PH102, 2014W, Lecture Notes: January 16, Thur, Class 4

Hydrogen Atom: Normalization, Electron whereabouts, spectral lines, and hydrogen-like atoms

Objectives:

- Recognize characteristics of radial and angular probability densities using n, l, m_l.
- Extend the Schrodinger Equation solutions of the hydrogen atom to the hydrogenlike atoms.
- Qualitatively understand relationships between various hydrogen atom models and spectral lines.

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The origin of angular momentum quantization

Radial Equation is

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E-\underbrace{U(r)\big)R\ -l(l+1)}R=0$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left[E-U(r)\ -\frac{l(l+1)\hbar^2}{2mr^2}\right]R=0 \quad \text{(e3.1)}$$

The total energy of the electron E = Kinetic E (radial) + Kinetic E (orbital) + $U(r)$

Put the expression of E into (e3.1), then (e3.2) becomes

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left[Kineric\ E\ (radial)+\ Kinetic\ E\ (orbital)\ -\frac{l(l+1)\hbar^2}{2mr^2}\right]R=0$$

$$Kinetic\ E\ (orbital)=\frac{l(l+1)\hbar^2}{2mr^2}$$

The orbital kinetic energy of the electron = $\frac{1}{2}m\,v_{orbital}^2 = \frac{L^2}{2mr^2}$

The angular momentum L of the electron = $L = mv_{orbital}r \rightarrow v_{orbital} = \frac{L}{mr}$

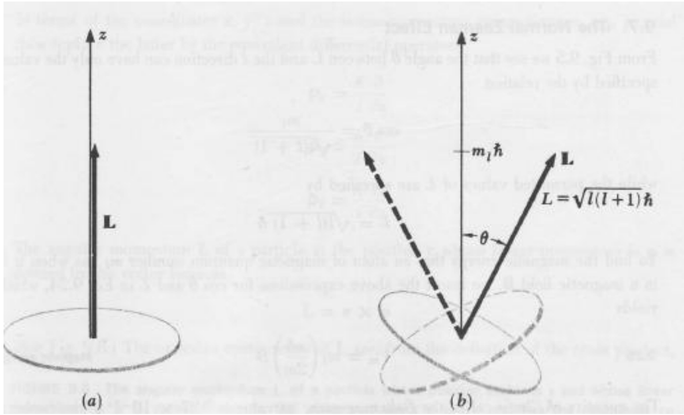
$$\frac{L^2}{2mr^2}=\frac{l(l+1)\hbar^2}{2mr^2}$$

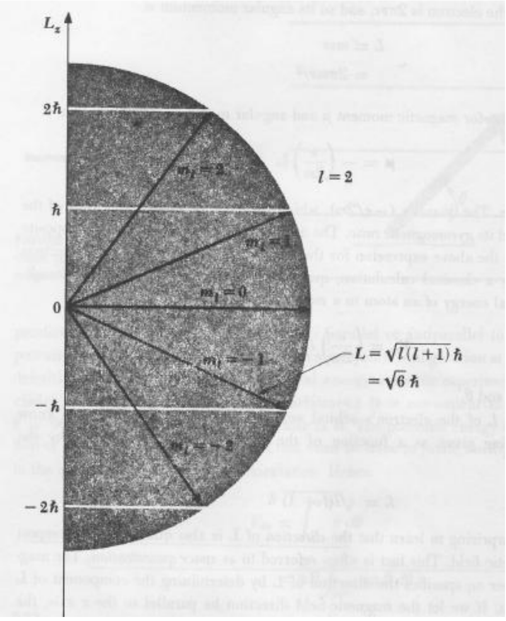
$$L^2=\ l(l+1)\hbar^2$$

$L=\ \sqrt{l(l+1)}\hbar$ → Electron angular momentum L is quantized

Angular momemtum L is defined as a vector L = r x p

- L is perpendicular to the plane in which the rotational motion takes place and follows the right hand rule.

- The amount is quantized and determined by the orbital angular quantum number, l. $L = \sqrt{l(l+1)}\hbar$
- The direction is also quantized and determined by the m_l $value$ with respect to the external magnetic field. The magnetic quantum number m_l specifies the direction of L determining the component of L in the magnetic field direction. If the magnetic field direction is parallel to the z-axis, then the component of L on the z-axis would be $L_z = m_l\hbar$.
- L can never be parallel to the z-axis because the amount of L is always greater than the largest m_l value allowed.
- Uncertainty principle explains the relationship between L and Lz.
- 



Three quantum numbers are defined so that the resulting wave functions can satisfy the Schrodinger Equation:

- Principal quantum number, n
- Orbital quantum number, l,
- Magnetic quantum number, m_l

where

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\,\hbar^2}\right)\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

$$L^2 = l(l+1)\hbar^2$$
$$L_z = m_l\hbar$$

where Bohr radius $a_0 = \frac{4\pi\varepsilon_0\,\hbar^2}{me^2}$= 0.053 nm or 0.53 A; and
Hydrogen atom's ground state energy, $E_1 = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right) = -13.6\ eV$

Wave function = $\psi(r,\theta,\phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}\mathbf{Y}_l^{m_l}$

where $\Theta_{l,m_l}\Phi_{m_l}$= $\mathbf{Y}_l^{m_l}$ (Spherical harmonics)

These relationships can be simply written using operator notations:

$$\mathbf{H}\psi_{n,l,m_l} = \boldsymbol{E_n}\psi_{n,l,m_l}$$
$$\mathbf{L^2}\psi_{n,l,m_l} = \boldsymbol{l(l+1)}\hbar^2\psi_{n,l,m_l}$$
$$\mathbf{L_z}\psi_{n,l,m_l} = \boldsymbol{m_l}\hbar\psi_{n,l,m_l}$$

Note. These equations can be applied to all systems where the Hamiltonian (H = T+V) has a spherical symmetry (remember that the hydrogen atom's potential energy has a spherical symmetry). In such a case, the wave function, ψ_{n,l,m_l}, is an eigenfunction of **H, $\mathbf{L^2}$, $\mathbf{L_z}$ and $\boldsymbol{E_n, L^2, and\ L_z}$ are all quantized.**

Normalization

The probability density of the hydrogen atom can be written as:

$$|\psi_{n,l,m_l}|^2 = R(r)^2\Theta(\theta)^2\Phi(\phi)^2$$

Normalization condition: $|\psi_{n,m,m_l}|^2\ over\ all\ space\ (dV = r^2 sin\theta\ drd\theta d\phi)$

$$\int |\psi_{n,l,m_l}|^2\,dV = \int |\psi_{n,l,m_l}|^2\, r^2 sin\theta\ drd\theta d\phi$$
$$= \int_0^\infty R(r)^2 r^2\,dr \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi$$

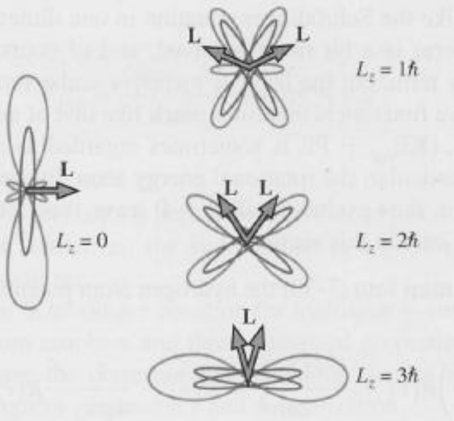
$$\begin{cases} \int_0^\infty R(r)^2 r^2\,dr = 1 \\ \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi = 2\pi \int_0^\pi \Theta(\theta)^2 sin\theta\ d\theta = 1 \end{cases}$$

Electron whereabouts: Angular directions $(\boldsymbol{\theta}, \boldsymbol{\varphi})$
Angular Probability Density

$$\Theta(\theta)^2\Phi(\phi)^2 \equiv \mathbf{Y}_l^{m_l *}\mathbf{Y}_l^{m_l}$$

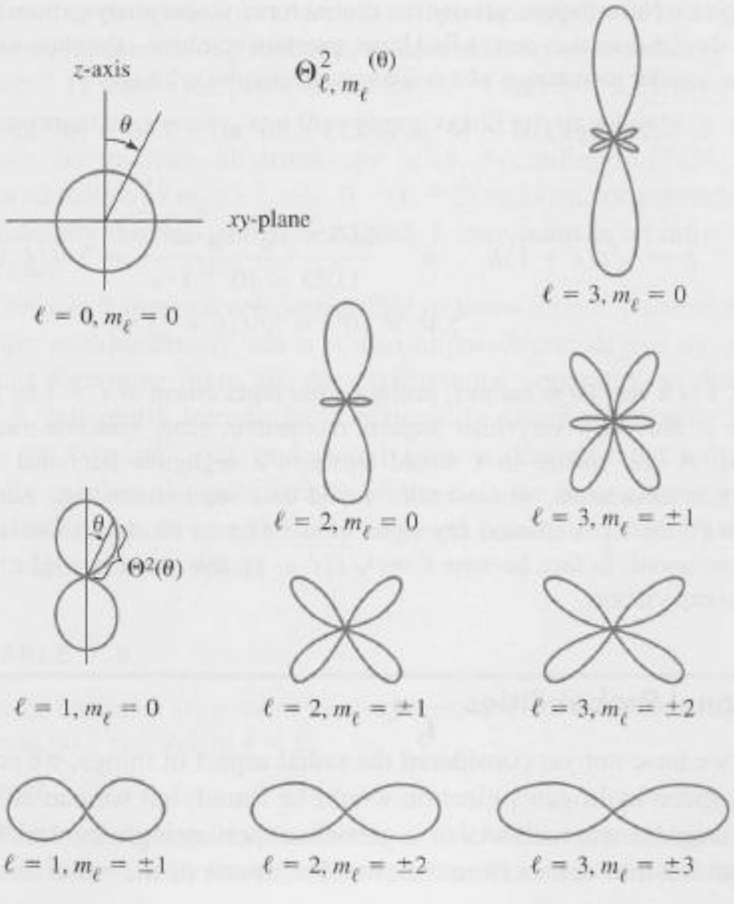
- The probability density is a diffuse cloud spread over space.
- The probability density extends farther from the origin (where the proton is) as n increases.
- The probability density should be symmetric along the ϕ axis.
- In s states where l = 0, the kinetic energy is solely radial, so the probability density is spherically symmetric. No orbital motion.
- Note that the electron is orbiting the place perpendicular to the direction of $L_z. See\ Figure\ on\ the\ right.$
- In p states where (l=1), three possible probability distributions: $L_z = 1, 0, -1$. See Figure below.
- In d states where (l=2), five possible probability distributions $L_z = 2, 1, 0, -1, -2$.

Figure 7.14 A crude correspondence to orbital motion.



- If l=0, the probability is the same in any direction.
- There is no probability at the center when $l \neq 0$. Take a look at the p, d, f orbitals as compared to s orbitals. In all $l \neq 0$ cases, as m_l increases, the probability density progressively changes from mostly along the z-axis to mostly in the xy-plane. See 7.14.
- In all $m_l \neq 0$ cases, the probability density is zero at the z-axis, suggesting that motion is more closely restricted to the xy-plane.
- All $m_l = \pm l$ cases have equatorial lobes, suggesting orbit near the xy-plane and becoming flatter as l increases.

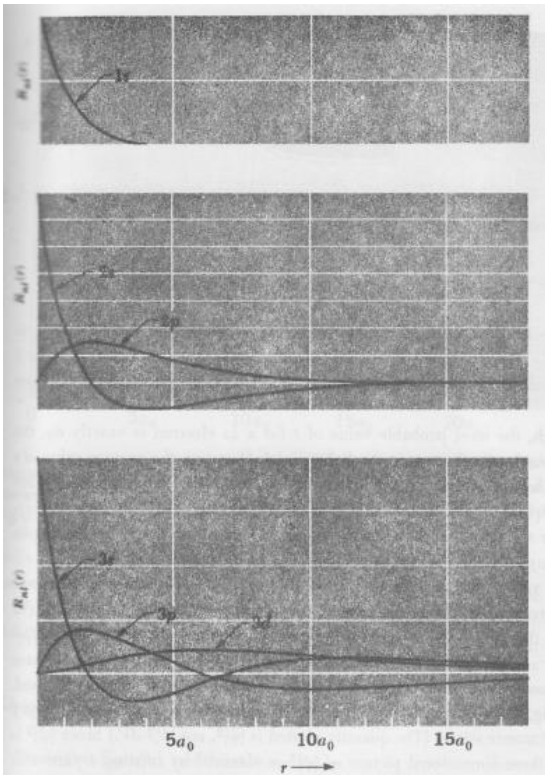
Figure 7.13 Angular probability densities for a central force.

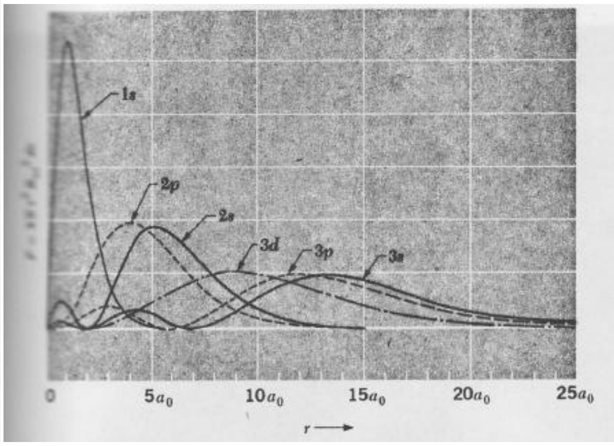


Electron's Whereabouts

Radial Probability Density

$$P(r)dr = R(r)^2 r^2 dr$$



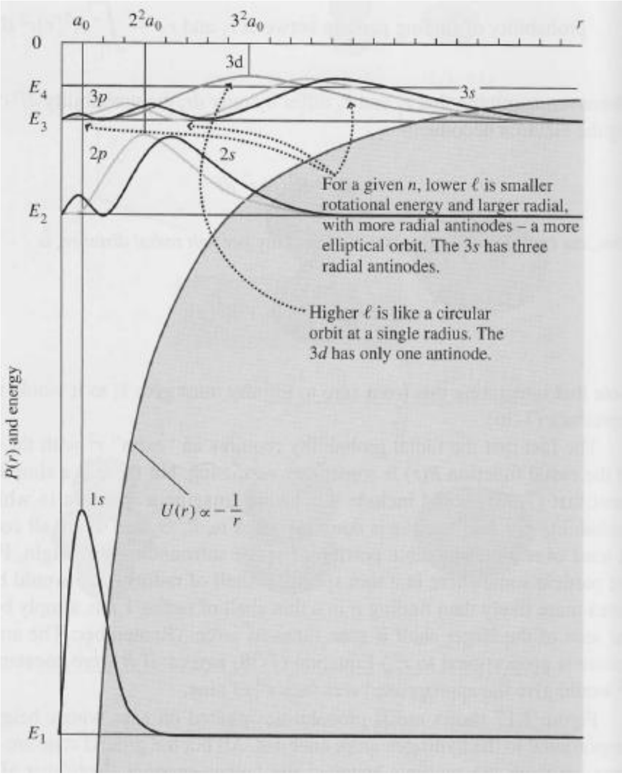


$R_{n,l}(r)$ $\qquad$ $r^2 R_{n,l}(r)^2$

- According to $R_{n,l}(r)$, there is a finite probability at the center for all *s* orbitals (*l*=0).
- Radial probabilities, $4\pi r^2 R_{n,l}(r)^2$, and energies are drawn in the hydrogen atom's Coulomb potential on the right.
- As n increases, the orbital radius increases.
- As n increases, the number of nodes in the same *l* orbital increases.
- When l = n-1, the most probable radius can be shown to have

  $r_{n,\,l=n-1}\,(\text{most probable}) = n^2 a_0$

  That is,
  $r_{10}\,(1s,\ \text{most probable}) = a_0$



For a given *n*, lower ℓ is smaller rotational energy and larger radial, with more radial antinodes – a more elliptical orbit. The 3*s* has three radial antinodes.

Higher ℓ is like a circular orbit at a single radius. The 3*d* has only one antinode.

r_{21} (2p, most probable) $= 4a_0$
r_{32} (3d, most probable) $= 9a_0$

The most probable r value is different from the expected r value since

The most probable r value is obtained when $\frac{dP(r)}{dr} = \frac{dr^2 R_{n,l}(r)^2}{dr} = 0$

And the expected r value is obtained when <r> = $\int_0^\infty r \cdot r^2 R_{n,l}(r)^2 dr$

- According to the radial probability distribution, the expected r value is larger than the most probable r value for a given orbital.

Hydrogenlike Atom

Hydrogen like atoms are atoms containing one electron but with a nucleus more than a single proton (Z*e*). The potential becomes

$$U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e \cdot Ze}{r} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

Example: ionized Helium where the nucleus has a charge of +2*e* and the orbiting electron has a charge of –*e*.

In that case,

$$E_{n\ hydrogen} = -\frac{m(e^2)e^2}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\ \hbar^2}\right)\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

$$E_{n\ hydrogenlike} = -\frac{m(Z^2e^2)e^2}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{Z^2e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\ \hbar^2}\right)\left(\frac{1}{n^2}\right) = -\left(\frac{Z^2e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{Z^2}{n^2}\right)$$

The most probable r vale for the orbital $l = n - 1$

$r_{n,\ l=n-1}$ (most probable) hydrogen $= n^2 a_0$

$r_{n,\ l=n-1}$ (most probable) hydrogenlike $= \frac{1}{Z} n^2 a_0$

Bound energies are deeper by Z^2, the orbital most probably radii smaller by $\frac{1}{Z}$

Hydrogen Atom Spectral Lines

The electron in the hydrogen atom is allowed to have the following energy levels:

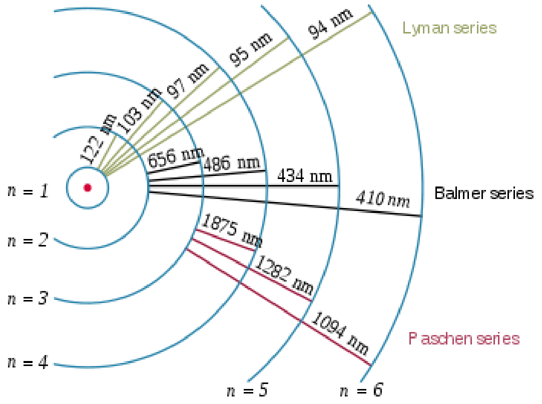
$$E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} = -\frac{e^2}{8\pi\varepsilon_0}\frac{me^2}{4\pi\varepsilon_0\hbar^2}\frac{1}{n^2} = -\frac{e^2}{8\pi\varepsilon_0\ a_0}\frac{1}{n^2} = (-13.6\ \text{eV})\frac{1}{n^2}$$

$$\text{Where } a_0(Bohr\ Radius) = \frac{me^2}{4\pi\varepsilon_0\hbar^2} = 0.0529 \text{ nm} = 0.529 \text{ A}$$

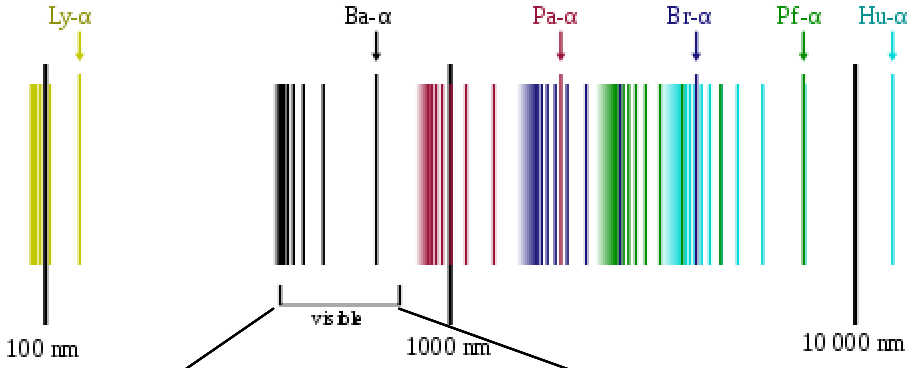
If the electron in the hydrogen atom occupies at a higher energy state, then the electron can transition from the higher to the lower energy state by emiting the photon of which energy equals the difference between the two energy states.

$$E_{photon} = \frac{h\,c}{\lambda} = E_{initial} - E_{final} = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

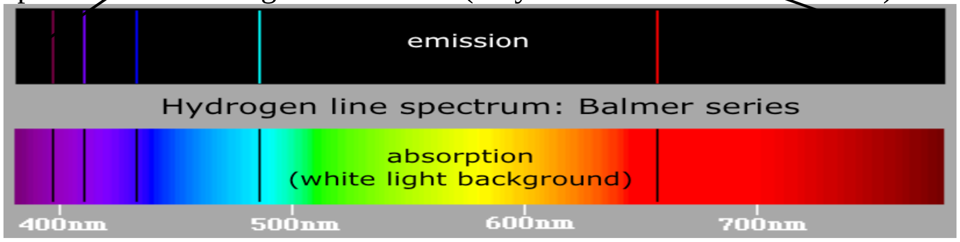
$$\frac{1}{\lambda} = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2 hc}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right) = 1.097\ x\ 10^7\ m^{-1}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

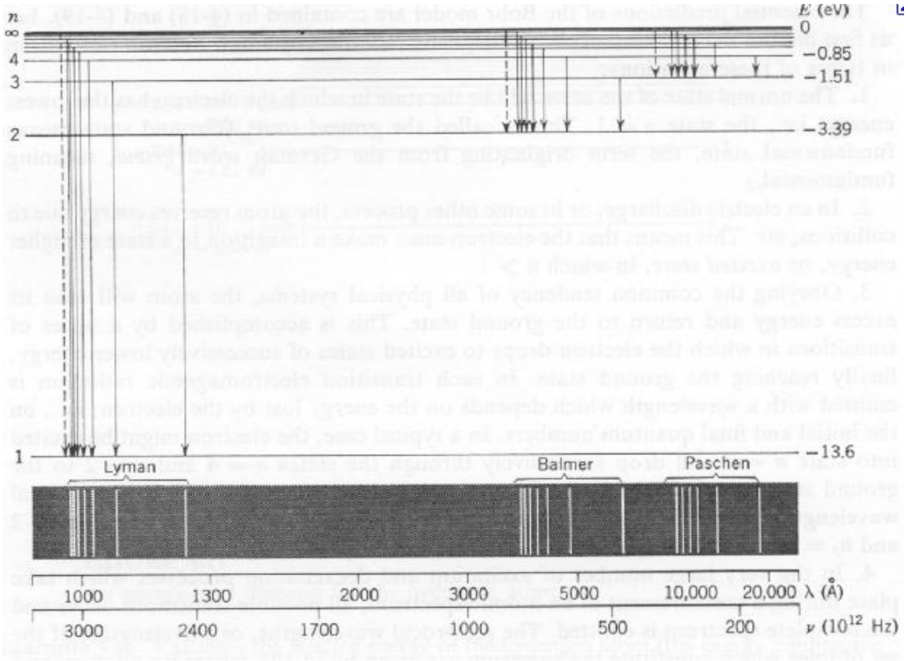


- When $n_{final} = 1$, $Lyman\ Series$ (discovered between 1905-1914)
- When $n_{final} = 2$, $Balmer\ Series$ (in 1885)
- When $n_{final} = 3$, $Pachen\ Series$ (in 1908)
- When $n_{final} = 4$, $Brackett\ Series$ (in 1922)
- When $n_{final} = 5$, $Pfund\ Series$ (in 1924)
- When $n_{final} = 6$, $Humphreys\ Series$ (in 1953)



Spectral lines in a logarithmic scale (only the Balmer series is visible).





From quantummechanics.ucsd.edu

Lyman Series ($n_{final} = 1$)

$n_{initial}$	λ (nm)
2	**122**
3	**103**
4	**97.3**
5	**95.0**
6	**93.8**
∞	**91.2**

Balmer Series ($n_{final} = 2$)

$n_{initial}$	λ (nm)
3	**656**
4	**486**
5	**434**
6	**410**
7	**397**
∞	**365**

Pachen Series (($n_{final} = 3$)

$n_{initial}$	λ (nm)
4	**1870**
5	**1280**
6	**1090**
7	**1020**
8	**954**
∞	**820**