Welcome back to PHY 3305

Today's Lecture:

Hydrogen Atom Pt 2

Wolfgang Ernst Pauli
1900 - 1958

# Last Lecture:

## Three Quantum Numbers and quantities they describe.

| | |
|---|---|
| n | energy |
| l | length of the angular momentum vector |
| $m_l$ | z-component of the angular momentum |

# Last Lecture:

The solutions of the 3D SWE, complete quantum numbers, can be written as

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,m_\ell}(r)\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

| $n$ | $l$ | $m_l$ | $R(r)$ | $\Theta(\theta)$ | $\Phi(\phi)$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | $\frac{2}{a_0^{3/2}}e^{-r/a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 0 | 0 | $\frac{1}{(2a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | 0 | $\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\sqrt{\frac{3}{2}}\cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | $\pm1$ | $\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\mp\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 0 | 0 | $\frac{2}{(3a_0)^{3/2}}\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | 0 | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$ | $\sqrt{\frac{3}{2}}\cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | $\pm1$ | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$ | $\mp\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 2 | 0 | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 2 | $\pm1$ | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\mp\sqrt{\frac{15}{4}}\sin\theta\cos\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 2 | $\pm2$ | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{\sqrt{15}}{4}\sin^2\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$ |

Ground state ($n=1$; $l = 0$; $m_l = 0$)

($n=2$; $l = 0, 1$; $m_l = 0, \pm1$)

($n=3$; $l = 0, 1, 2$; $m_l = 0, \pm1, \pm2$)

# Probability Densities

For the hydrogen atom the probability density (volume) is given by

$$|\psi(r, \theta, \phi)|^2$$

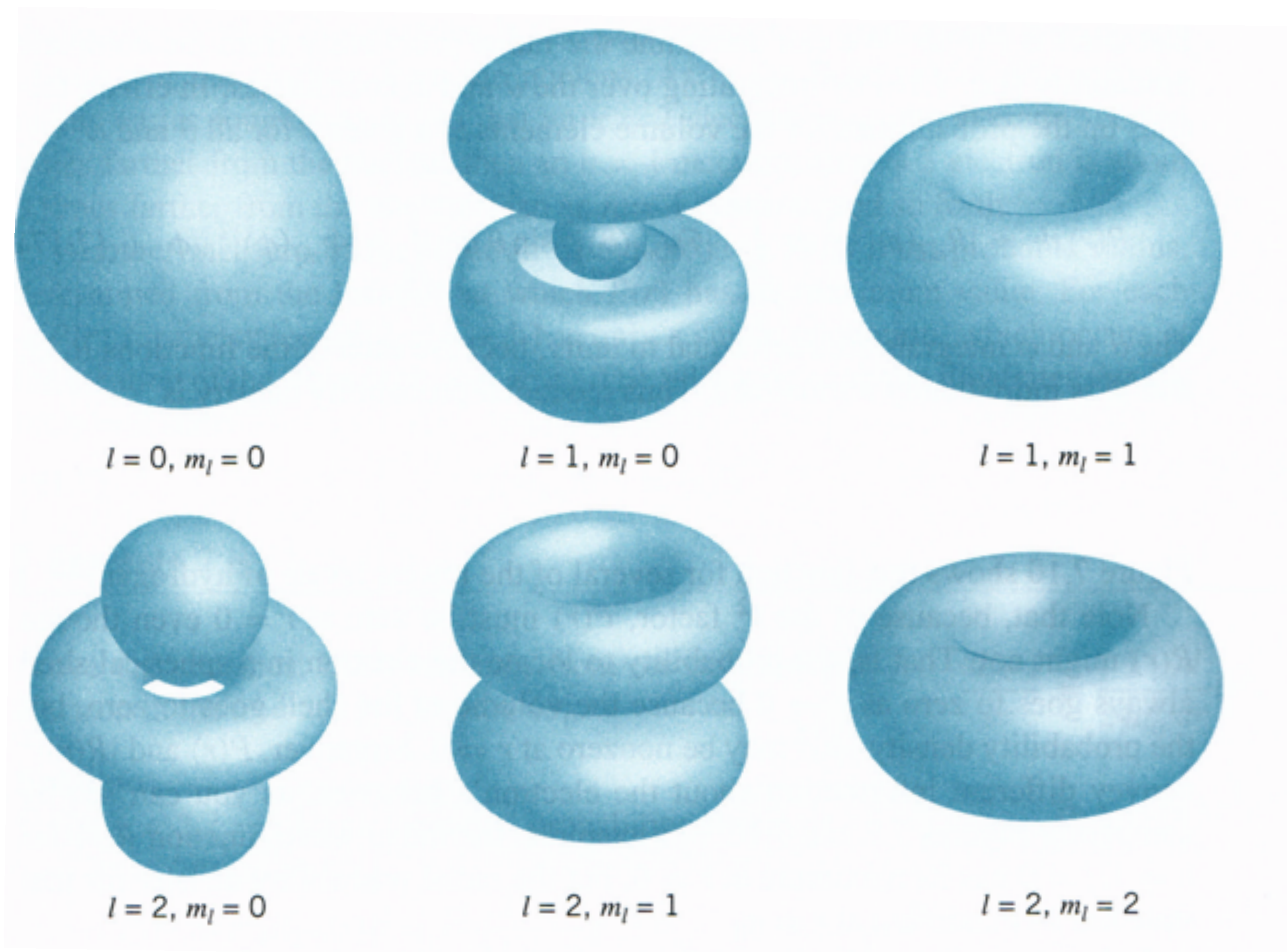
To compute the probability of finding the electron in any spacial interval, you must integrate.

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

volume element

$$|\psi_{n,l,m_l}(r,\theta,\phi)|^2 \, dV = |R_{n,l}(r)|^2 |\Theta_{l,m_l}(\theta)|^2 |\Phi_{m_l}(\phi)|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Representations of probability density for different sets of quantum numbers. The diagrams represent surfaces for which the probability has the same value.



$$|\psi_{n,l,m_l}(r,\theta,\phi)|^2\,dV = |R_{n,l}(r)|^2|\Theta_{l,m_l}(\theta)|^2|\Phi_{m_l}(\phi)|^2 r^2 \sin\theta\,dr\,d\theta\,d\phi$$

# Radial Probability

How do we find the probability of finding the electron a certain distance from the nucleus, regardless of $\theta$ and $\varphi$?

$$P(r)dr = r^2|R|^2 dr \int_0^{\pi} |\Theta|^2 \sin\theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi$$

where $\Theta$ and $\Phi$ are normalized functions.

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

And the radial probability (per unit distance) becomes

$$P(r) = \frac{dP}{dr} = r^2R^2(r)$$

# Example:  Most Likely Distance

What is the most likely distance from the origin of an electron in the n=2, l=1 state?

$$R(r)_{2,1,\pm 1} = \frac{1}{\sqrt{3}(2a_0)^{\frac{3}{2}}} \frac{r}{a_0} e^{\frac{-r}{2a_0}}$$

**Step 1:** Calculate the radial probability density

$$P(r) = r^2 |R_{2,1}(r)|^2 = r^2 \frac{1}{24a_0^3} \frac{r^2}{a_0^2} e^{-r/a_0}$$

$$P(r) = r^2|R_{2,1}(r)|^2 = r^2 \frac{1}{24a_0^3}\frac{r^2}{a_0^2}e^{-r/a_0}$$

**Step 2:** Find the maximum of the function. How do we do this?

Set the first derivative to zero.

$$\frac{dP(r)}{dr} = \frac{1}{24a_0^5}\frac{d}{dr}(r^4 e^{-r/a_0}) = \frac{1}{24a_0^5}\left[4r^3 e^{-r/a_0} + r^4\left(-\frac{1}{a_0}\right)e^{-r/a_0}\right] = 0$$

$$\frac{1}{24a_0^5}e^{-r/a_0}\left(4r^3 - \frac{r^4}{a_0}\right) = 0$$

$$4 - \frac{r}{a_0} = 0$$

$$\boxed{r = 4a_0}$$

# Angular Probability Density

How would we find the angular part of the probability density?

$$P(\theta,\phi) = |\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi)|^2$$

| $n$ | $l$ | $m_l$ | $R(r)$ | $\Theta(\theta)$ | $\Phi(\phi)$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | $\frac{2}{a_0^{3/2}}e^{-r/a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 0 | 0 | $\frac{1}{(2a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | 0 | $\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\sqrt{\frac{3}{2}}\cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | $\pm 1$ | $\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\mp\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 0 | 0 | $\frac{2}{(3a_0)^{3/2}}\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | 0 | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$ | $\sqrt{\frac{3}{2}}\cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | $\pm 1$ | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$ | $\mp\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 2 | 0 | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 2 | $\pm 1$ | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\mp\sqrt{\frac{15}{4}}\sin\theta\cos\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 2 | $\pm 2$ | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{\sqrt{15}}{4}\sin^2\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$ |

Note: The l = 0 wave functions are spherically symmetric, no dependence on angle.

# Example: Angular Probability Density

For the n=2, l=1 wave functions, find the direction in space at which the maximum probability occurs when $m_l = \pm 1$.

| $n$ | $l$ | $m_l$ | $R(r)$ | $\Theta(\theta)$ | $\Phi(\phi)$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | $\frac{2}{a_0^{3/2}} e^{-r/a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 0 | 0 | $\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | 0 | $\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$ | $\sqrt{\frac{3}{2}} \cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | $\pm 1$ | $\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$ | $\mp \frac{\sqrt{3}}{2} \sin\theta$ | $\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$ |
| 3 | 0 | 0 | $\frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | 0 | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$ | $\sqrt{\frac{3}{2}} \cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | $\pm 1$ | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$ | $\mp \frac{\sqrt{3}}{2} \sin\theta$ | $\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$ |
| 3 | 2 | 0 | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$ | $\sqrt{\frac{5}{8}} (3\cos^2\theta - 1)$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 2 | $\pm 1$ | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$ | $\mp \sqrt{\frac{15}{4}} \sin\theta\cos\theta$ | $\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$ |
| 3 | 2 | $\pm 2$ | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$ | $\frac{\sqrt{15}}{4} \sin^2\theta$ | $\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$ |

$$
\begin{aligned}
P(\theta, \phi) &= |\Theta_{\ell, m_\ell}(\theta)\Phi_{m_\ell}(\phi)|^2 \\
&= \frac{3}{4}\sin^2\theta \left(\frac{1}{2\pi} e^{\pm i\phi} e^{\mp i\phi}\right) \\
&= \frac{3}{8\pi}\sin^2\theta
\end{aligned}
$$

To find the maximum, we set $dP/d\theta = 0$ and solve.

$$P(\theta, \phi) = \frac{3}{8\pi} \sin^2 \theta$$

$$\frac{dP}{d\theta} = \frac{3}{4\pi} (\sin\theta \cos\theta) = 0$$

$$\theta = 0, \pi, \frac{\pi}{2}$$

However, in this case, the maxima occurs at

$$\boxed{\theta = \frac{\pi}{2}}$$

Take the second derivative to find which is min and which is max.

| $n$ | $l$ | $m_l$ | $R(r)$ | $\Theta(\theta)$ | $\Phi(\phi)$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | $\frac{2}{a_0^{3/2}}e^{-r/a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 0 | 0 | $\frac{1}{(2a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | 0 | $\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\sqrt{\frac{3}{2}}\cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 2 | 1 | ±1 | $\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\mp\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 0 | 0 | $\frac{2}{(3a_0)^{3/2}}\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | 0 | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$ | $\sqrt{\frac{3}{2}}\cos\theta$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 1 | ±1 | $\frac{8}{9\sqrt{2}(3a_0)^{3/2}}\left(\frac{r}{a_0}-\frac{r^2}{6a_0^2}\right)e^{-r/3a_0}$ | $\mp\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 2 | 0 | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$ | $\frac{1}{\sqrt{2\pi}}$ |
| 3 | 2 | ±1 | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\mp\sqrt{\frac{15}{4}}\sin\theta\cos\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ |
| 3 | 2 | ±2 | $\frac{4}{27\sqrt{10}(3a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{\sqrt{15}}{4}\sin^2\theta$ | $\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$ |

Note: The probability densities are cylindrically symmetric - No dependence on $\varphi$.

# Spectral Lines

Spectroscopic observations demonstrate that hydrogen emits only certain wavelengths of light known as **spectral lines**.

656 nm
486 nm
434 nm
410 nm

The formula that yields the observed patterns was found by school teacher Johann Balmer (1885, trial & error).

$$\frac{1}{\lambda} = 1.097 \times 10^7 m^{-1} (\frac{1}{4} - \frac{1}{n^2})$$

for n = 3, 4, 5, ....

We can rearrange this formula to a more convenient form.

$$\lambda = (364.5nm)\frac{n^2}{n^2-4}$$ for n = 3, 4, 5, ....

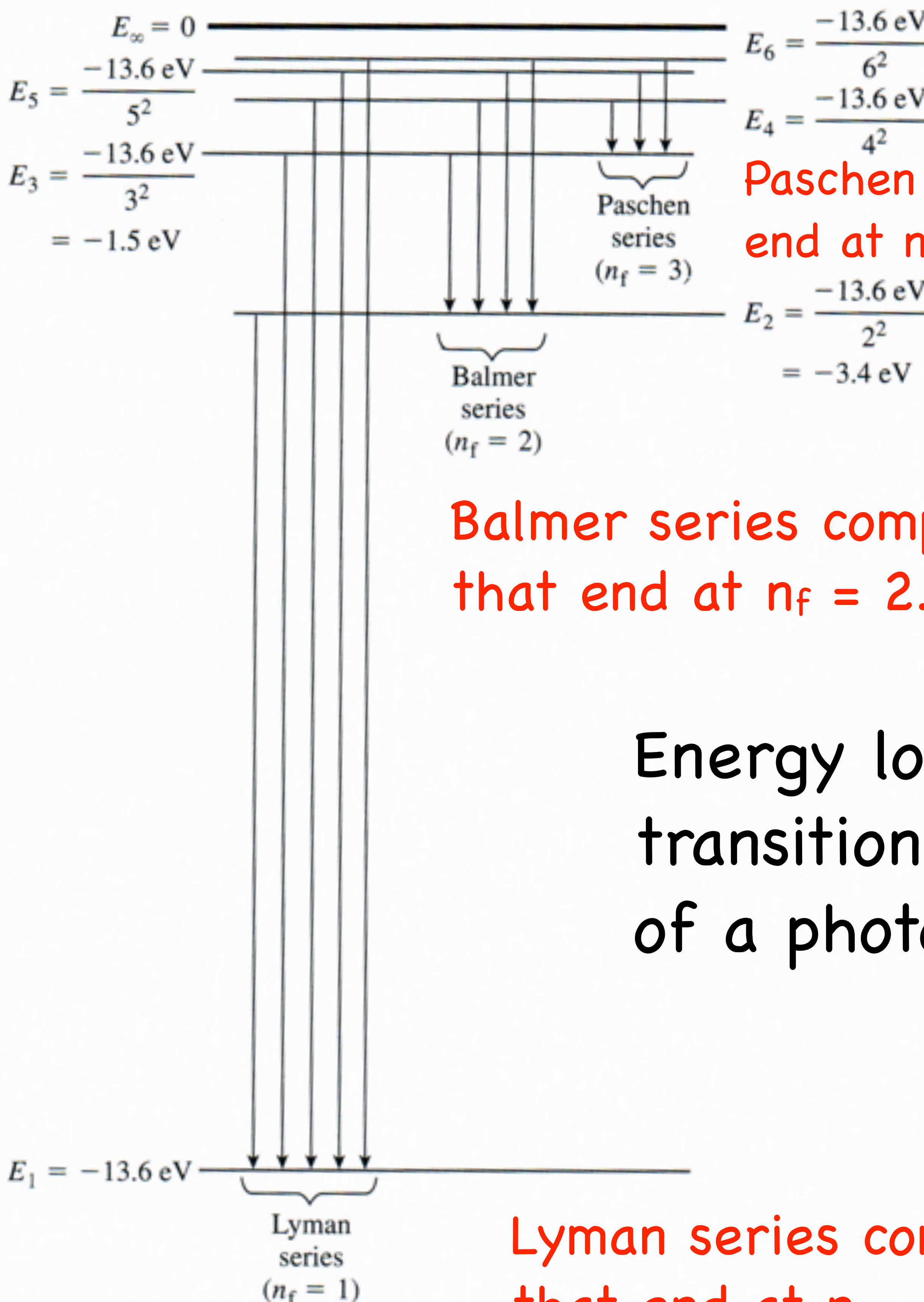
This formula is known as the **Balmer formula** and the lines it fits are called the **Balmer series**.

As we saw earlier, the energy levels in hydrogen are quantized.

$$E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} \quad \text{where} \quad n = 1, 2, 3, \ldots$$

which simplifies to

$$E_n = \frac{-13.6\ \text{eV}}{n^2} \qquad n = 1, 2, 3, \ldots$$




Paschen series comprises all transitions that end at $n_f = 3$.

Balmer series comprises all transitions that end at $n_f = 2$.

Energy lost by the downward transition is emitted in the form of a photon.

Lyman series comprises all transitions that end at $n_f = 1$.

We can rearrange this formula to a more convenient form.

This is the series limit. $n_0 = 2$

$$\lambda = (364.5nm)\frac{n^2}{n^2 - 4}$$ for n = 3, 4, 5, ....

This formula is known as the **Balmer formula** and the lines it fits are called the **Balmer series**.

More generally, we can write

$$\lambda = \lambda_0 \frac{n^2}{n^2 - n_0^2}$$ for $n = n_0+1, n_0+2, n_0+3, \ldots$

$\lambda_0$ = **series limit** - the shortest wavelength possible in a transition from a higher initial energy level to the final level.

## What will an electron in the $n_i = 3$ state do? Will it transition to the $n_f = 2$ state or the $n_f = 1$ state?

It may do either. The outcome is governed by probabilities.

## If the electron is in a stationary state, why would it transition at all?

Even in a vacuum, there are always spontaneously fluctuating magnetic fields, **VACUUM FLUCTUATIONS**. These fluctuations perturb the atom in such a way that it causes the electron to seek a lower energy.

The atom can also be induced to jump to a higher energy level. One way to accomplish this is to strike the atom with a photon. This requires the photon to have precisely the energy difference from one atomic level to another.

# Example: Paschen Series

The wavelength of the series limit of the Paschen series is 820.1 nm. What are the three longest wavelengths of the Paschen series?

**Step 1:** Identify the correct limits for the Paschen series.

$$\lambda = \lambda_0 \frac{n^2}{n^2 - n_0^2}$$

$$\lambda = (820.1\, nm) \frac{n^2}{n^2 - 3^2}$$

## **Step 2:** Do the calculations.

$$\lambda = (820.1\, nm)\frac{n^2}{n^2 - 3^2}$$

n=4:

$$\lambda = (820.1\, nm)\frac{4^2}{4^2 - 3^2} = 1875\, nm$$

n=5:

$$\lambda = (820.1\, nm)\frac{5^2}{5^2 - 3^2} = 1281\, nm$$

n=6:

$$\lambda = (820.1\, nm)\frac{6^2}{6^2 - 3^2} = 1094\, nm$$

# The end
# (for today)