Theoretical Spectroscopy

I. The Hydrogen Atom

Astronomical Spectroscopy Ch. 3

Prequel

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A large part of what we have learn about our Universe is by studying and looking at line emission. It is therefor important to understand where it comes from and the physical processes behind it.

We have done the simple model of line emission coming from two levels. Now we find ourselves diving deeper into the Universe--but in the other direction! Into the world of atomic particles and quantum physics we will have to explore in order to find a better description of line emission...

Not your great-great-great grandfather's physics

Some familiar relationships still hold true in the Quantum Physics, whereas somethings are pretty different. In a closed system, we still find:

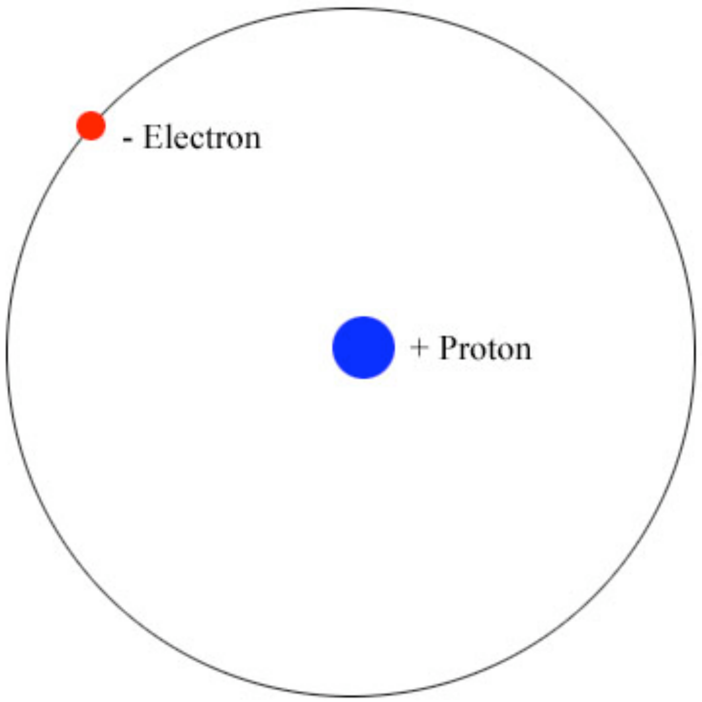
- Mass-Energy, momentum, angular momentum, and electric charge are conserved (Just sometimes not how you think)
- As the size grows, the predictions of QM match those of classical behavior (correspondence principle)

But some things are very different

- *Action is quantized by an amount of* $\hbar = h/2\pi$
- *Actions less than* $\hbar$ *do not exist and cannot be distinguished even if they did*
- *Two particles with half-integral spin cannot be identical*

Classical Look at the Hydrogen Atom (or so what's the problem?)

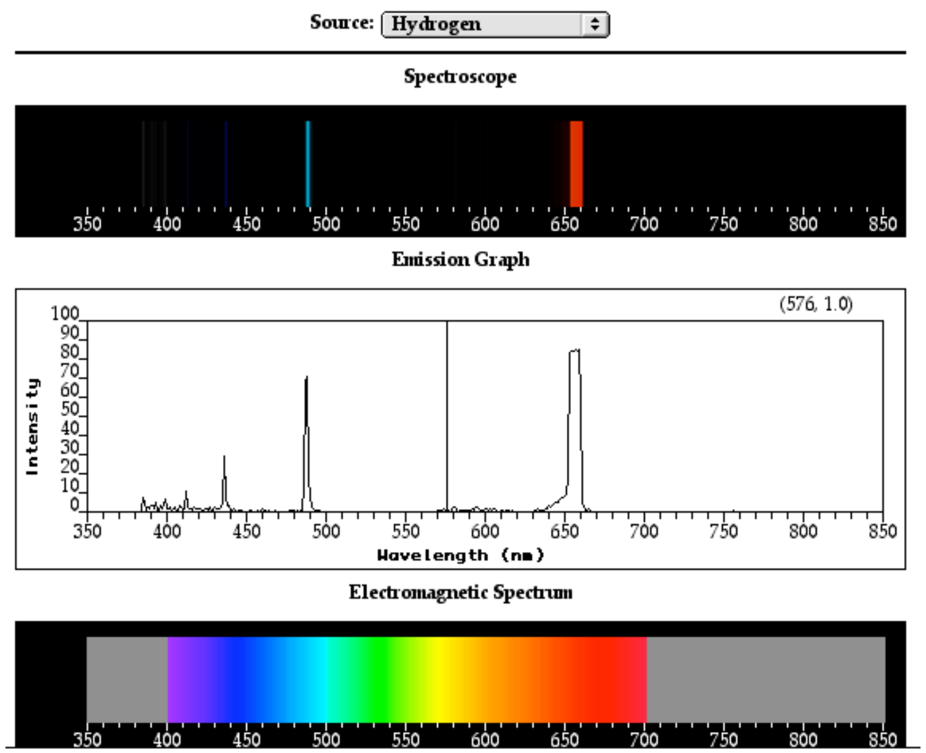
The classical view of the hydrogen atom is an electron orbiting around a proton and kept in placed by the electrical attraction between the two particles

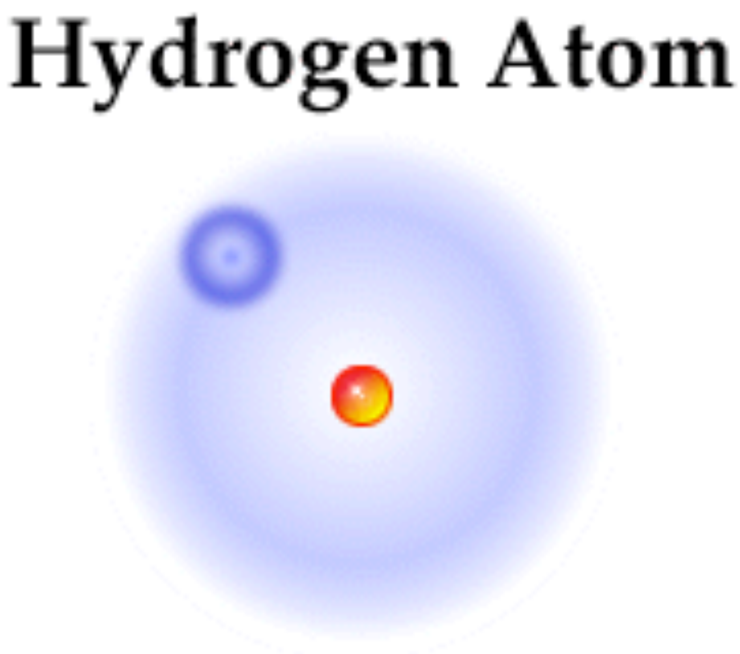


However, in classical mechanics the electron could orbit anywhere around the proton

$$1/2mv^2 - e^2/r = 0$$

The Hydrogen Atom





Observations of an excited hydrogen atoms indicated emission only occurs at certain specific wavelengths. For some reason, the states of the atom were set at specific levels which

Schrödinger Equation

In QM, the Hamiltonian for a electron orbiting a nucleus:

$$\hat{H} = \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

The Schrödinger equation is found by setting $\hat{H}\Psi = E\Psi$, where Ψ is the the wavefunction and in atomic units gives:

$$\left[-\frac{1}{2\mu}\nabla^2 - \frac{Z}{r} - E\right]\psi(\underline{r}) = 0$$

NB: In atomic units, ħ, e, and $4\pi\varepsilon_o$ are all equal to 1.

Solution to the Schrödinger Equation

The Schrödinger equation for the hydrogen atom can be solved analytically in spherical coordinates and has the following form:

$\Psi = R_{nl}(r)\ Y_{lm}(\theta,\phi)$

where $R_{nl}(r)$ is given by Laguerre Polynomials and $Y_{lm}(\theta,\phi)$ are spherical harmonics.

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These are functions specified by integers!

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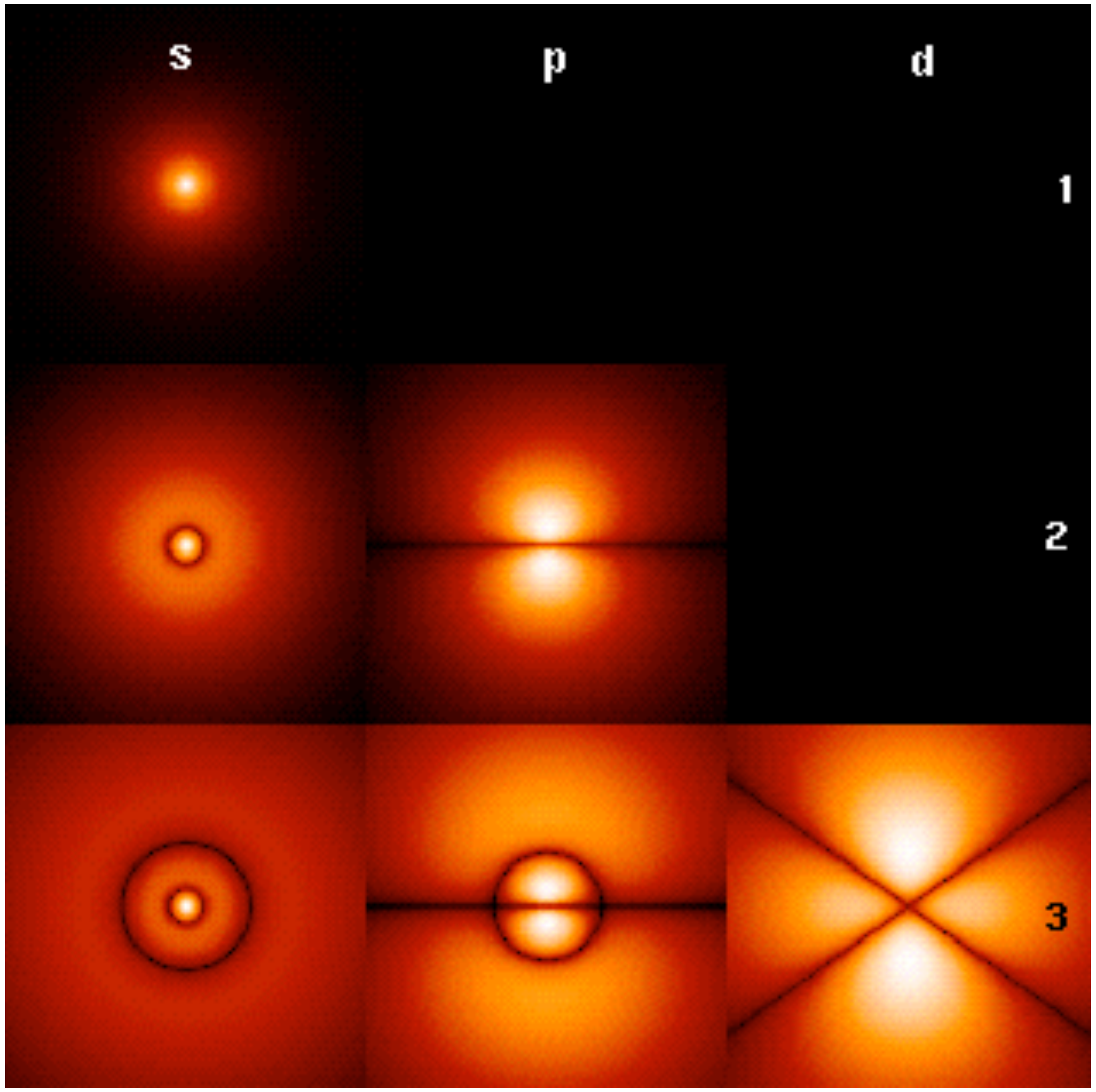
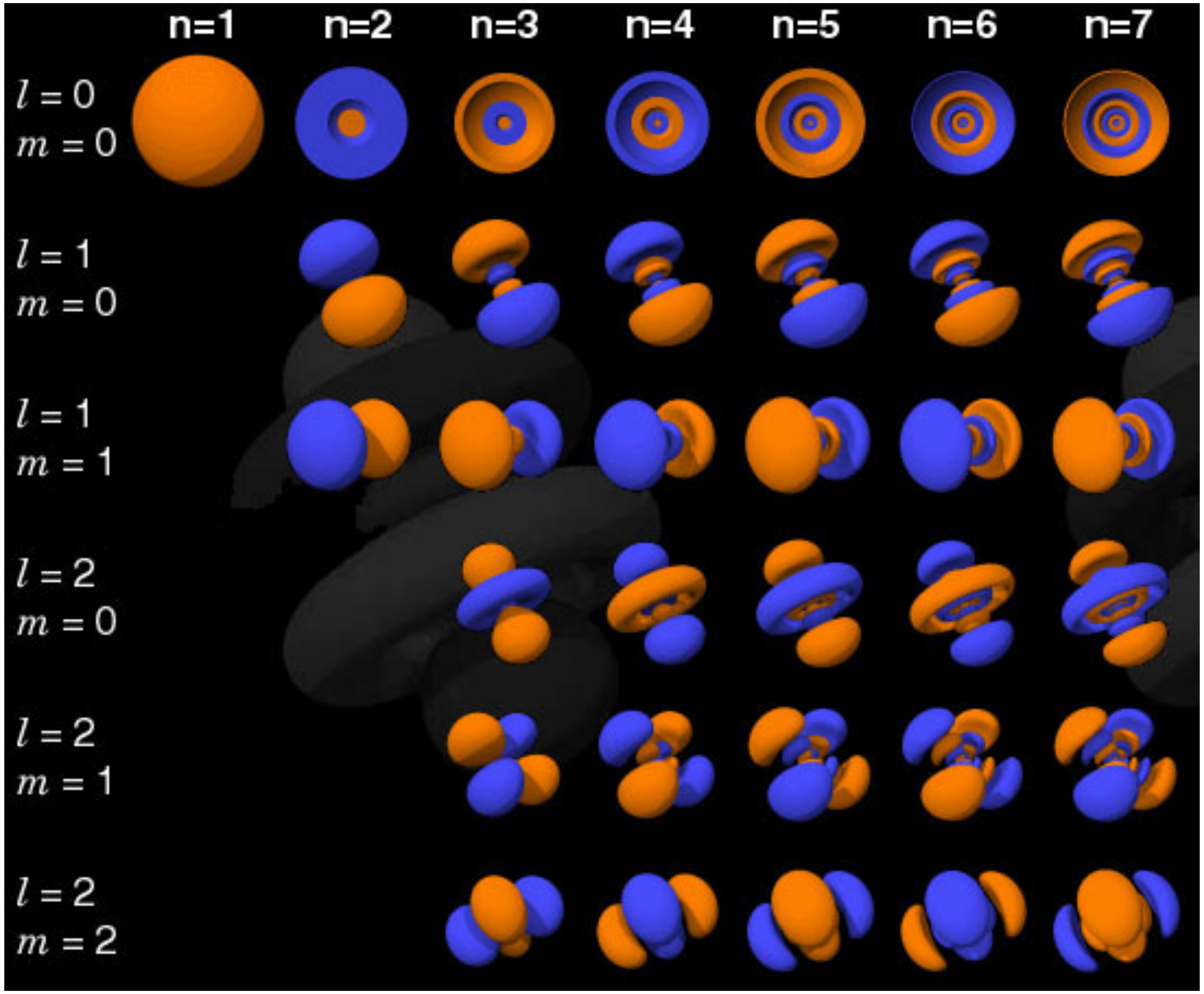
Orbits



More Orbits



Quantum Numbers

n	The principle quantum number. It takes the values n = 1, 2, 3, …, ∞. n determines the energy of the atom according to eq. 6.6.
l	The electron orbital angular momentum quantum number. The actual momentum is given by $h[l(l+1)]^{1/2}/2\pi$. l can take the values of 0, 1, 2, …, n – 1. It is perhaps useful to think of these as orbits of different shape.
m	The magnetic quantum number. It determines the behaviour of the energy levels in the presence of a magnetic field. $Mh/2\pi$ is the projection of the electron orbital angular momentum quantum number, given by l, along the z-axis, of the system. It can take (2l + 1) values –l, –l +1, …, 0, l – 1, l.
s	The electron spin quantum number. Electron spin angular momentum is given by $h[s(s+1)]^{1/2}$, which for a 1-electron system equals $h\sqrt{3}/2\pi$ because an electron always has spin one-half.
s_z	Gives the projection of the electron spin quantum number, s, along the z-axis of the system. This projection is actually $hs_z/2\pi$. In general s_z can take $(2s+1)$ values given by –s, –s +1, …, s – 1, s. For a 1-electron system, this means s_z can take one of two values $-1/2$ or $+1/2$.

Various states are denoted by their nl quantum numbers. The l states are typically given by letters such that the ground state is 1s

0	1	2	3	4	5	6	7	8	…
s	p	d	f	g	h	i	k	l	…

Energy Levels

The energy level of a single level is given by:

$$E_n = -\frac{\mu Z^2 e^4}{8h^2\varepsilon_0^2}\frac{1}{n^2} = -R\frac{Z^2}{n^2}$$

where: R is the Ryberg constant and given by:

$$R_H = \frac{\mu}{m_e}R_\infty = \left(\frac{M_H}{M_H + m_e}\right)R_\infty$$

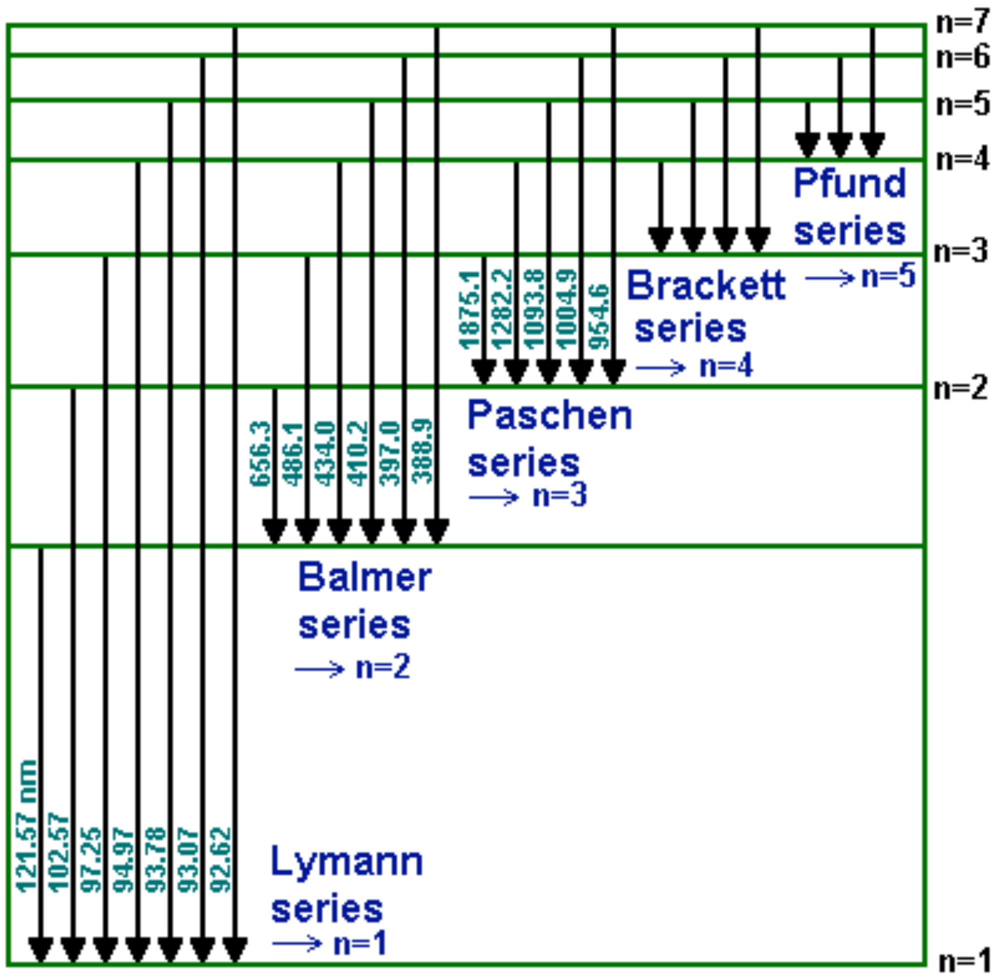
and R_∞=109737.31 cm^{-1} and R_H=109677.581 cm^{-1}.

Energy Levels (cont.)

For a photon emitted between a transition between two levels, the wavelength of the photon will be:

$$\frac{1}{\lambda} = \frac{1}{hc}\left(E_{n_1} - E_{n_2}\right) = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), n_1 < n_2$$

Transitions in H



				range/cm^{-1}		Range/Å	
n_1	name	symbol	region	$n_2 = n_1 + 1$	$n_2 = \infty$	$n_2 = n_1 + 1$	$n_2 = \infty$
1	Lyman	Ly	UV	82 257	109 677	1 216	912
2	Balmer	H	visible	15 237	27 427	6 563	3 646
3	Paschen	P	IR	5 532	12 186	18 077	8 206
4	Brackett	Br	IR	2 468	6 855	40 519	14 588
5	Pfund	Pf	IR	1 340	4 387	74 627	22 795
6	Humphreys	Hu	IR	808	3 047	123 762	32 819

The first line in any series is typically named α, followed by β, γ, and so on. The names of the series are after their discoverer. The diagram on the left is also referred to as a Grotian diagram.

Example: Hα

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- Calculate λ for an $n=3 \rightarrow n=2$ transition

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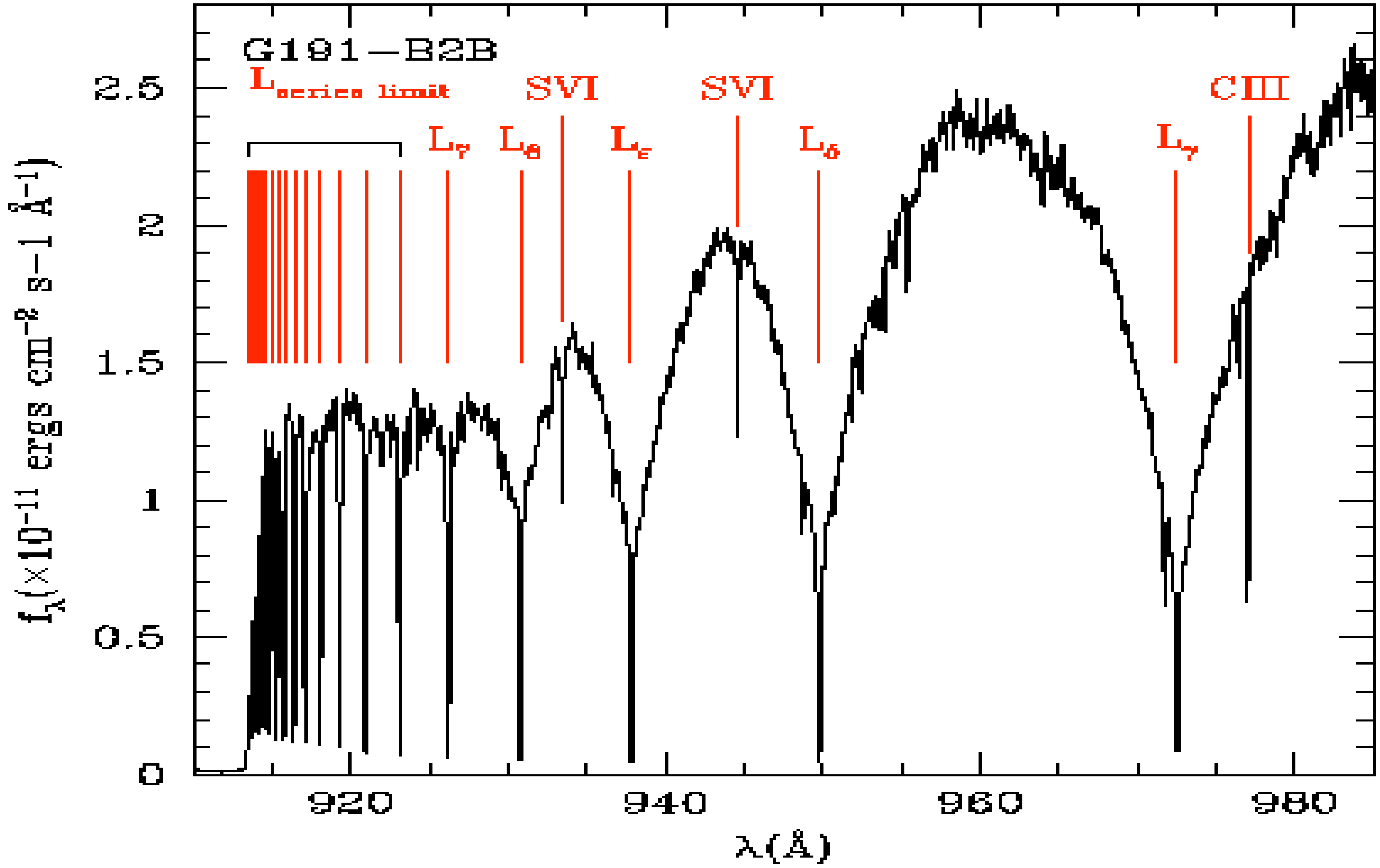
- Calculate λ for an n=3→n=2 transition
- Answer: λ=6562.75

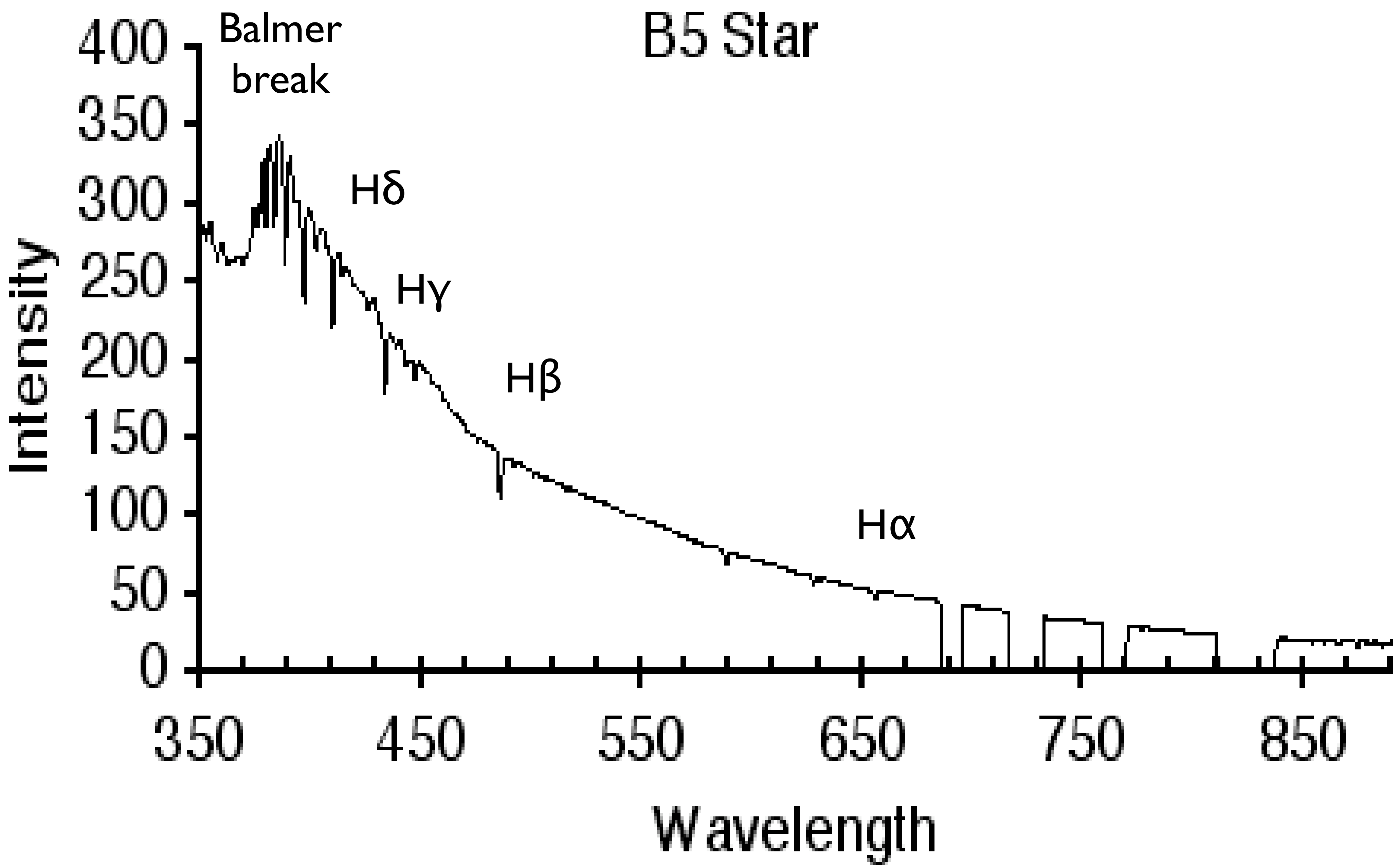
Lyman Lines

In a hot white dwarf



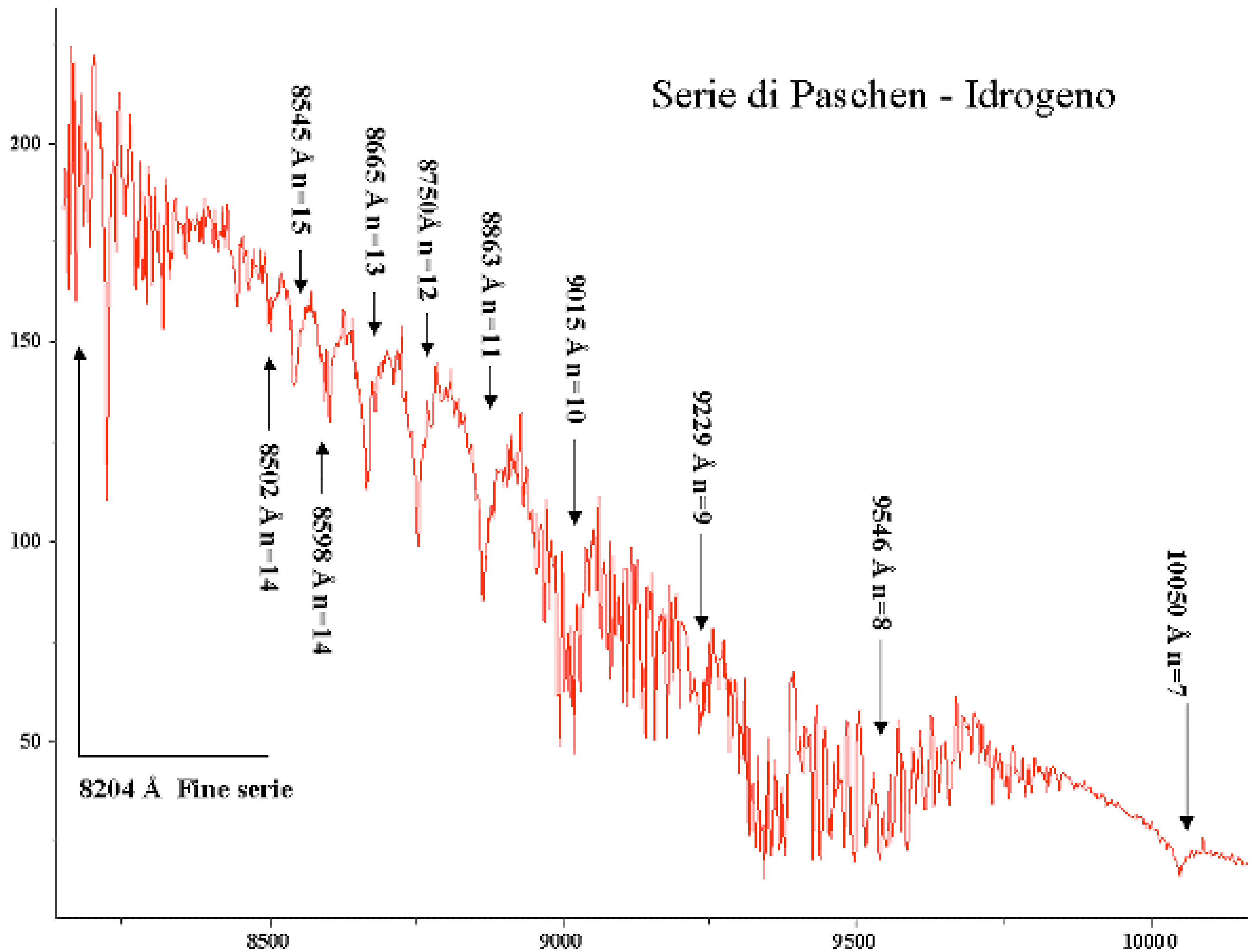
Balmer Lines

In a hot white dwarf



Paschen Lines

In a B star



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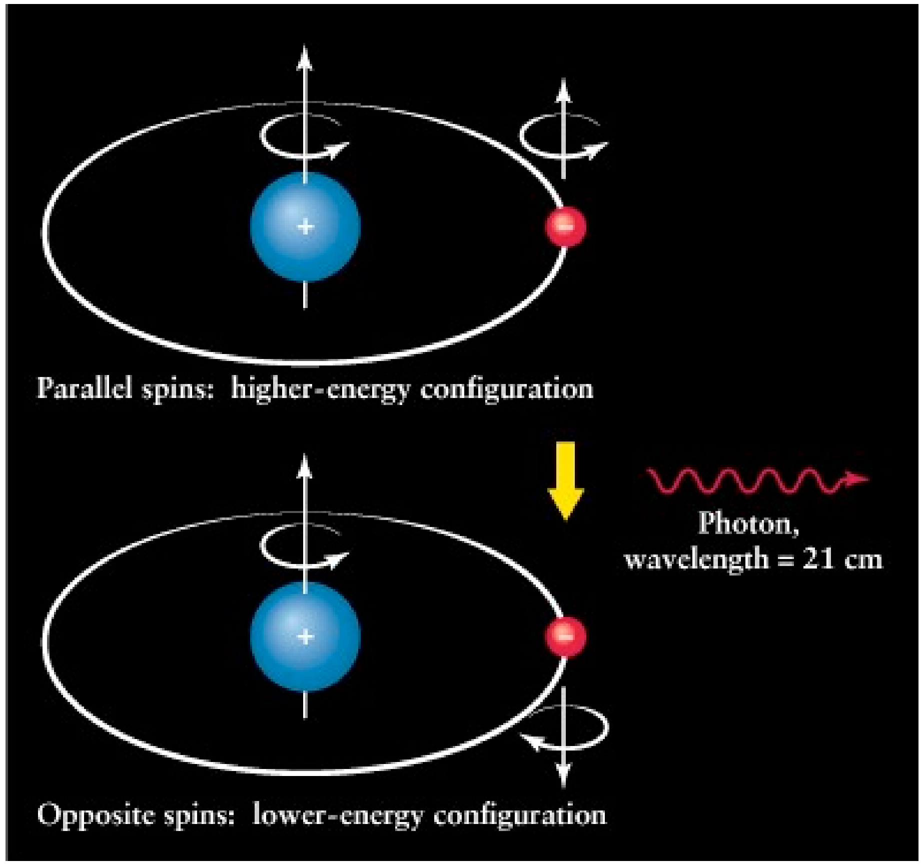
- Answer: λ=6564.95 Å

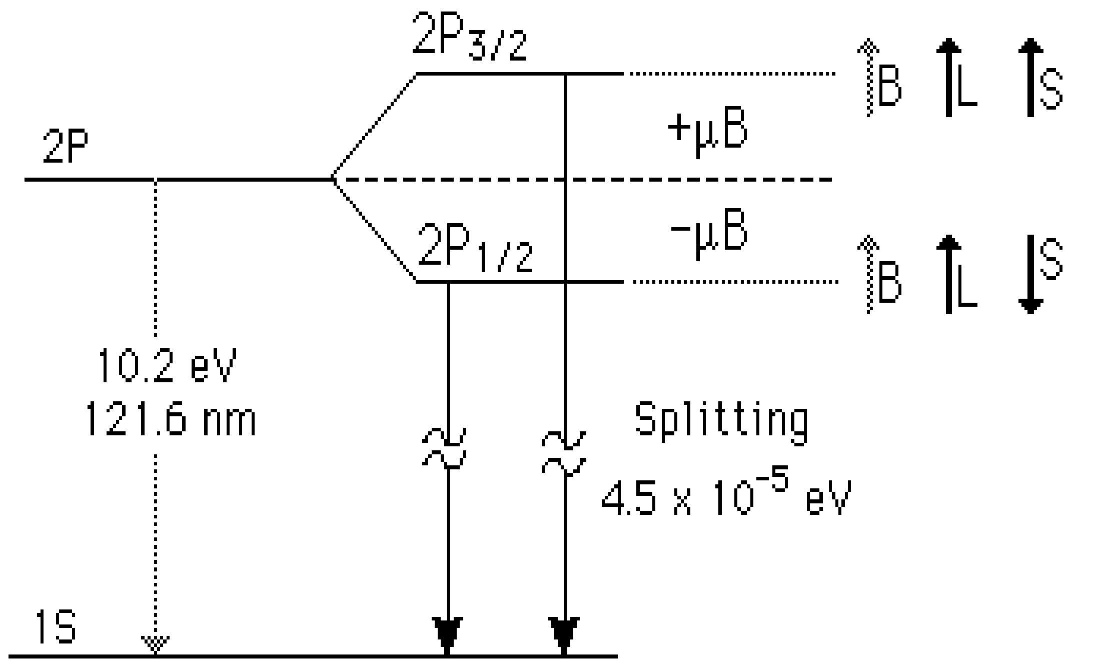
Angular Momentum

- Angular momentum is a vector!
- Total Electron angular momentum
  - $\underline{j}=\underline{l}+\underline{s}$
  - l is Electron orbit angular moment
  - s is Electron spin angular momentum
- Final Angular Momentum
  - $\underline{f}=\underline{j}+\underline{i}$
  - i is the spin of the nucleus
- In QM, the addition of two vectors like:
  - L=l1+l2
  - L=|l1-l2|,|l1-l2|+1...|l1+l2|
  - so l1=2, l2=3, then L=1,2,3,4,5



Fine Structure of Hydrogen

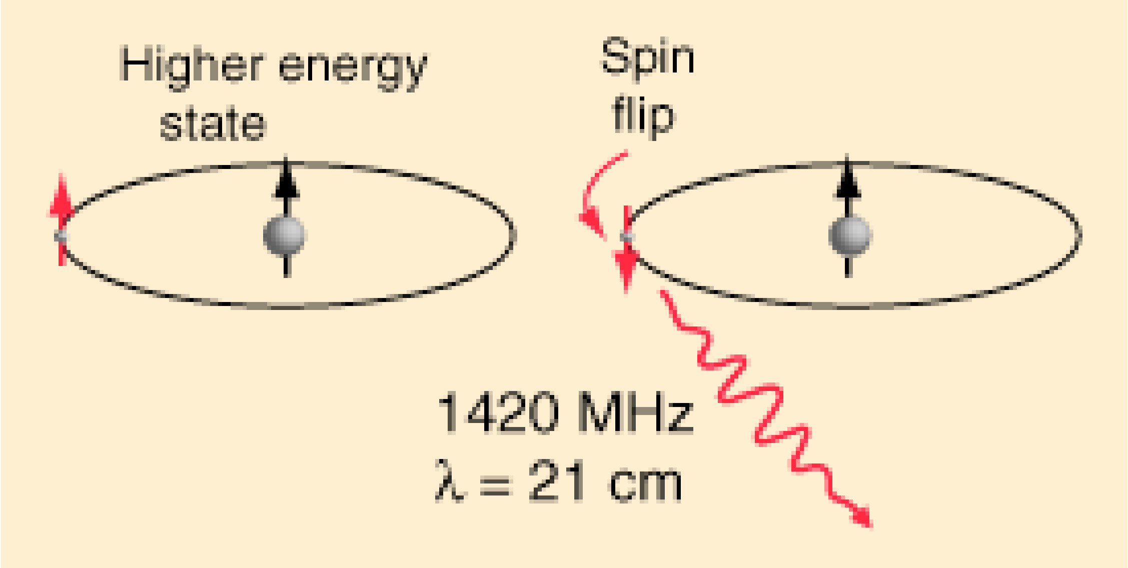
Fine structure is due to a relativistic treatment of the motion of the electron around the atom and the magnetic moments of the orbits.

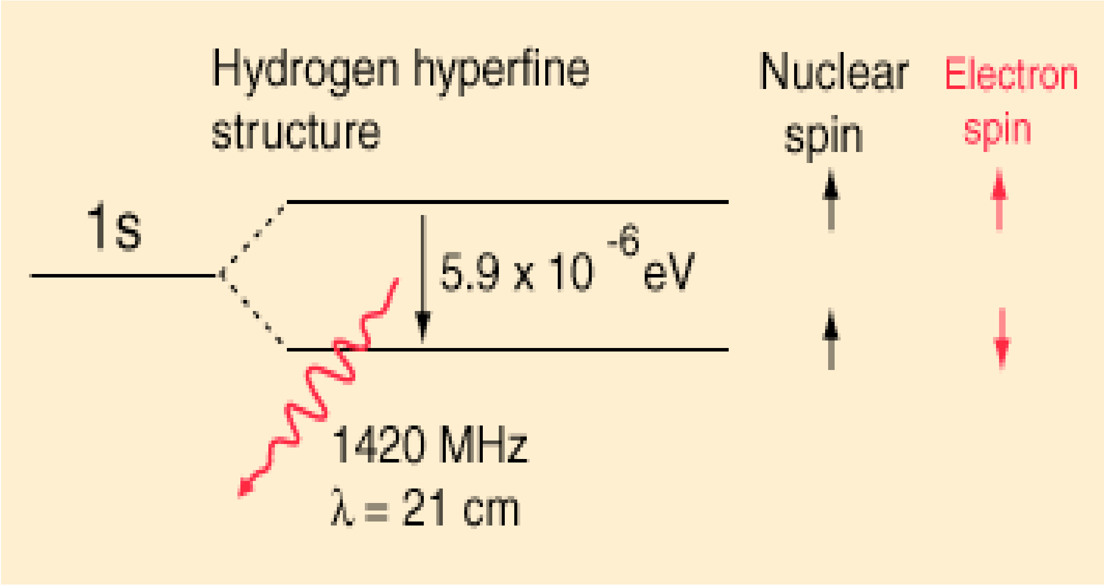


So the angular moment can be $j=l+s$. s has a value of 1/2 and l can range from 0...∞ depending on n, with the other requirement $j>0$

Hyperfine Structure of hydrogen

One more source of lines in the hydrogen atom is the angular moment between the spin nucleus, i, and the total electron angular momentum j, such that the final angular momentum f=j ±1/2, giving f=0,1. The energy difference between these two levels produces a photon with λ=21 cm





Allowed Transitions

For hydrogen, transitions between any level are allowed, but not all transitions are observed between all states. Transitions are governed by selection rules which can be derived from quantum mechanics. These rules are:

- Δn any
- $\Delta l = \pm 1$
- $\Delta s = 0$ (always true for H)
- $\Delta j = 0$

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- Answer:
  - 2s - 3p, 2p-3s, 2p-3d are allowed
  - 2s-3s, 2p-3p, and 2s-3d are not allowed