

**PH102, 2012W, Lecture Notes: January 17, 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.

**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 ( $dV = r^2 \sin\theta \, dr d\theta d\phi$ )

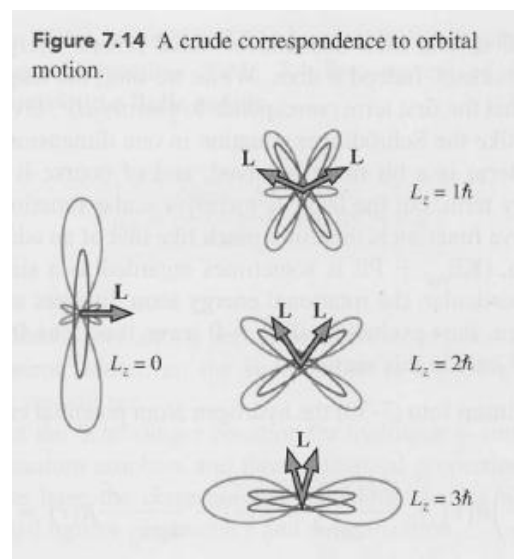
$$\begin{aligned} \int |\psi_{n,l,m_l}|^2 dV &= \int |\psi_{n,l,m_l}|^2 r^2 \sin\theta \, dr d\theta d\phi \\ &= \int_0^\infty R(r)^2 r^2 \, dr \int_0^\pi \Theta(\theta)^2 \sin\theta \, d\theta \int_0^{2\pi} \Phi(\phi)^2 \, d\phi \end{aligned}$$

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

**Electron whereabouts: Angular directions ( $\theta, \phi$ )**  
**Angular Probability Density**

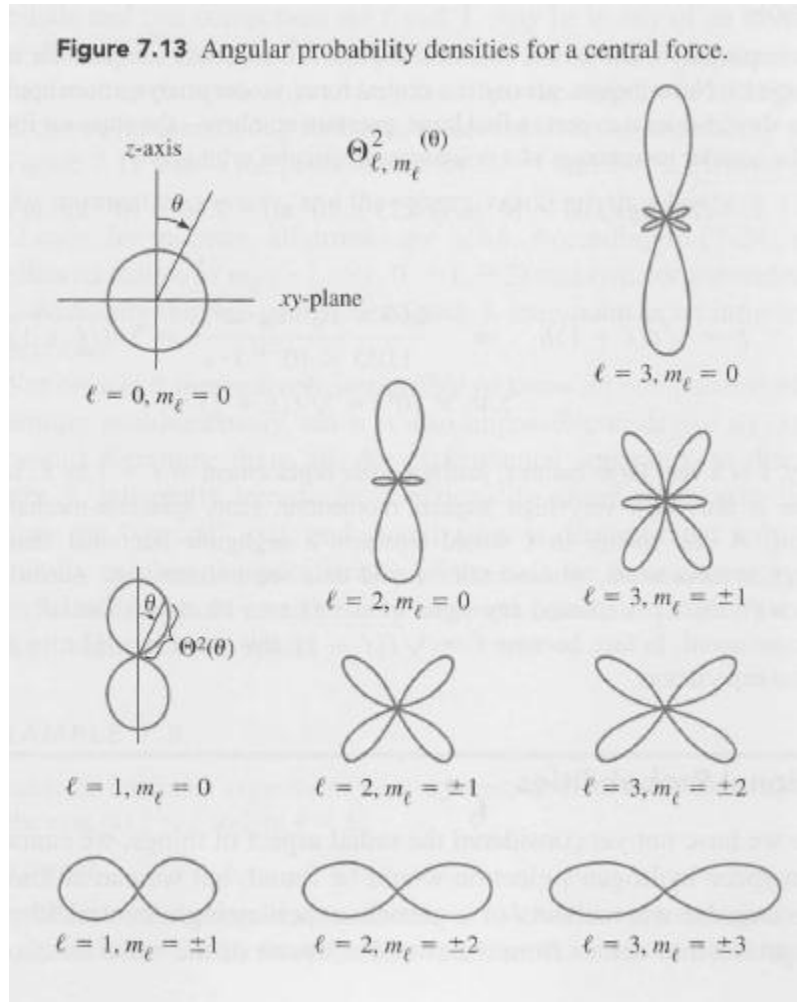
$$\Theta(\theta)^2 \Phi(\phi)^2 \equiv \mathbf{Y}_l^{m_l*} \mathbf{Y}_l^{m_l}$$

- 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  $\phi$  axis.
- In  $s$  states where  $l = 0$ , the kinetic energy is solely radial, so the probability density is spherically symmetric. No orbital motion.



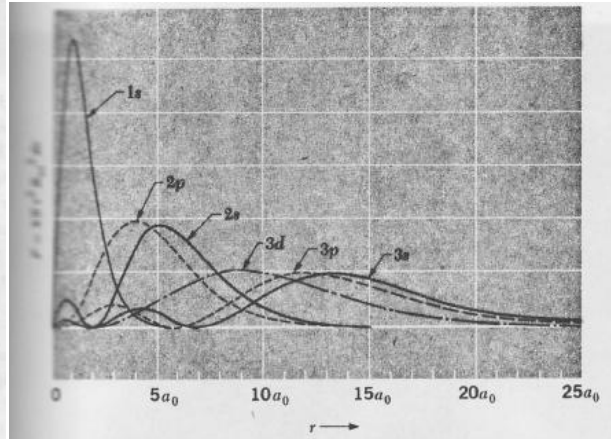
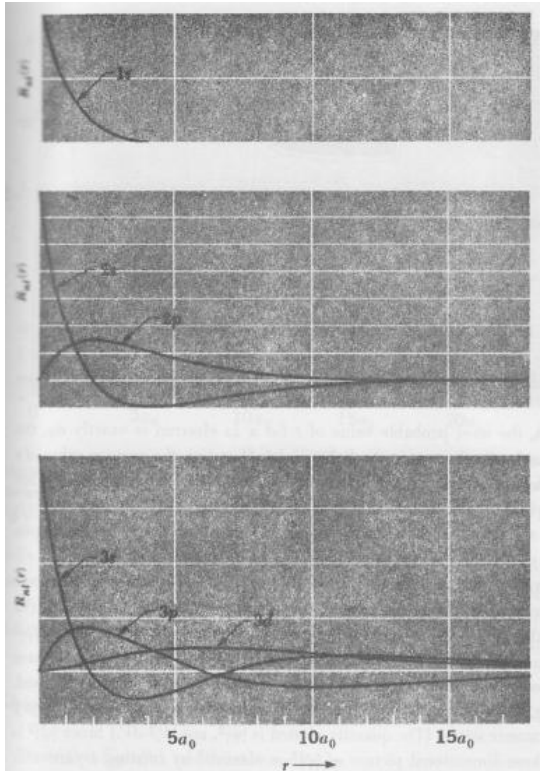
- Note that the electron is orbiting the place perpendicular to the direction of  $L_z$ . See Figure on the right.
- In p states where ( $l=1$ ), three possible probability distributions:  $L_z = 1, 0, -1$ . See Figure below.
- In d states where ( $l=2$ ), five possible probability distributions  $L_z = 2, 1, 0, -1, -2$ .

- 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.



**Electron's Whereabouts**  
 Radial Probability Density

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



$R_{n,l}(r)$

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

- 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

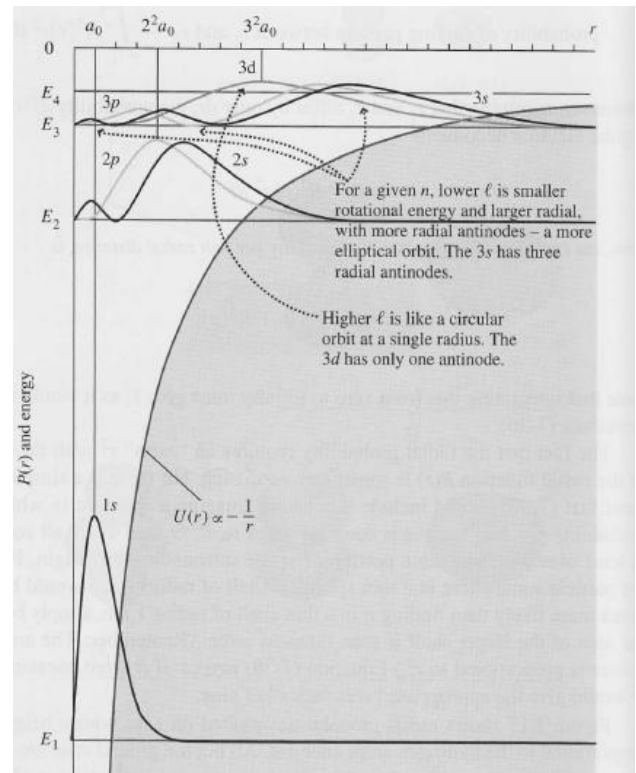
$$r_{n, l=n-1} (\text{most probable}) = n^2 a_0$$

That is,

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

$$r_{21} (2p, \text{ most probable}) = 4a_0$$

$$r_{32} (3d, \text{ most probable}) = 9a_0$$



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  $\langle r \rangle = \int_0^\infty r \cdot r^2 R_{n,l}(r)^2 dr$

- 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 ( $Ze$ ). The potential becomes

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e \cdot Ze}{r} = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

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

In that case,

$$E_{n \text{ hydrogen}} = -\frac{m(e^2)e^2}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\epsilon_0}\right) \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right) \left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\epsilon_0 a_0}\right) \left(\frac{1}{n^2}\right) = -13.6 \text{ eV} \left(\frac{1}{n^2}\right)$$

$$E_{n \text{ hydrogenlike}} = -\frac{m(Z^2 e^2)e^2}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2}\right) = -\left(\frac{Z^2 e^2}{8\pi\epsilon_0}\right) \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right) \left(\frac{1}{n^2}\right) = -\left(\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}\right) \left(\frac{1}{n^2}\right) = -13.6 \text{ eV} \left(\frac{Z^2}{n^2}\right)$$

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

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

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

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:

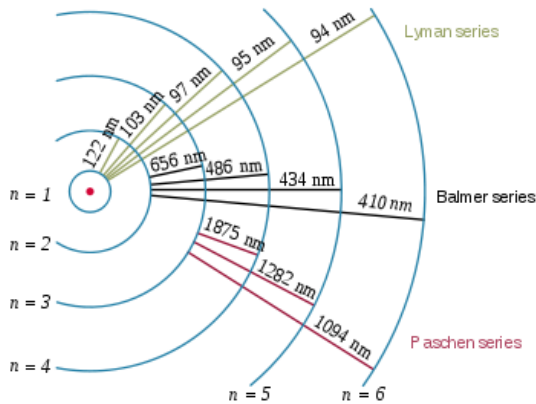
$$E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0} \frac{me^2}{4\pi\epsilon_0\hbar^2} \frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{1}{n^2} = (-13.6 \text{ eV}) \frac{1}{n^2}$$

$$\text{Where } a_0 \text{ (Bohr Radius)} = \frac{me^2}{4\pi\epsilon_0\hbar^2} = 0.0529 \text{ nm} = 0.529 \text{ \AA}$$

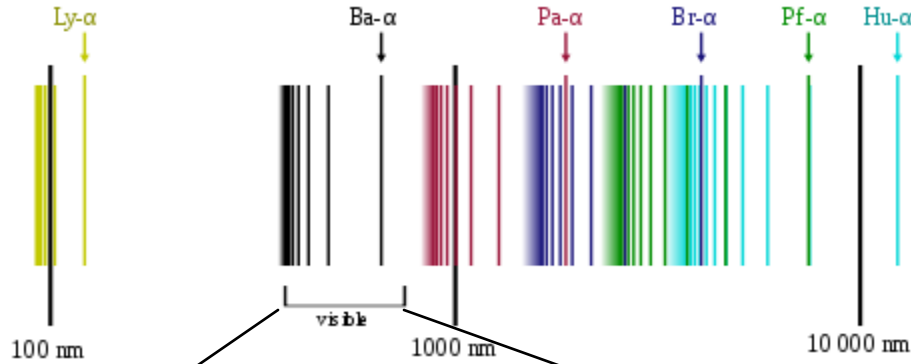
If the electron in the hydrogen atom occupies at a higher energy state, then the electron can transition from the higher to the lower energy state by emitting the photon of which energy equals the difference between the two energy states.

$$E_{\text{photon}} = \frac{hc}{\lambda} = E_{\text{initial}} - E_{\text{final}} = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right)$$

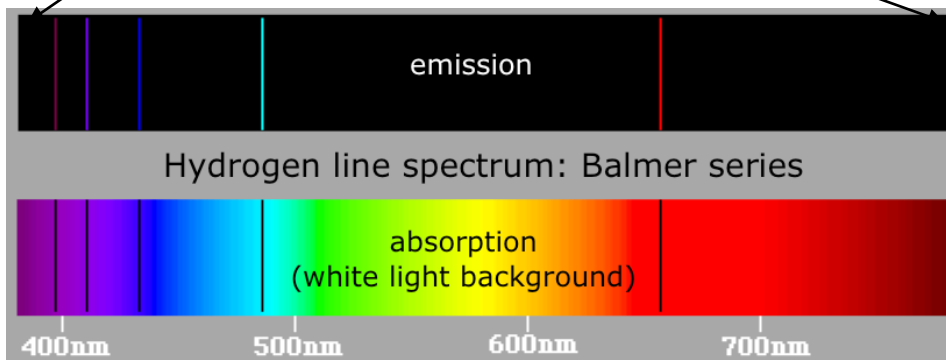
$$\frac{1}{\lambda} = \frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2 hc} \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) = 1.097 \times 10^7 \text{ m}^{-1} \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right)$$

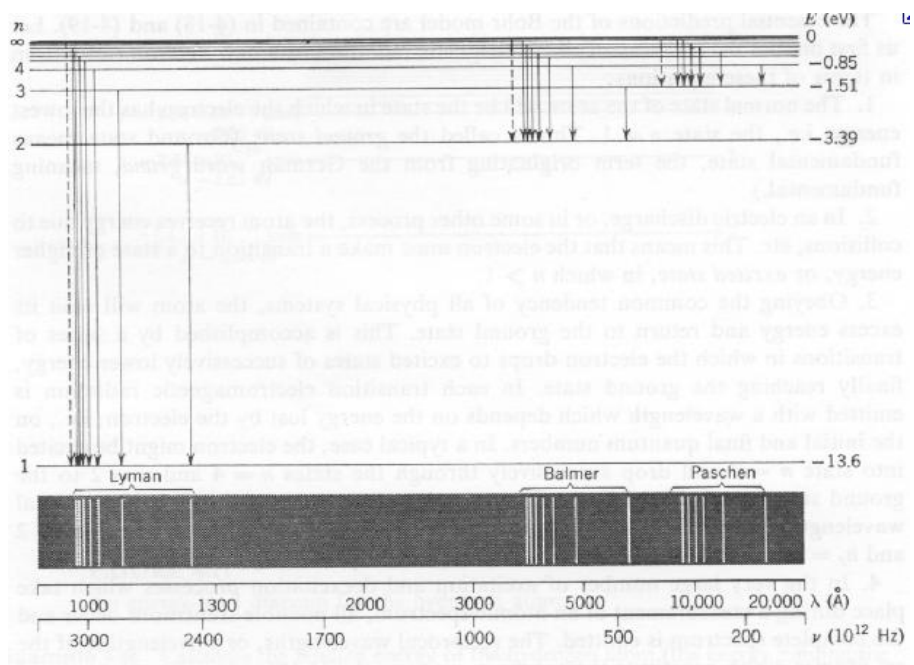


- When  $n_{\text{final}} = 1$ , *Lyman Series* (discovered between 1905-1914)
- When  $n_{\text{final}} = 2$ , *Balmer Series* (in 1885)
- When  $n_{\text{final}} = 3$ , *Paschen Series* (in 1908)
- When  $n_{\text{final}} = 4$ , *Brackett Series* (in 1922)
- When  $n_{\text{final}} = 5$ , *Pfund Series*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



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





From

quantummechanics.ucsd.edu

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

| $n_{initial}$ | $\lambda$ (nm) |
|---------------|----------------|
| 2             | 122            |
| 3             | 103            |
| 4             | 97.3           |
| 5             | 95.0           |
| 6             | 93.8           |
| $\infty$      | 91.2           |

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

| $n_{initial}$ | $\lambda$ (nm) |
|---------------|----------------|
| 3             | 656            |
| 4             | 486            |
| 5             | 434            |
| 6             | 410            |
| 7             | 397            |
| $\infty$      | 365            |

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

| $n_{initial}$ | $\lambda$ (nm) |
|---------------|----------------|
| 4             | 1870           |
| 5             | 1280           |
| 6             | 1090           |
| 7             | 1020           |
| 8             | 954            |
| $\infty$      | 820            |