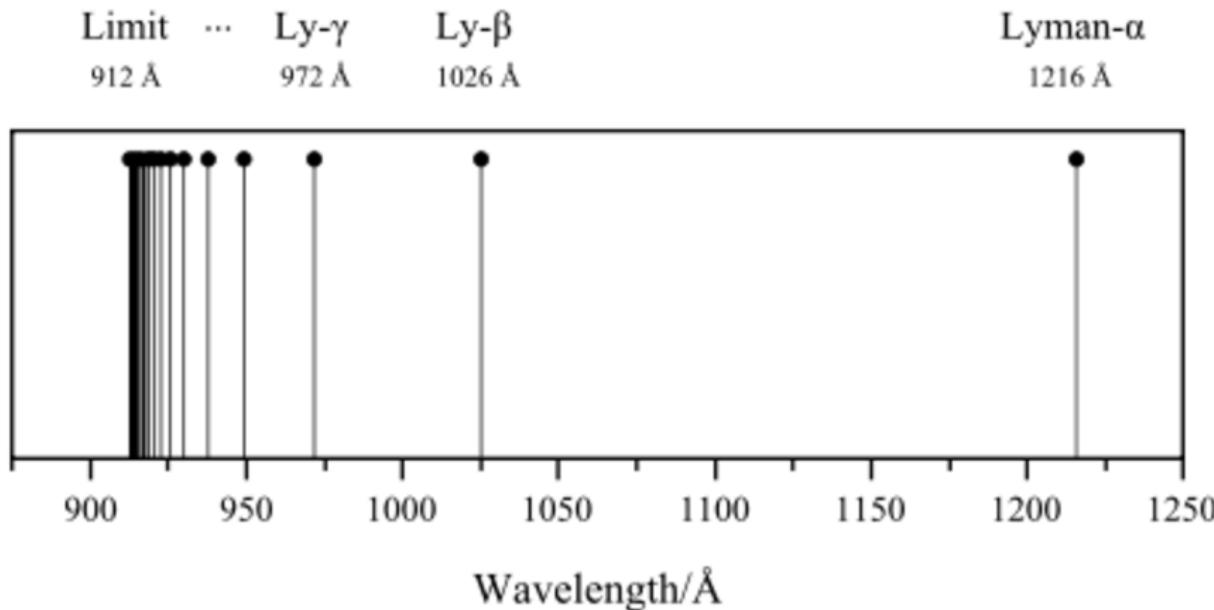
$$\begin{array}{ccc} & n'=1 & n'=2 \\ n=2 & 1216 \text{ \AA} & (\text{Ly}\alpha) \end{array}$$

$$n=3 \quad 1026 \text{ \AA} \quad (\text{Ly}\beta) \quad 6563 \text{ \AA} \quad (\text{H}\alpha)$$

$$n=4 \quad 973 \text{ \AA} \quad (\text{Ly}\gamma) \quad 4861 \text{ \AA} \quad (\text{H}\beta)$$

$$n=5 \quad 950 \text{ \AA} \quad (\text{Ly}\delta) \quad 4342 \text{ \AA} \quad (\text{H}\gamma)$$

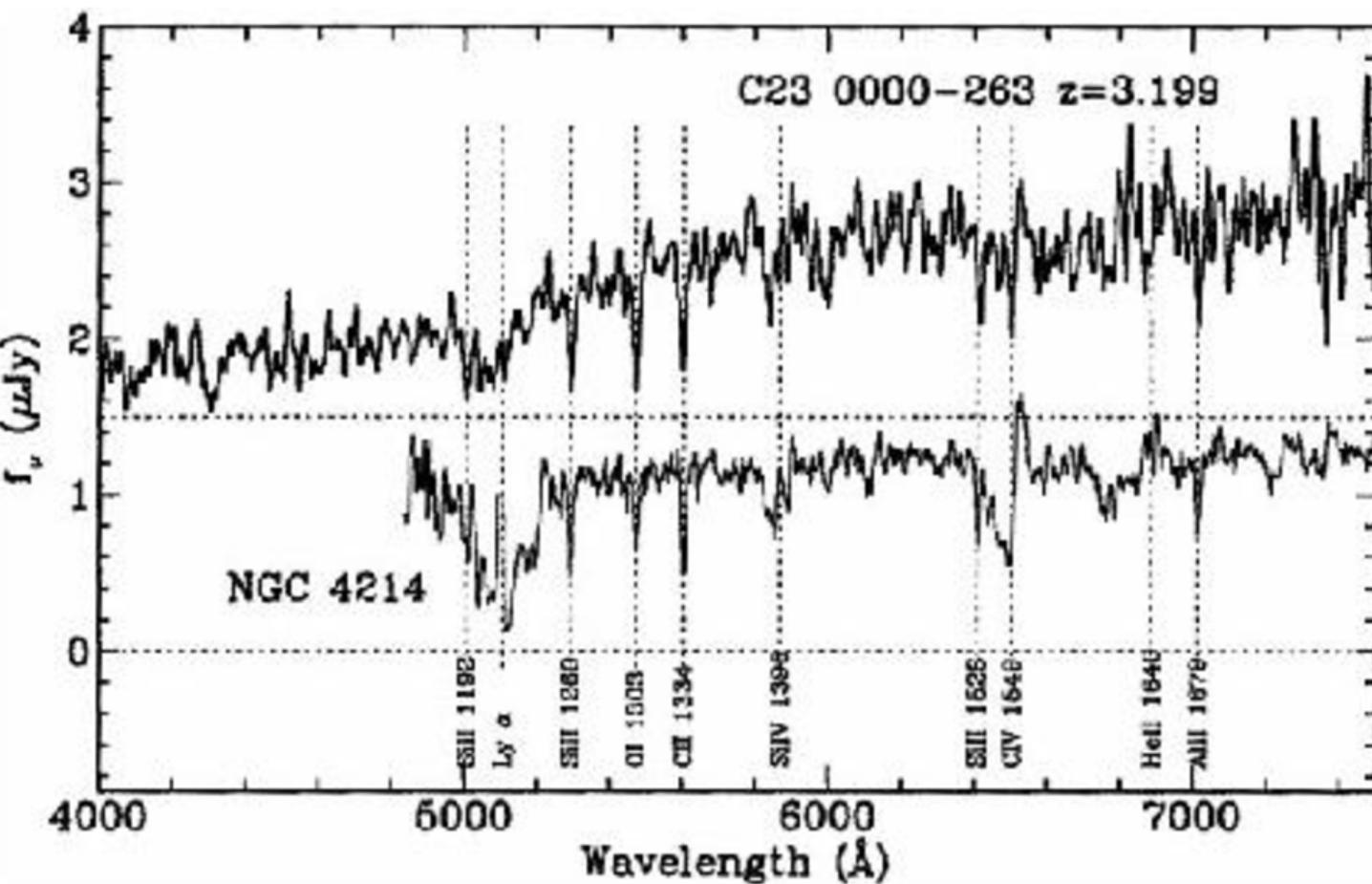
Lyman limit



The limit for $n' \rightarrow n$ with $n' \rightarrow \infty$ is $912 \text{ \AA} = 13.6 \text{ eV}$: H ionization energy

For galactic sources the Lyman break is far-ultra violet which is blocked by earth atmosphere.

For extragalactic sources $\lambda_{\text{obs}} = (1+z) \lambda_{\text{emit}}$ and the limit is shifted in optical and infrared



High-z forming galaxy:
UV rest frame, but
optical observer frame

Local star
forming galaxy
red-shifted for
comparison

Lyman break galaxies

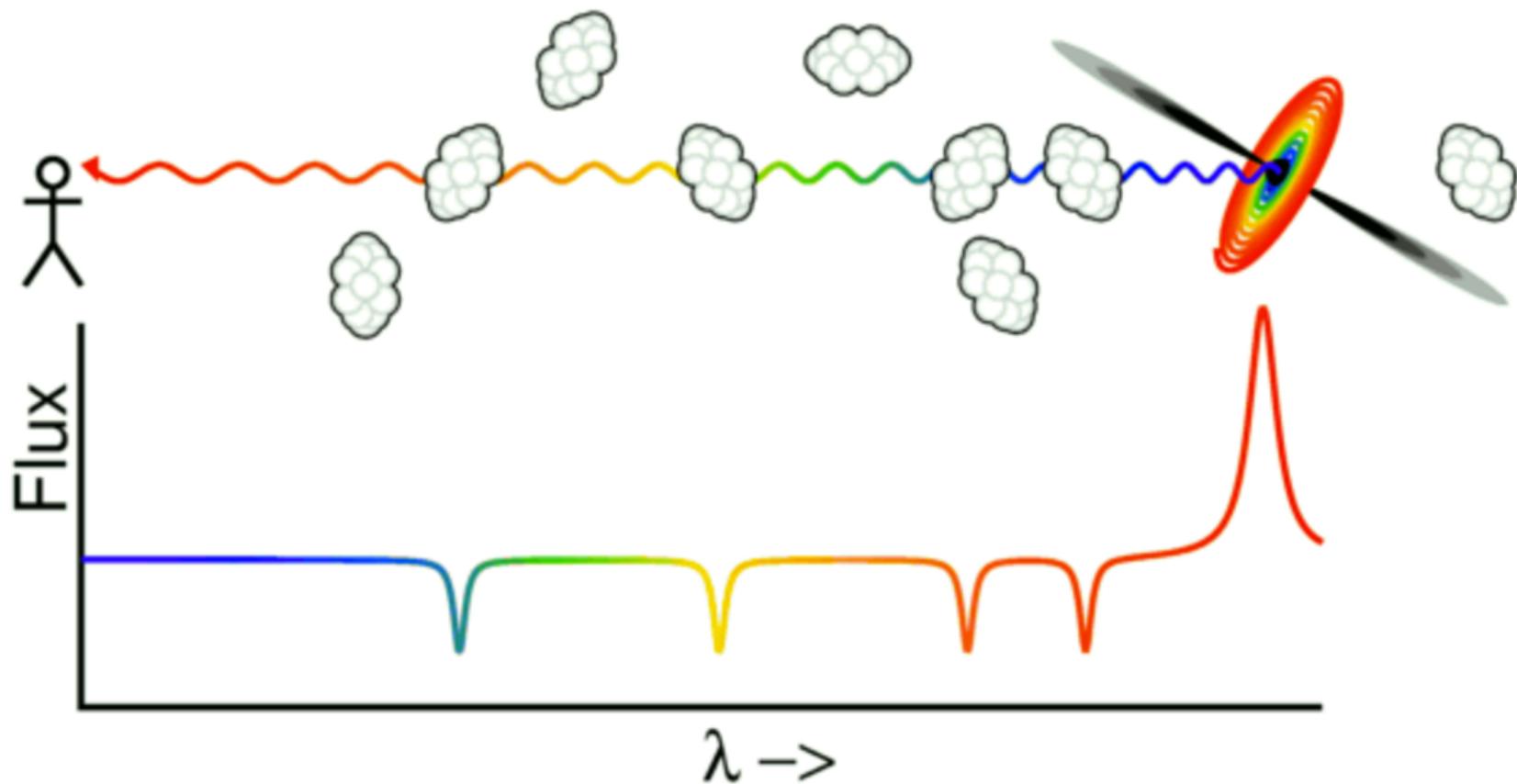
Searching for high-z star forming galaxies, finding the position of
the Lyman limit (also called Lyman limit) :

Star forming galaxies with hot stars that emit UV

Neutral hydrogen around stars absorbs UV at $\lambda < 912 \text{ \AA}$

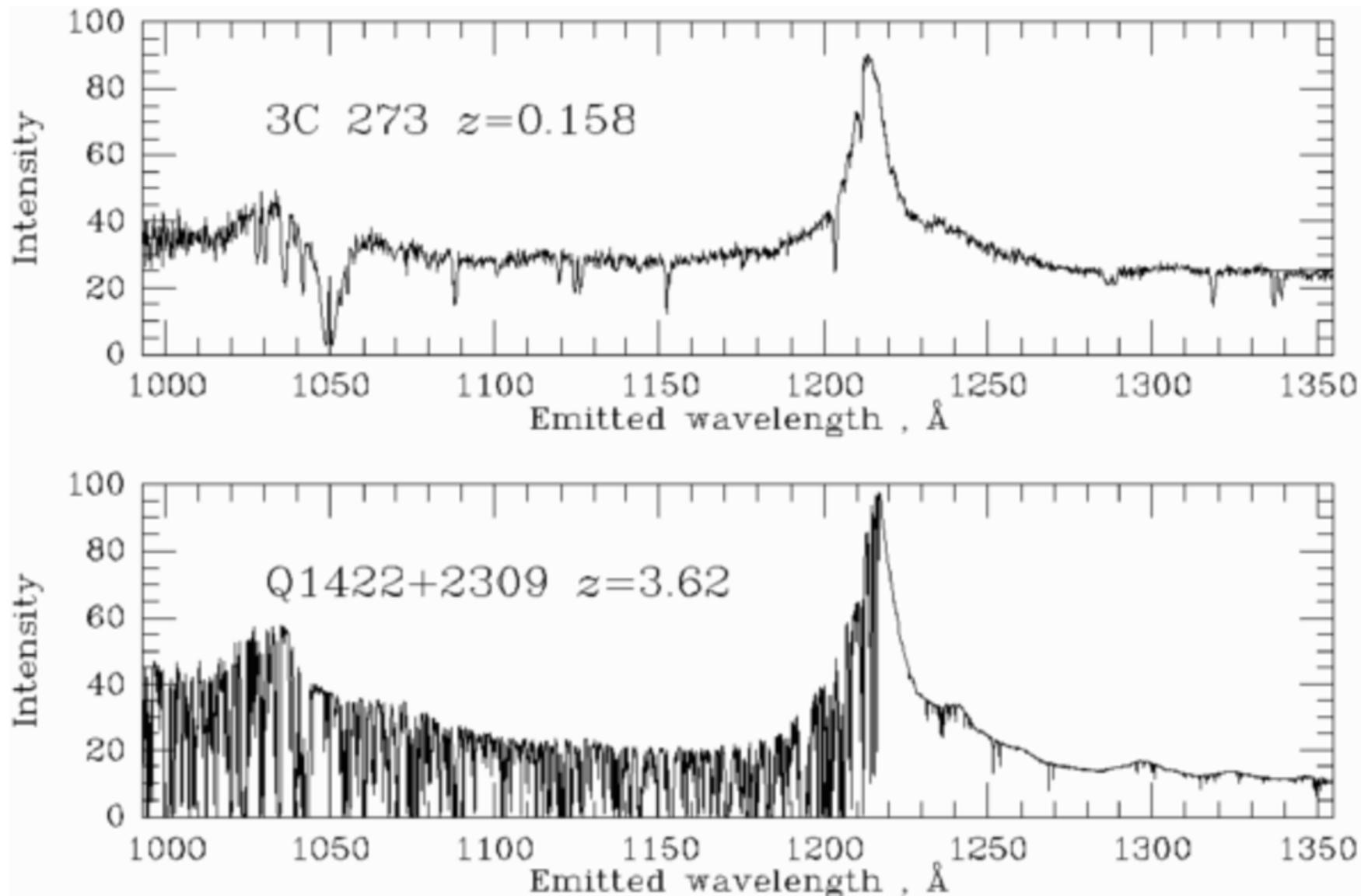
At $z=3-4$ the Lyman limit is in optical: the galaxy appears brighter
in optical ($\lambda > \text{break}$) and very dim in UV ($\lambda < \text{break}$)

Lya forest



Overdense regions along the line of sight: abundant in neutral H absorbs light from quasars or gamma-ray bursts :

Lya forest



We can study H distribution in universe

X-Ray Notation & Iron line

In nuclear/atomic physics an electron shell corresponds to a principal energy level “n”.

The closest shell to the nucleus is called the "1st shell" (also called "K shell"), followed by the "2shell" (or "L shell"), then the "3 shell" (or "M shell"), and so on farther and farther from the nucleus. The labels K, L, M shells are typical of X-ray spectroscopy.

The difference between the s,p,d,... notation and the K,L,M... notation is that the first refers to the *orbital* of the electron, whereas the second refers to the principal quantum number **n**.

Example:
K shell → 1s orbital
L shell → 2s & 2p orbitals
M shell → 3s, 3p & 3d orbitals

And so on...

One says that the K shell has 1 subshell, L shell has 2 subshells (2s &2p), M shell has three subshells (3s, 3p, 3d) etc.

Fluorescent Iron K line

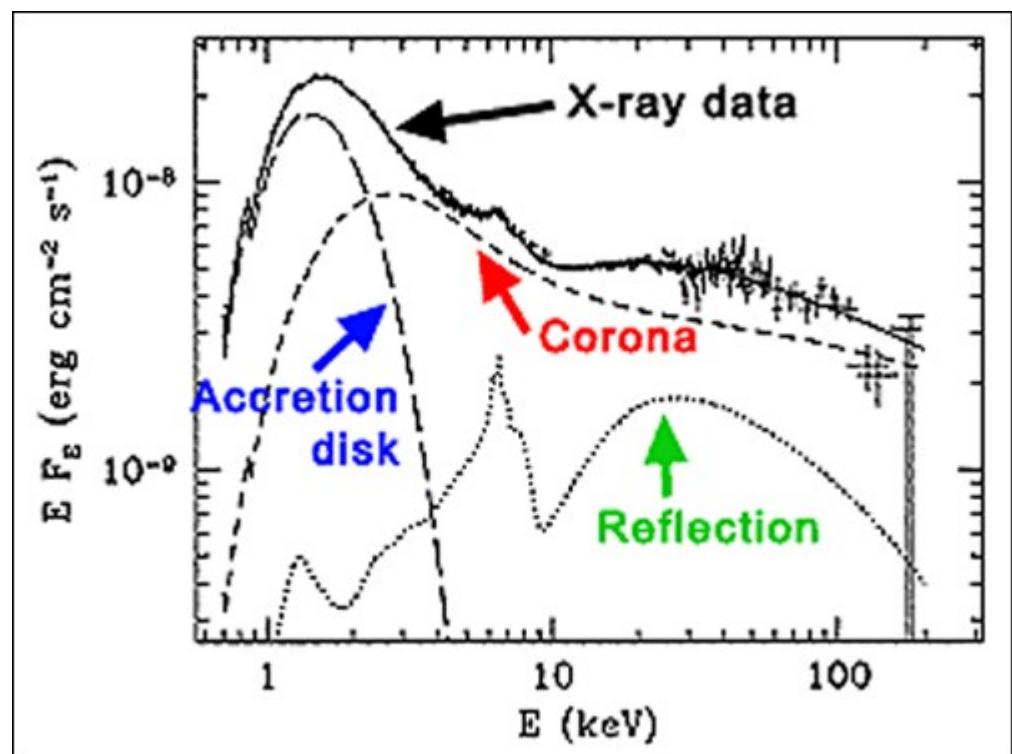
K-alpha emission lines result when an electron transitions to the innermost "K" shell ($n=1$, orbital 1s) from a 2p orbital of the L shell ($n=2$, 2s or 2p). K-alpha is typically by far the strongest X-ray spectral line for an element bombarded with energy sufficient to cause maximally intense X-ray emission. Such X-ray line photons are produced when an atom, or ion, of a heavy element, is left in an excited state following ejection from an inner K- or L-shell by an incident X-ray photon of sufficient energy. The ion may return to a lower energy state by emitting an electron from a higher shell (the 'Auger effect') or by a radiative transition. The relative probability of a radiative transition is referred to as the fluorescence yield. For K-shell electrons the fluorescence yield increases with atomic number; the largest product of element abundance and yield, by a factor of about 5, occurs for iron.

The energy of the line depends on the atomic charge Z : $E = (10.2\text{eV})(Z - 1)^2$

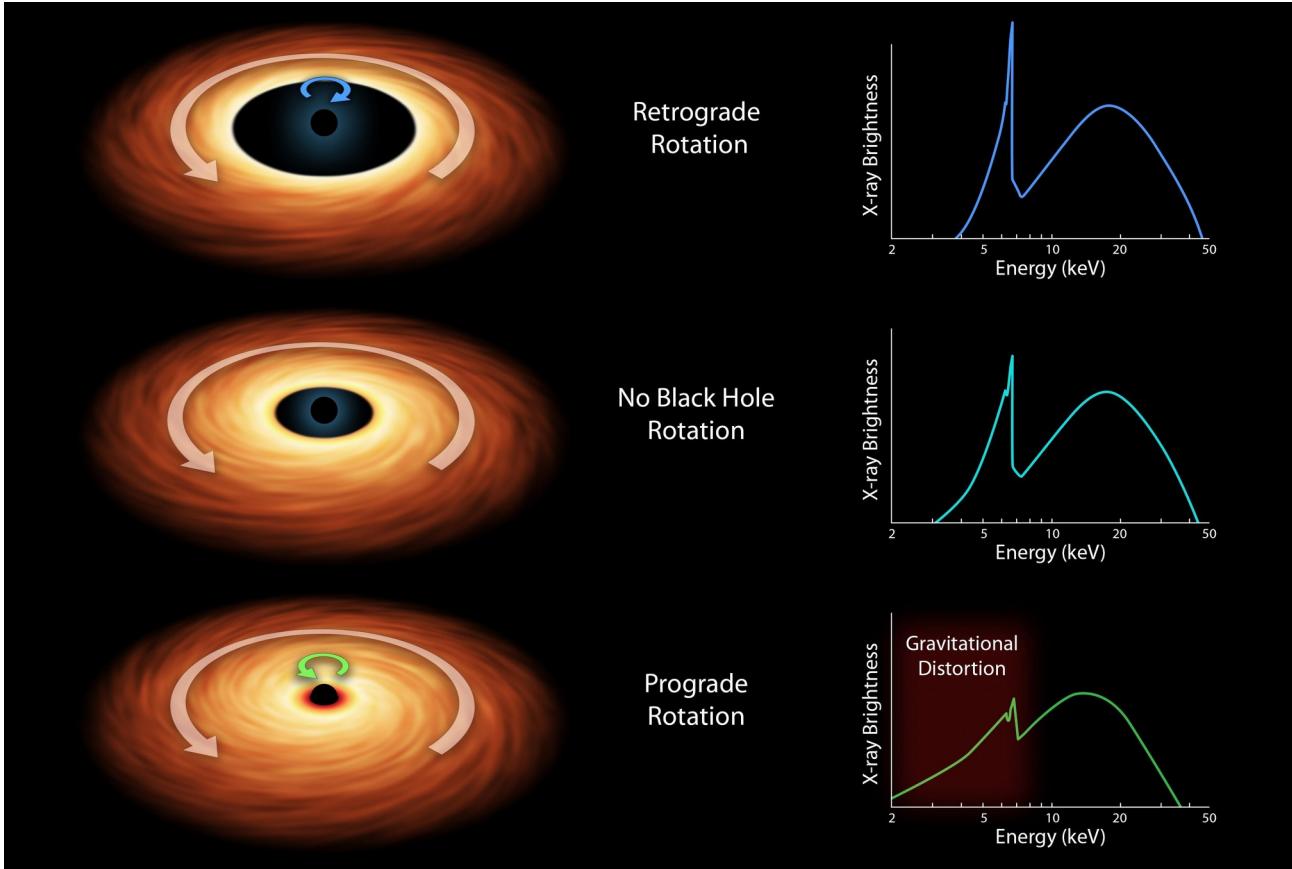
In X-ray binaries and AGNs, K-alpha Iron line emission is seen prominently.

Since Fe has $Z=26$, then $E \sim 6.4 \text{ keV}$.

(The line is actually a doublet, with slightly different energies depending on LS coupling as we will see later).



Iron K line to probe Strong Gravity



The shape of the Fe K-alpha line can be used to determine the rotation of black holes which is an important parameter to measure.

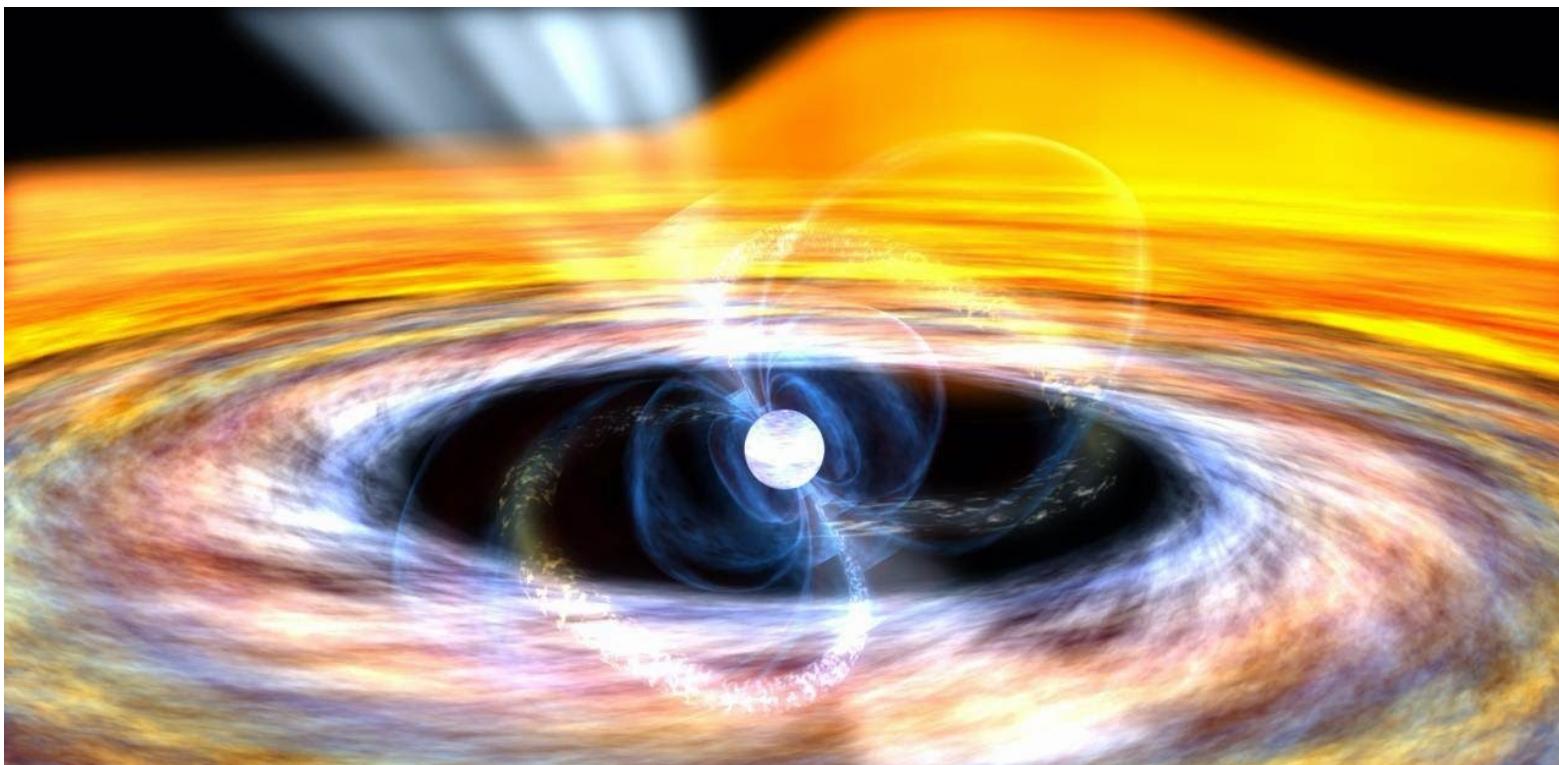
It has implications for the black hole formation, but also cosmological implications.

Doppler broadening due to the Keplerian accretion disk motion of the irradiated gas smears the Iron K-alpha line.

The truncation of the disk, due to general relativistic effects (known as the Innermost Stable Circular Orbit) determines how fast the gas rotates and thus the shape of the line.

More on Physics with Iron line

- The **energy** of the K α Fe line (from 6.4 to 6.7 keV) tells about the ionization state of the iron, and thus the temperature of the disk.
- The **luminosity** of the line tells about the amount of iron, and thus about the abundance of metals of the disk.
- The **width** of the line tells about the velocities of the irradiated material forming the line.
- The **profile** (symmetric, double horned, skewed) tells about Doppler boosting and gravitational redshift.
- If the accretor is a *neutron star* then you can infer the strength of the neutron star **magnetic field** by looking at the truncation radius.



The Spin: Lifting the energy degeneracy

Non-relativistic Schrödinger eq. predicts that H-atom energy levels depend only on ``n''. But

- 1) When observed at high resolution the H spectrum shows very closely spaced doublets
- 2) Stern-Gerlach experiment showed that a beam of atom is split by an inhomogeneous magnetic field B in given directions.

Argue for the presence of an intrinsic angular momentum, which is quantized: the spin.

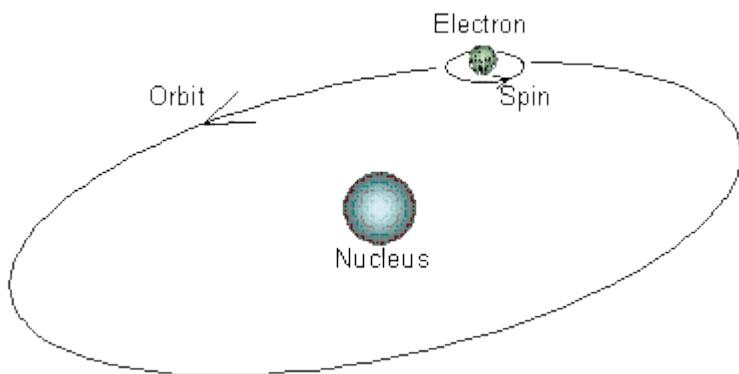
the electron spin has only 2 values along z-axis : $\pm \hbar/2$

Quantum number $s=1/2$ and $m_s = \pm 1/2$ (equivalent of ``l'' and ``m'' of orbital angular momentum)

Remember that given an arbitrary axis z , then the secondary quantum number m_s is defined as:

$$s_z = m_s \hbar \quad \text{with } m_s = -s, -s+1, \dots, s \quad (\text{i.e., } 2s+1 \text{ values})$$

Spin-Orbit Coupling



Consider an electron bound in an atom.
The electron moves around the nucleus and
so there is a certain orbital angular momentum

But the electron has also an intrinsic angular momentum due to its spin.

The spin and orbital angular momentum can interact giving rise to the so-called spin-orbit coupling.

Let's call the total spin angular momentum and orbital angular momentum as **S** and **L**

$$S = \sum_i s_i \quad L = \sum_i l_i$$

Now let's see what happens in an hydrogen atom (but the same is true in any atom) when we let **S** and **L** interact.

The Spin-Orbit coupling

Intrinsic magnetic dipole moment is

$$\vec{\mu}_s = -g_s \frac{e}{2m_e c} \vec{S}$$

Where from the Dirac eq. the g-factor is: $g_s \approx 2$

Electron sees a current loop from proton:

- 1) \rightarrow magnetic field
- 2) \rightarrow energy is different for different spin states:

$$E = -\vec{\mu}_s \cdot \vec{B}$$

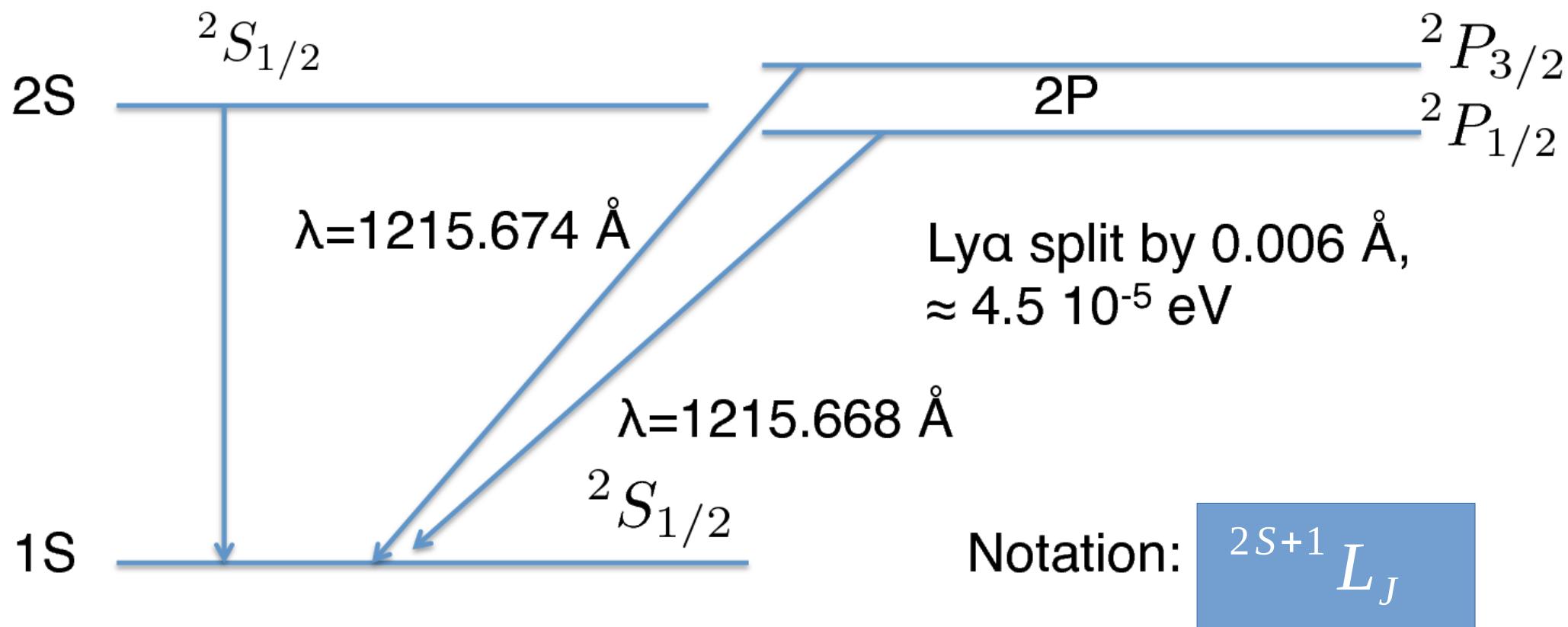
Fine structure in spectrum!

Fine structure in H spectrum

Total angular momentum is $\vec{J} = \vec{S} + \vec{L}$ $|\ell - s| \leq j \leq \ell + s$

The associated quantum number j can take the values:

$j = l \pm \frac{1}{2}$, for each state " $l \neq 0$ ". For $l=0$: $j= \frac{1}{2}$. + relativistic corrections: level with same j have same energy. Now energy depends on n and j : splitting!



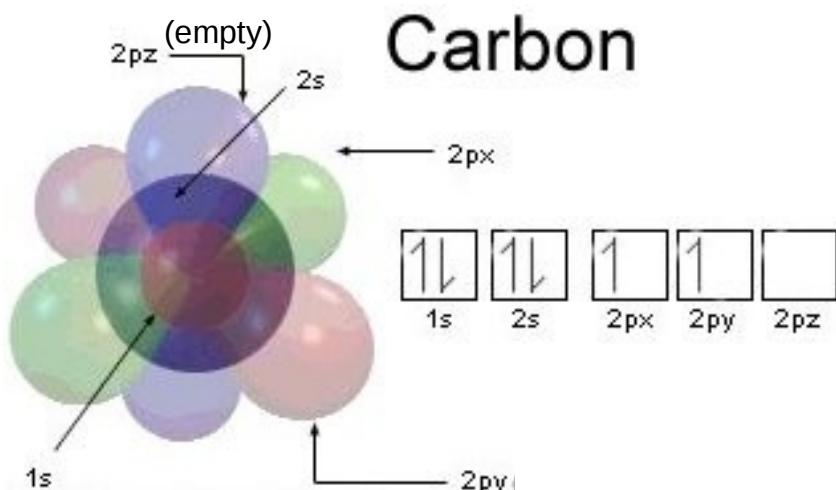
L =	0	1	2	3	4	5	6	7...	$2S+1 L_J$
Nomenclature:	S	P	D	F	G	H	I	K...	

The **multiplicity** of an energy level is defined as $2S+1$.

States with multiplicity 1, 2, 3, 4, 5 are respectively called singlets, doublets, triplets, quartets and quintets.

For example, the ground state of the carbon atom is a 3P state. The superscript three indicates that the multiplicity $2S+1 = 3$ (triplet).

The total spin $S = 1$. This spin is due to two unpaired electrons, each filling one degenerate orbital. The triplet consists of three states with spin components +1, 0 and –1 along the direction of the total orbital angular momentum, which is also 1 as indicated by the letter P. The total angular momentum J can vary from $L+S = 2$ to $L-S = 0$ in integer steps, so that $J = 2, 1$ or 0.



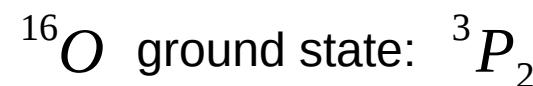
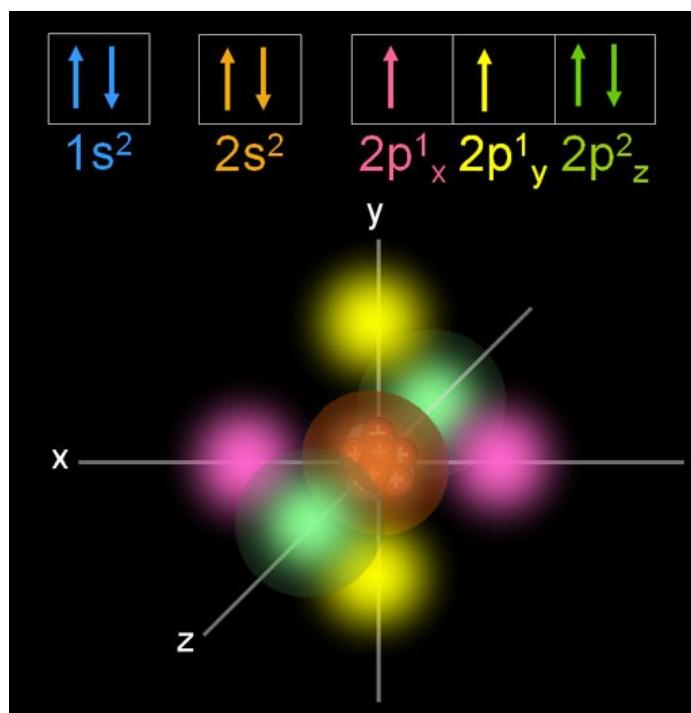
The ordering of the energies increases with increasing J. Therefore the ground state of carbon is:

^{12}C ground state: 3P_0

$L =$	0	1	2	3	4	5	6	7...	$2S+1 L_J$
Nomenclature:	S	P	D	F	G	H	I	K...	

However, when the outer shell is **more** than half-full, then the ordering is with decreasing J.

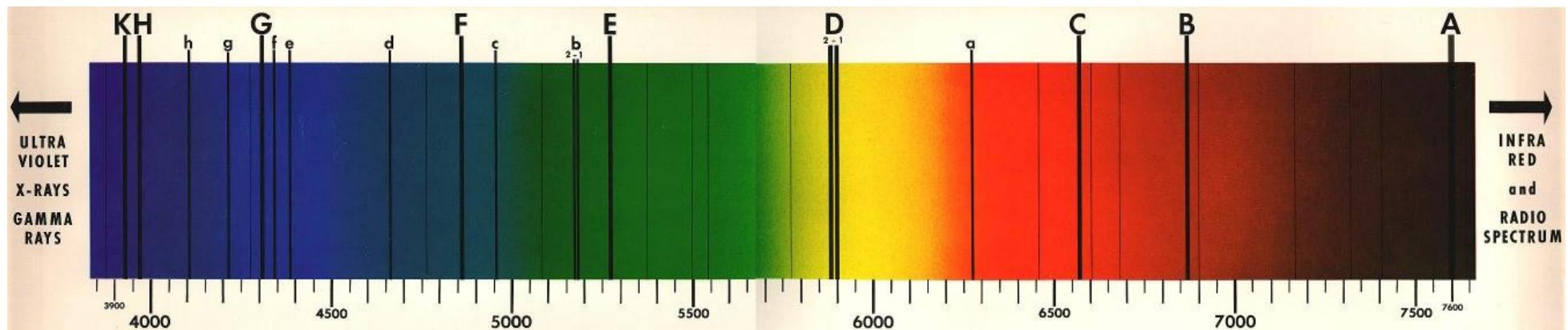
For oxygen O, we have 8 electrons and the p orbitals are more than half full. The total spin $S = 1$. The multiplicity is $2S+1 = 3$ so again it's a triplet. Since electrons fill more than half orbitals then the largest J is the ground state. Therefore:



Which term represents the ground state?
Use **Hund's Rules**:

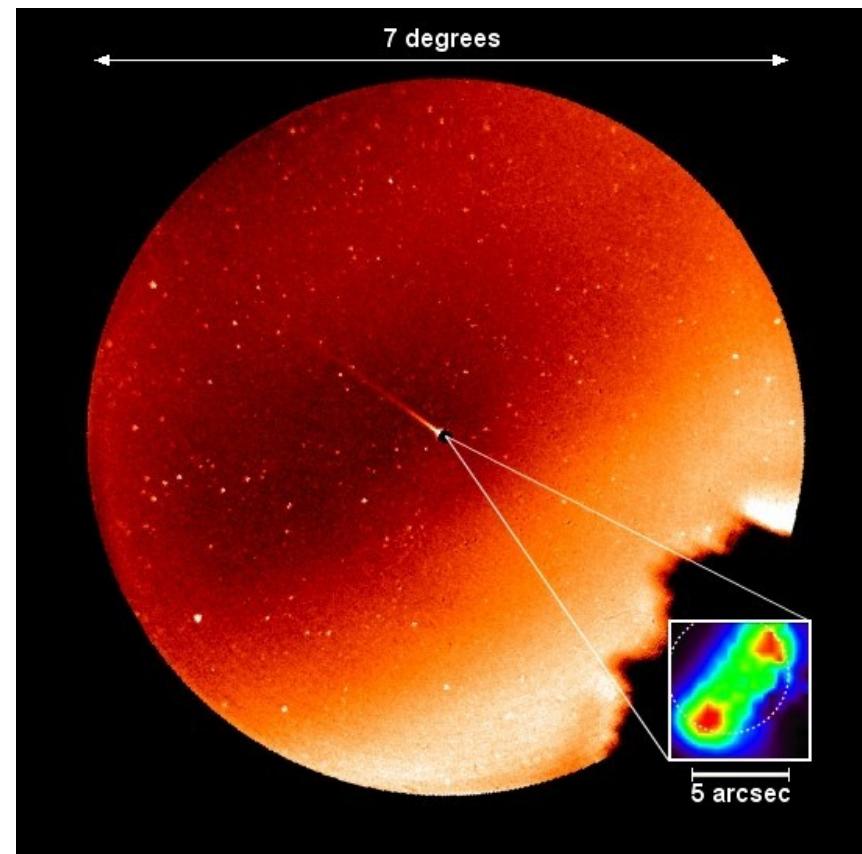
- 1) The term with the highest multiplicity is lowest in energy.
- 2) For a term of given multiplicity, the greater the value of L, the lower the energy.

The fine structure is also responsible for the famous Sodium doublet in the Sun spectrum:



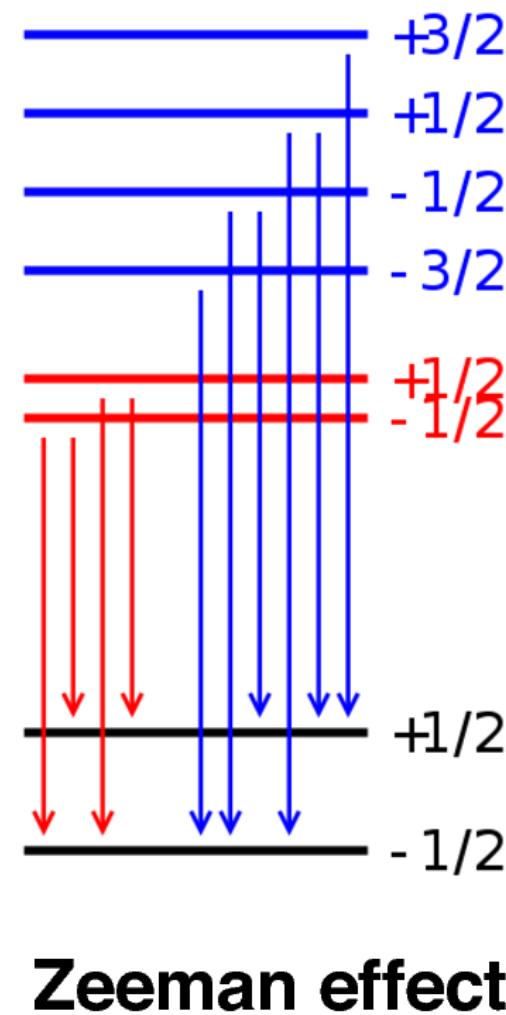
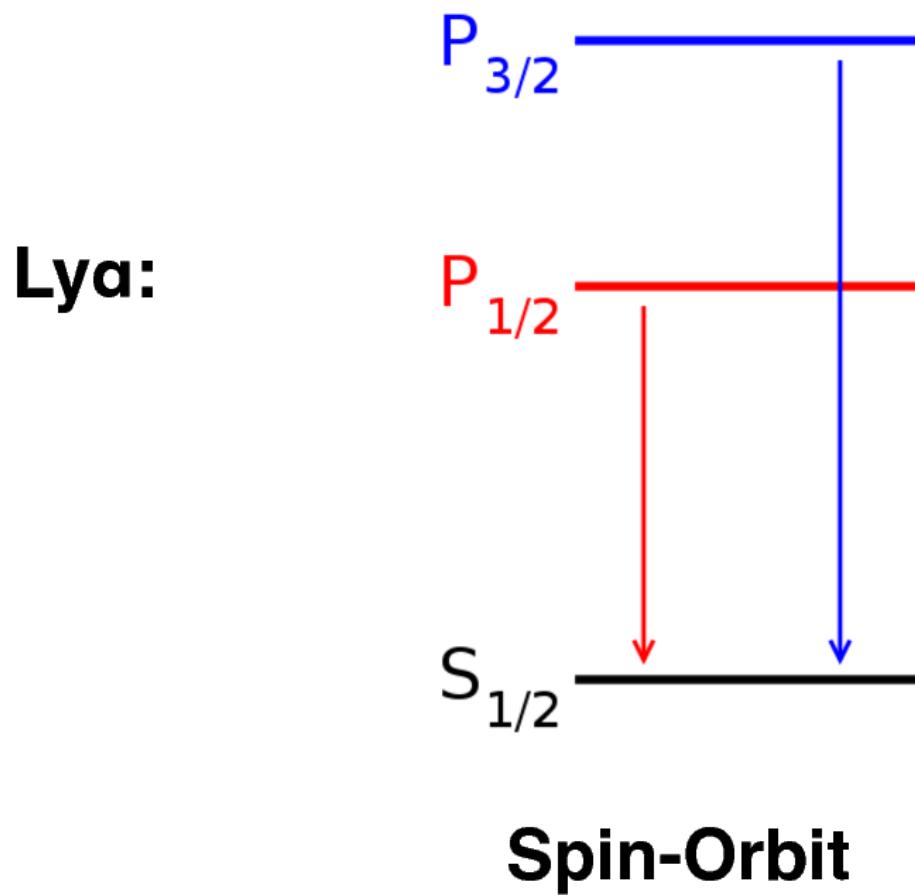
The same fine structure is seen in this image of Mercury: the Sun particles are channeled by the planet's magnetic field onto the equatorial region and cause an ejection of sodium (Na) that generates a tail visible from Earth.

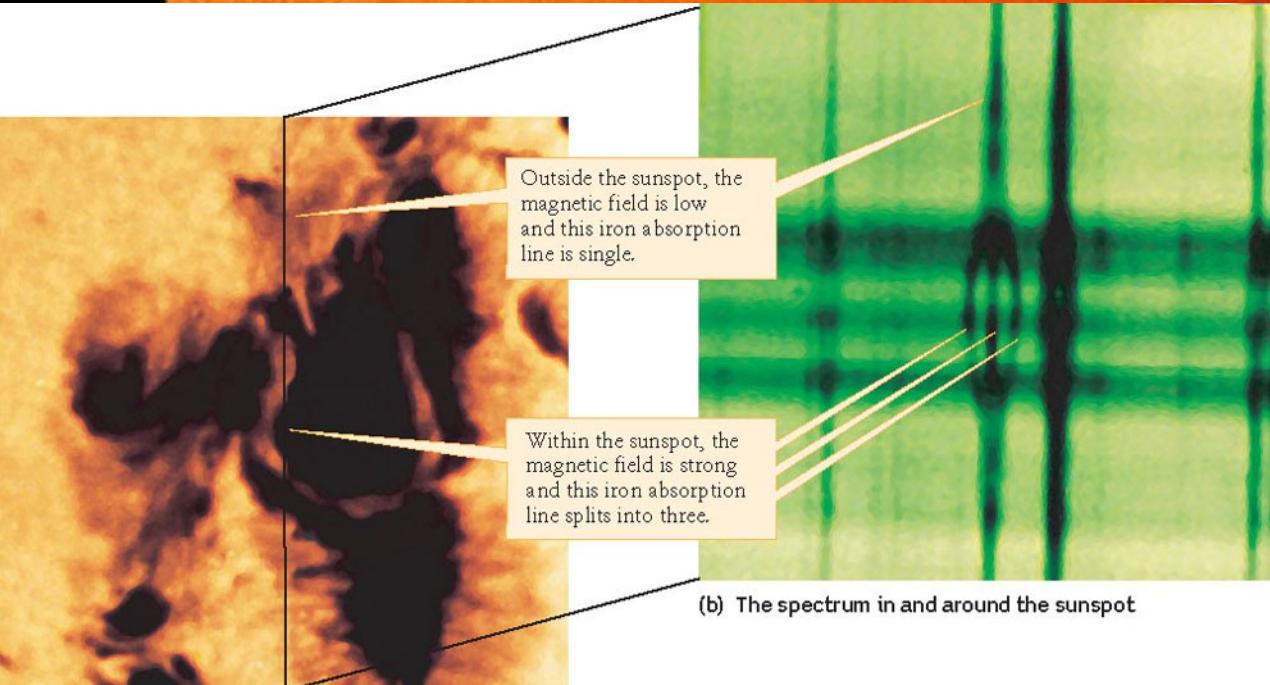
The planet Mercury looks like a comet!



Zeeman effect

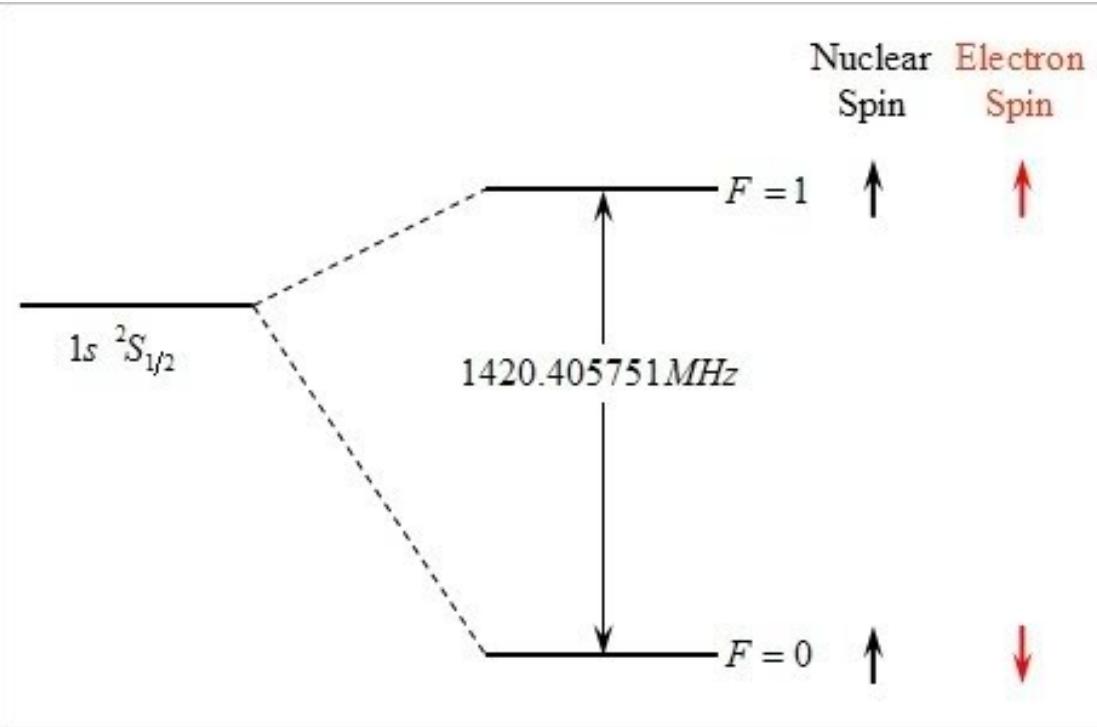
In the presence of a magnetic field the `` m_j '' degeneracy is lifted,
Energy depends now on n, j and m_j .
The splitting is proportional to B : we can measure its strength!





Sun's mean B field~ 1 G
Sunspots B field ~ 1,000-10,000 G

Zeeman effect is easily visible in spectral absorption lines!



Hyperfine structure has energy shifts typically orders of magnitude smaller than those of a fine-structure shift

At Hydrogen atom has spin $\mathbf{S} = 1/2$, and the $^2S_{1/2}$ ground state has orbital angular momentum $\mathbf{L}=0$. So there should be no spin-orbit coupling. However, the nucleus (a proton) has nuclear spin $\mathbf{I}=1/2$ and the total angular momentum $\mathbf{F}=\mathbf{S}+\mathbf{I}$. This is the hyperfine structure

The radiative transition from $F=1$ to $F=0$ gives rise to the famous hydrogen 21 cm emission line, extensively observed in astronomy, even if it has a transition rate of $(10^7 \text{ years})^{-1}$.

Hyperfine structure

Due to interaction of the nucleus spin with the internally generated Magnetic and electric fields.

e.g. in H electron creates a current that generates B, which interact with the proton magnetic dipole.

Now energy depends on the relative orientation of the the proton and the electron spin.

For hydrogen:

$$\Delta E_{\text{hyperfine}} = \left(\frac{m_e}{m_p} \right) \Delta E_{\text{spin-orbit}} \sim 10^{-7} \text{eV}$$

21cm radiation

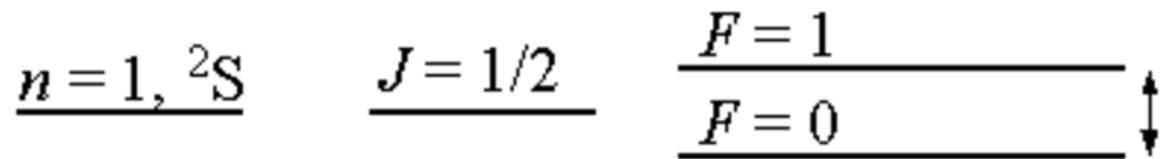
Ground state of hydrogen ($n=1$) has $2 \times 1^2 = 2$ states.

Correspond to different orientations of the electron spin relative to the proton spin.

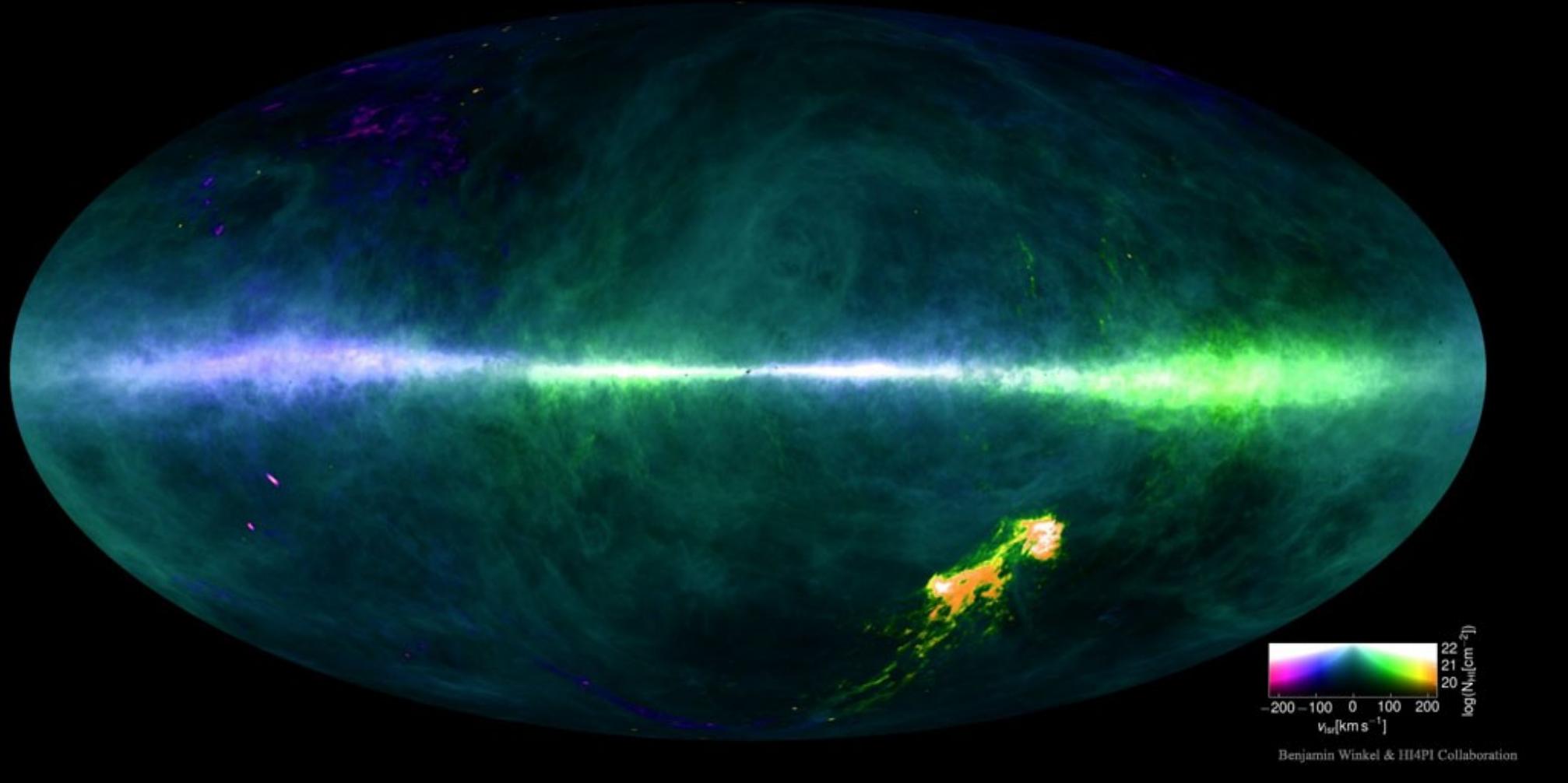
Very slightly different energies - *hyperfine splitting*.

Energy difference corresponds to a frequency of 1420 MHz, or 21cm wavelength.

Very important for radio astronomy, because neutral hydrogen is so abundant in the Universe.



Spin-flip transition
once every 10^7 yr



21 cm map of the galaxy carried with the Effelsberg and Parkes radio telescopes

The bright band in the middle is the galactic plane, rich of neutral hydrogen.
The bright patch in the bottom right corresponds to the Large and Small Magellanic Clouds.

Selection Rules for Radiative Transitions

Some energy levels are connected by strong radiative transitions; in other cases, radiative transitions between the levels may be extremely slow. The strong transitions always satisfy what are referred to as the selection rules for electric dipole transitions.

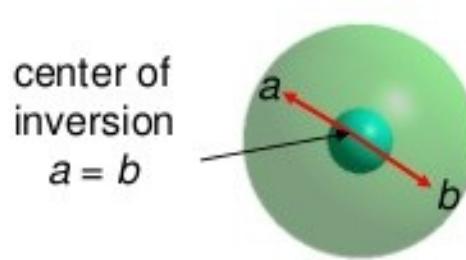
The strongest transitions are electric dipole transitions. These are transitions satisfying the following selection rules:

1. Parity must change.
2. $\Delta L = 0, \pm 1$.
3. $\Delta J = 0, \pm 1$, but $J = 0 \rightarrow 0$ is forbidden.
4. Only one single-electron wave function $n\ell$ changes, with $\Delta\ell = \pm 1$.
5. $\Delta S = 0$: Spin does **not** change.

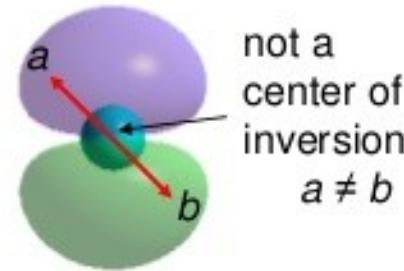
Orbital Parity

Symmetry of orbitals and molecules is of great importance, and we should be able to determine whether orbitals are *gerade* (*g*) or *ungerade* (*u*) (from German for even or odd).

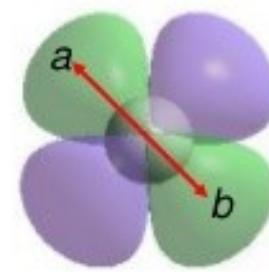
Parity (*g* or *u*) of atomic orbitals:



s-orbital
gerade (*g*)



p-orbital
ungerade (*u*)



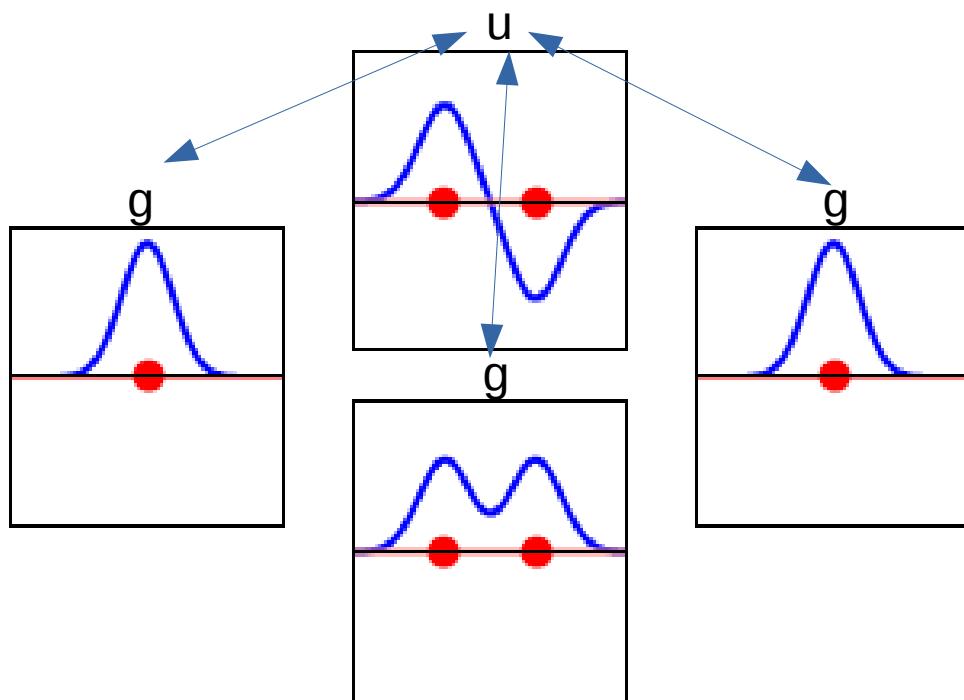
d-orbital
gerade (*g*)

Transitions $g \rightarrow g$ and $u \rightarrow u$ are not allowed

Only transitions that change parity ($g \rightarrow u$) and ($u \rightarrow g$) are allowed.

Orbital Parity II

The electron wavefunction oscillates according to the Schroedinger wave equation and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy.



We allow only $g \rightarrow u$ and $u \rightarrow g$ transitions

(Blue curve: real part of the wave equation)
(Red curve: imaginary part)

Boltzmann Equation

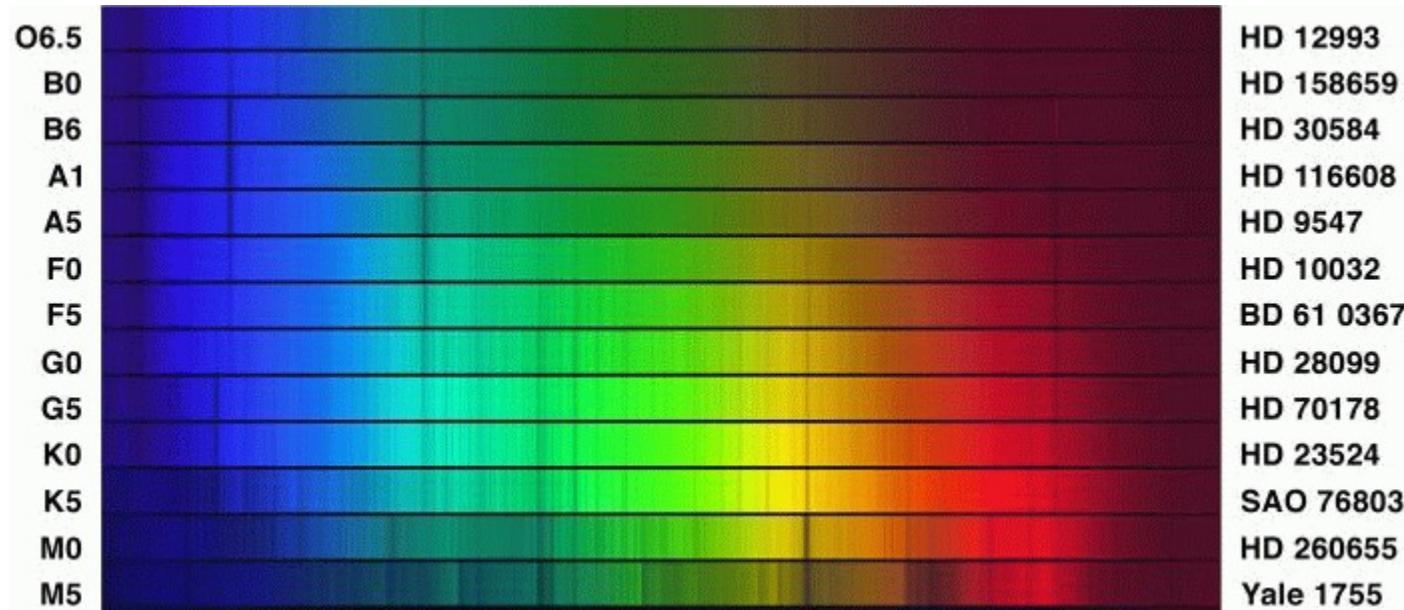
The relative populations of the various atomic levels is difficult to determine general except for the case of atoms in **thermal equilibrium**. In that case the fraction of all the atoms of a given sort which are in level n₁ and n₂ has the simplest form:

$$\frac{N_b}{N_a} = \left(\frac{g_b}{g_a} \right) \left(e^{-(E_b - E_a)/kT} \right)$$

The first term includes factors describing the degeneracy of each energy level. In a hydrogen atom, there are g = 2 ways that an atom can exist at the n=1 energy level, and g = 8 ways that an atom can arrange itself at the n=2 energy level.

The second factor on the right-hand side depends on two quantities: the difference in energy between the two states, and the temperature T of the gas within which the atom sits. The Boltzmann equation assumes that the atoms are primarily excited by collisions with other particles the atoms are immersed in a gas at thermal equilibrium, so that the kinetic energies and velocities of particles is described by a Maxwell-Boltzmann distribution

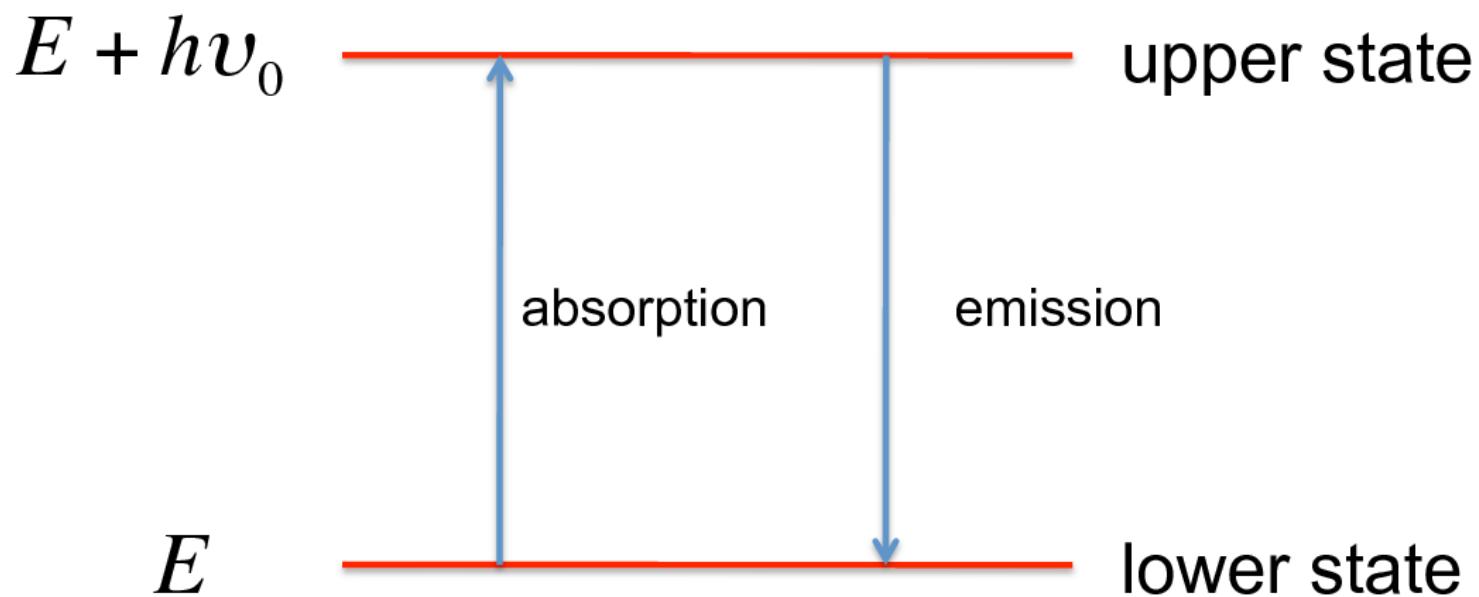
Small digression on Balmer lines



If our atom model is correct, then by using Boltzmann equation one should find that the Balmer lines (the strong dark bands in the A1 spectral type star for example) should be prominent when the corresponding population of hydrogen is excited in the correct state. Consider the first three lines of the Balmer series: Halpha ($n=3 \rightarrow n=2$), Hbeta ($n=4 \rightarrow n=2$) and Hgamma ($n=5 \rightarrow n=2$). Can you explain why the Hbeta and Hgamma lines are strongest in the A1 spectral type? Check also what happens to the Halpha. (A1 temperature $\sim 10,000$ K. B0 temperature $\sim 25,000$ K, F0 temperature $7,000$ K).

Einstein A & B co-efficients

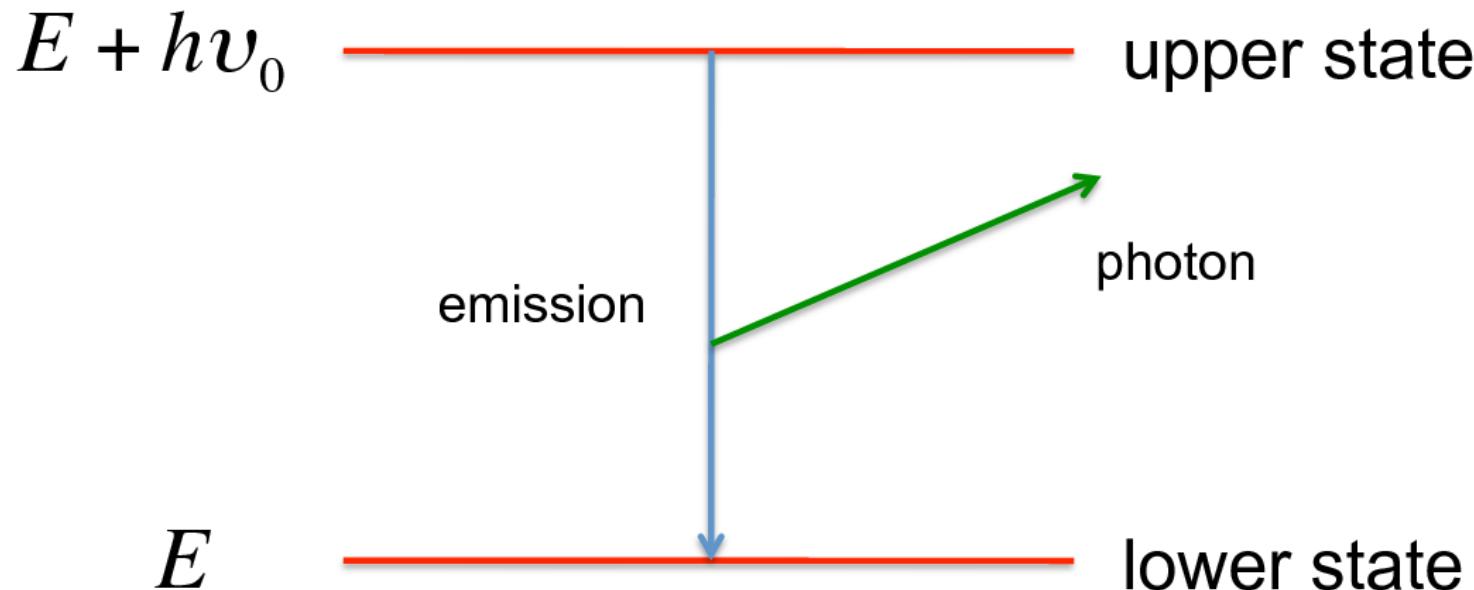
Consider interaction of radiation with a very simple “2-level” atom:



Lower state statistical weight g_1
Upper state statistical weight g_2

Consider balance
between emission /
absorption processes

Spontaneous emission

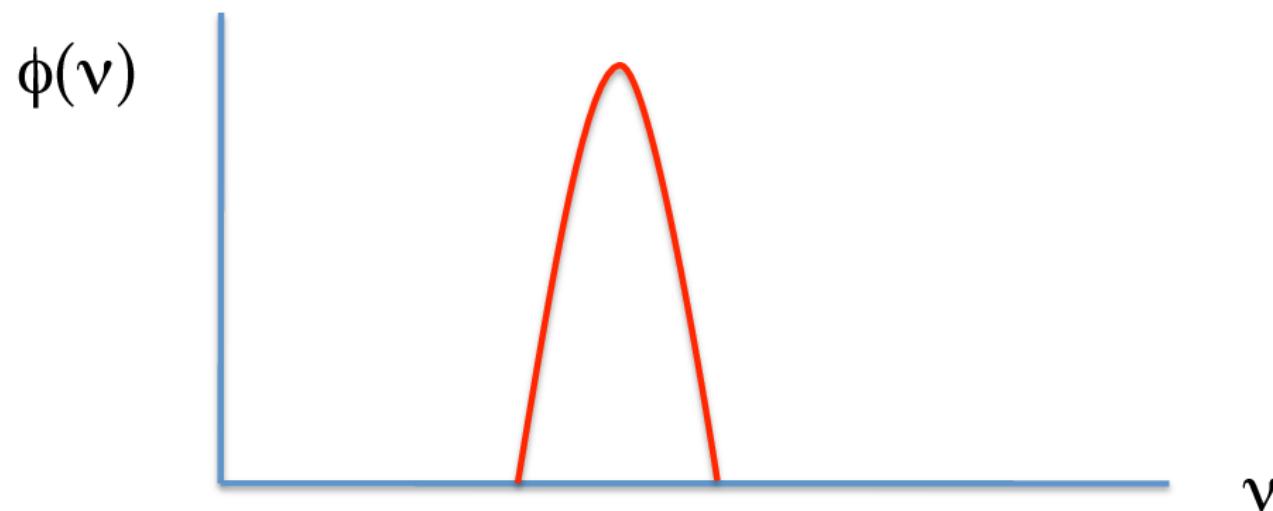


Define the **spontaneous emission** coefficient, A_{21} , as probability per unit time that the system in level 2 drops to level 1 with emission of a photon

Note: units s^{-1} , “spontaneous” means independent of radiation field

Absorption

Actual transitions are not infinitely sharp (e.g. quantum mechanical uncertainty between ΔE and Δt , but also classical effects). Define the relative probability that a photon will be absorbed via *line profile function*



$$\int_0^{\infty} \phi(v) dv = 1$$

Absorption

Define the Einstein B co-efficient:

$B_{12}\bar{J}$ = probability per unit time that the atom absorbs a photon and transitions from level 1 to 2

$$\bar{J} \equiv \int_0^{\infty} J_{\nu} \phi(\nu) d\nu$$

i.e. the weighted average of the intensity in the region of the spectrum that can produce a transition

Stimulated emission

Although we will not prove it here, “obvious” processes of absorption / spontaneous emission, on their own, are not consistent with a Planck form for blackbody emission.
homework!

Need an additional process: **stimulated emission**, emission of a photon stimulated (“catalyzed”) by existing radiation.
Define:

$B_{21}\bar{J}$ = transition probability per unit time for
stimulated emission

Relations between Einstein co-efficients

Let n_1 and n_2 be number densities of atoms in level 1 and level 2 respectively. In thermal equilibrium (which implies steady state):

- “upward” transitions (absorption)
- “downward” transitions (spontaneous / stimulated emission)

...must balance

$$n_1 B_{12} \bar{J} = n_2 A_{21} + n_2 B_{21} \bar{J}$$



$$\bar{J} = \frac{A_{21}/B_{21}}{(n_1/n_2)(B_{12}/B_{21}) - 1}$$

Relations between Einstein co-efficients

But... know that in thermal equilibrium number densities of atoms in states 1 and 2 satisfy Boltzmann Law

$$\frac{n_1}{n_2} = \frac{g_1 \exp(-E/kT)}{g_2 \exp[-(E + h\nu_0)/kT]} = \frac{g_1}{g_2} \exp(h\nu_0/kT)$$



$$\bar{J} = \frac{A_{21}/B_{21}}{(g_1 B_{12}/g_2 B_{21}) \exp(h\nu_0/kT) - 1}$$

Finally use the fact that in thermal equilibrium, the mean intensity is just the Planck function

$$\bar{J} = B_\nu \quad \dots \text{must be true at any temperature}$$

Relations between Einstein co-efficients

Implies finally:

$$g_1 B_{12} = g_2 B_{21}$$

$$A_{21} = \frac{2h\nu^3}{c^2} B_{21}$$

“Einstein relations”, “principle of detailed balance”

Most important point:

- connect **atomic properties**: relations between the microscopic absorption and emission properties of atoms
- apply **irrespective** of whether atoms are in thermal equilibrium with radiation

Inverted population: Maser

- generally

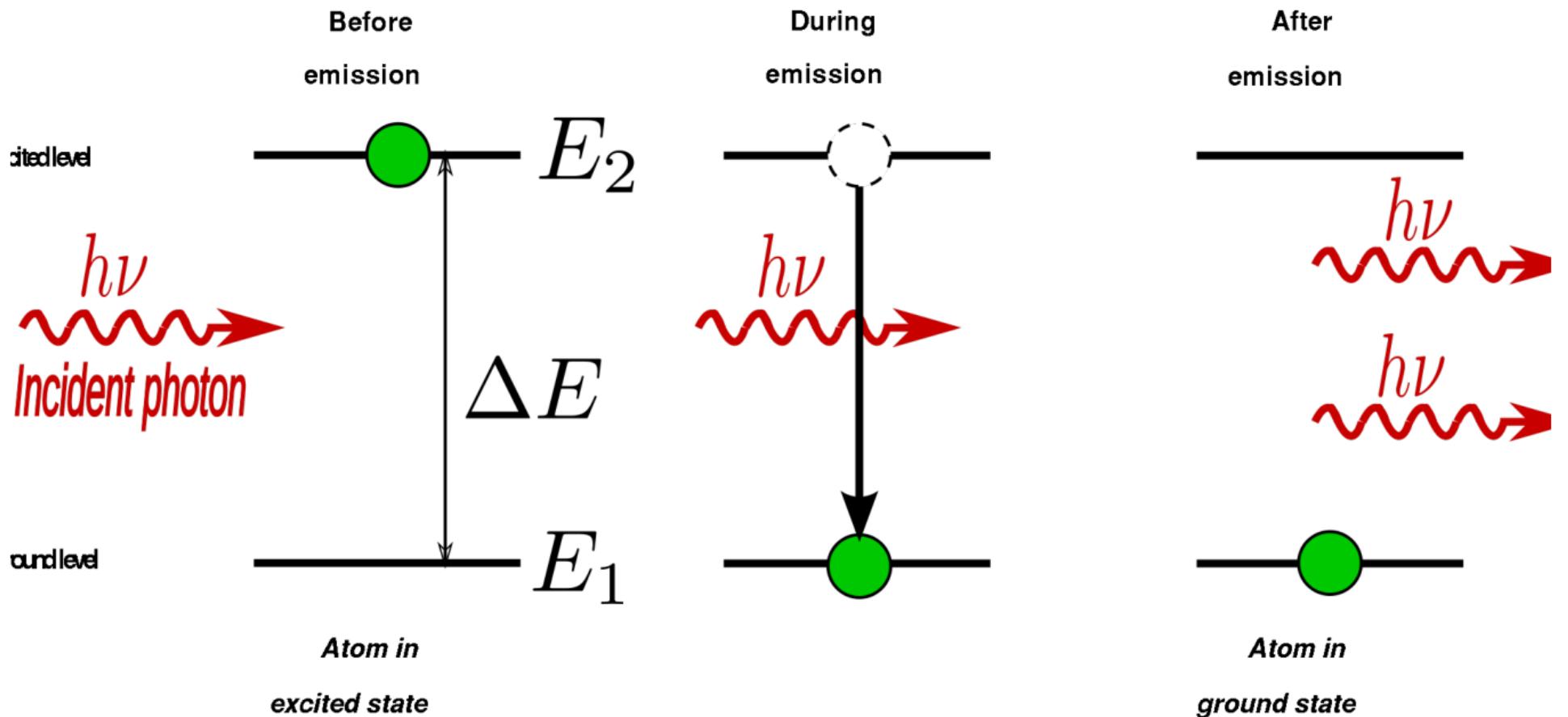
$$\frac{n_1}{g_1} > \frac{n_2}{g_2} \quad \text{Normal population}$$

- In some cases however

$$\frac{n_1}{g_1} < \frac{n_2}{g_2} \quad \text{inverted population}$$

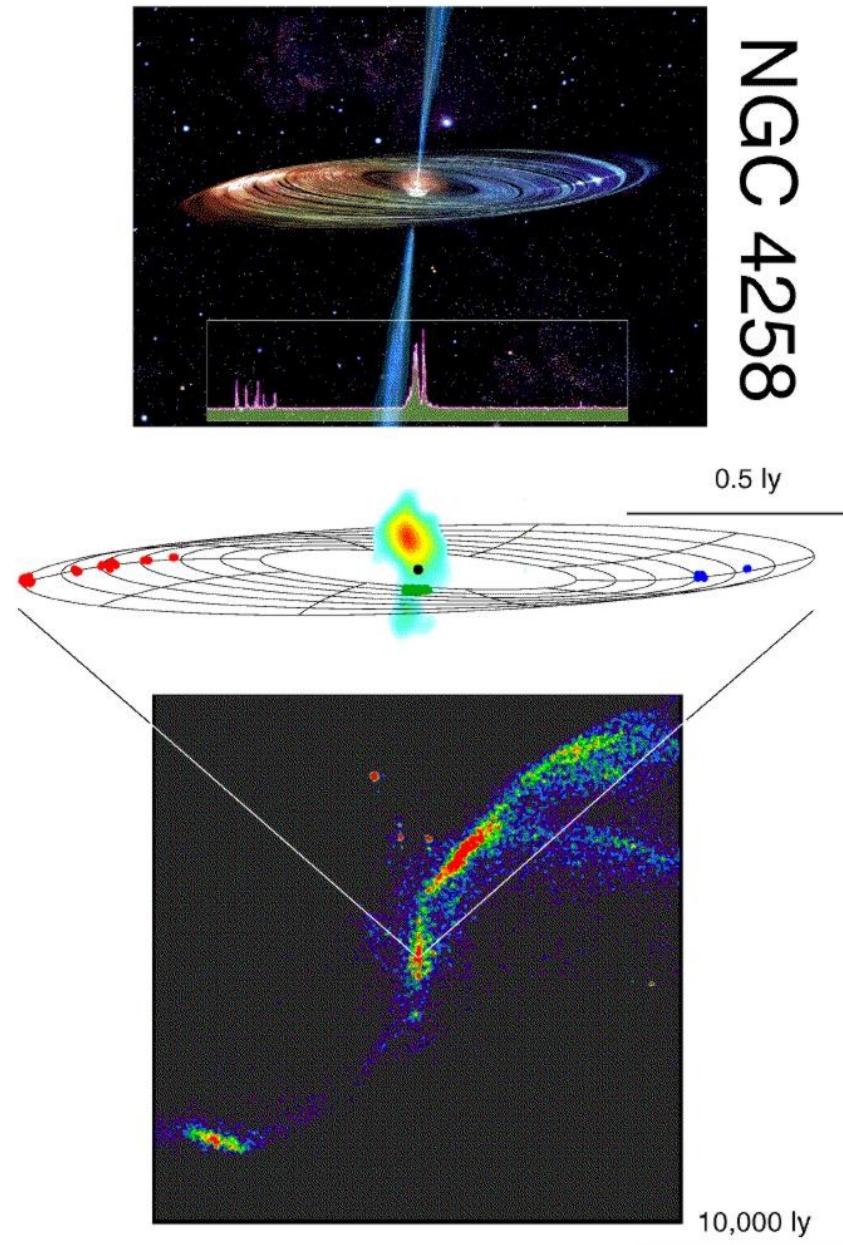
And the absorption coef <0! Light is amplified along the path! E.g. water maser in AGN disc.

Same phase, polarisation, direction and v



$$E_2 - E_1 = \Delta E = h\nu$$

To be continued next week...



Water masers are found predominantly in Seyfert 2 or LINER galaxies and are currently the only resolvable tracers of warm dense molecular gas in the inner parsec of AGN.

Because they are associated with nuclear activity, the most likely model for exciting the maser emission is X-ray irradiation of molecular gas by the central engine

Regardless of the masing molecule, there are a few requirements that must be met for a strong maser source to exist. One requirement is a radio continuum background source to provide the radiation amplified by the maser, as all maser transitions take place at radio wavelengths. The masing molecule must have a pumping mechanism to create the population inversion, and sufficient density and path length for significant amplification to take place.