

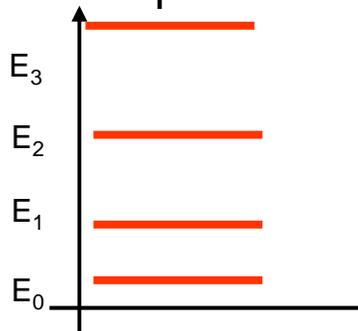
# Chapter 8: Spectra

***Special Note: Professor Heinz will be lecturing on this chapter. He may not necessarily follow these notes. I provide them for completeness.***

- In this Chapter we want to study the phenomena of atomic spectra. There are several topics that we will cover:
  - Spontaneous Emission of Photons.
  - Spectral Lines
  - Absorption Lines
  - Physics of spin
- Some of these topics we being studies experimentally before, during, (and after) the development of quantum mechanics. These phenomena are difficult to explain with classical physics and were part of the body of evidence that pointed the way toward quantum mechanics.

# Energy-Level Diagrams

- When considering spectral lines (and absorption lines) it is use to have a picture of the energy levels of the atom or bound system that you are considering.
- These are very simple diagrams but they contain useful information. We depict them as a two-dimensional diagram



- The vertical axis is the energy. We place a horizontal line at each energy-level of our bound system. The horizontal direction has no meaning.
- Let's make energy diagrams for the three bound systems that we have looked at in the last chapter
- (1) Electron in a Box

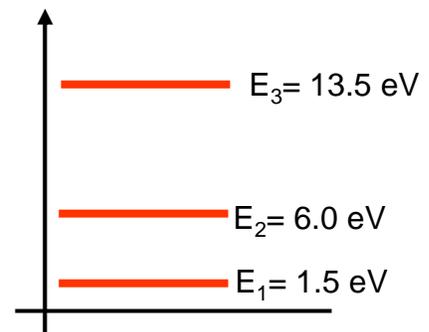
➤ Let's take  $L=0.50$  nm

➤ We saw in the last chapter the energy levels are:

$$E_n = \frac{n^2 h^2}{8mL^2} = n^2 E_1 \quad n = 1, 2, 3, \dots$$

$$E_1 = \frac{h^2}{8mL^2} = \frac{(hc)^2}{8mc^2 L^2} =$$

$$= \frac{(1240 \text{ eV} \cdot \text{nm})^2}{8(511,000 \text{ eV}/c^2)c^2 (0.5 \text{ nm})^2} = 1.5 \text{ eV}$$



# Energy Level Diagrams

- (2) Simple harmonic Oscillator:
  - Take  $\omega$  such that  $\hbar\omega = 4.0 \text{ eV}$
  - In the last chapter we saw that the energy levels for a simple harmonic oscillator is

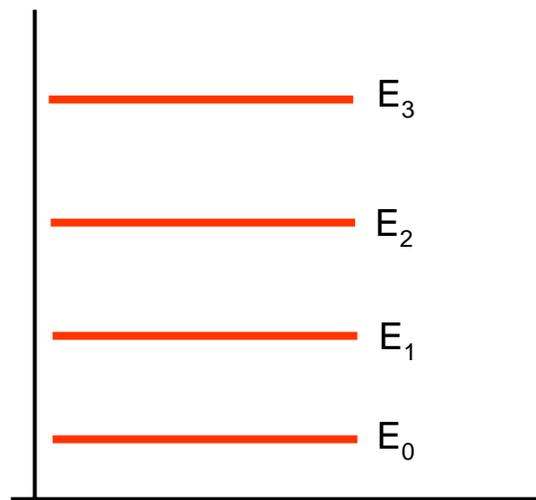
$$E = \hbar\omega\left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, \dots$$

$$E_0 = \frac{1}{2}\hbar\omega = 2.0 \text{ eV}$$

$$E_1 = \frac{3}{2}\hbar\omega = 6.0 \text{ eV}$$

$$E_2 = \frac{5}{2}\hbar\omega = 10.0 \text{ eV}$$

$$E_3 = \frac{7}{2}\hbar\omega = 14.0 \text{ eV}$$



- (3) Bohr's Model of hydrogen
  - Remember, one of the things the Bohr model did reasonable well was predict the energy levels of H.
  - These levels are:

$$E = -\frac{ke^2}{2a_0n^2} = -\frac{13.6 \text{ eV}}{n^2} \quad n = 0, 1, 2, \dots$$

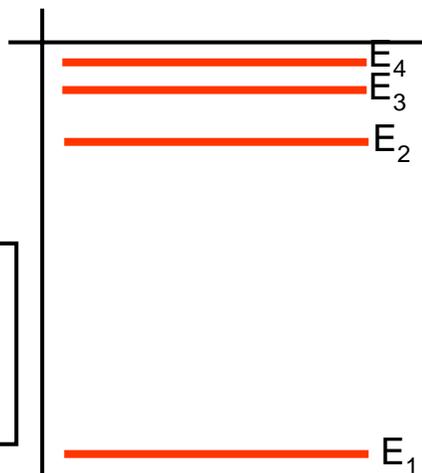
$$E_1 = -13.6 \text{ eV}$$

$$E_2 = -3.4 \text{ eV}$$

$$E_3 = -1.5 \text{ eV}$$

$$E_4 = -0.85 \text{ eV}$$

Notice how each bound has a different Energy-level diagram



# Spontaneous Emission

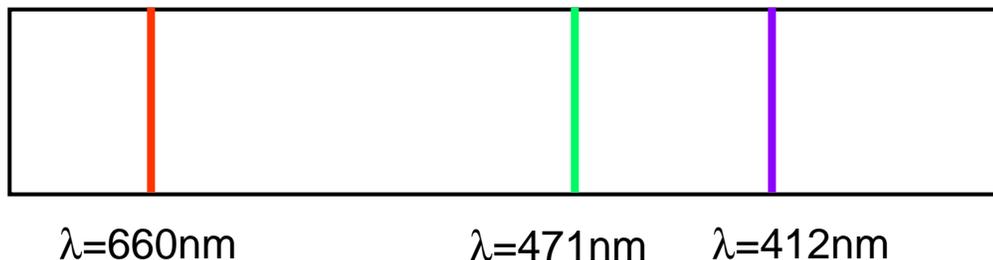
- There is an interesting phenomena that this called “spontaneous emission”.
  - Photon emitted from an atom as an electron makes a transition from one energy-level to another.
- Recall what we said in the last chapter
  - If the quanta has a definite energy value it must be in a state which is an energy eigenvector.
  - Energy Eigenvectors do not change with time
    - This was a consequence of the time-evolution rule
- The electric field of an electron can be thought of as the electric field due to a charge density which is given by the wave function.
  - A static charge density cannot radiate EM waves (photons)...and thus lose energy.
- These points seem to indicate that an electron at one energy-level should not spontaneously make a transition to a lower energy-level
  - What’s going on?
  - This is an effect of ***Relativistic Quantum Mechanics***.
    - The electron in the higher energy-levels is being hit by small quantum fluctuations which prevent it from being ***exactly*** in an energy eigenvector...so it has a small probability of radiating a photon and transitioning into a lower state.
  - Note: *Pauli Exclusion Principle* also plays a role (later)

# Spectral Lines

- One interesting consequence of bound systems, which have discrete energy levels, and spontaneous emissions is the phenomena of **spectral lines**.
- Since the photons take away the excess energy of an electron when it makes a transition from its starting energy level to a lower one, only *certain* energies of photons are allowed.
  - If only certain energies are allowed...only certain wavelengths are allowed:
    - $E = hc/\lambda$
  - The allowed energies correspond to the differences between energy levels

$$E_{\gamma} = (E_{\text{initial}} - E_{\text{final}}) = \frac{hc}{\lambda}$$

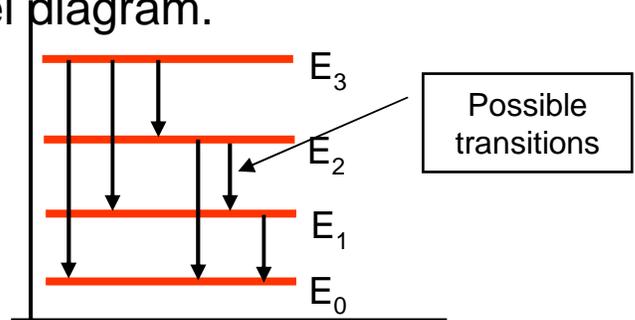
- We can take the light emitted from these atoms and measure the wavelength
  - Pass it through a prism for example.
  - We would see “lines” from the specific wavelengths that are present.



# Spectra For Different Systems

- The great thing about spectral lines is
  - They allow you to measure the energy levels (at least difference) for a bound system.
  - Each bound system has a different energy level structure
    - e.g. box, harmonic oscillator, hydrogen
    - Different atoms have different levels
  - Spectral lines can there give you insight into the system that is emitting the photons...is it a “box” or an “oscillator”.
- Consider the energy levels for a simple harmonic oscillator and its energy-level diagram.

$$E_n = \hbar\omega(n + \frac{1}{2}) \quad n = 0, 1, 2, \dots$$



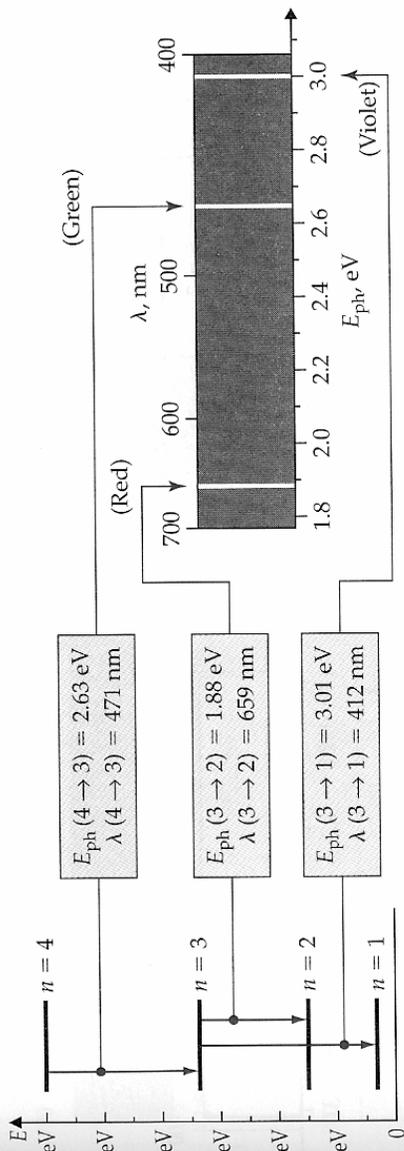
- The possible energies of the photons correspond to

$$\lambda = \frac{hc}{E_\gamma} = \frac{hc}{E_f - E_i} = \frac{hc}{\hbar\omega(n_f - n_i)} = \frac{2\pi c/\omega}{(n_f - n_i)}$$

- Similarly for a box and the hydrogen atom we get:

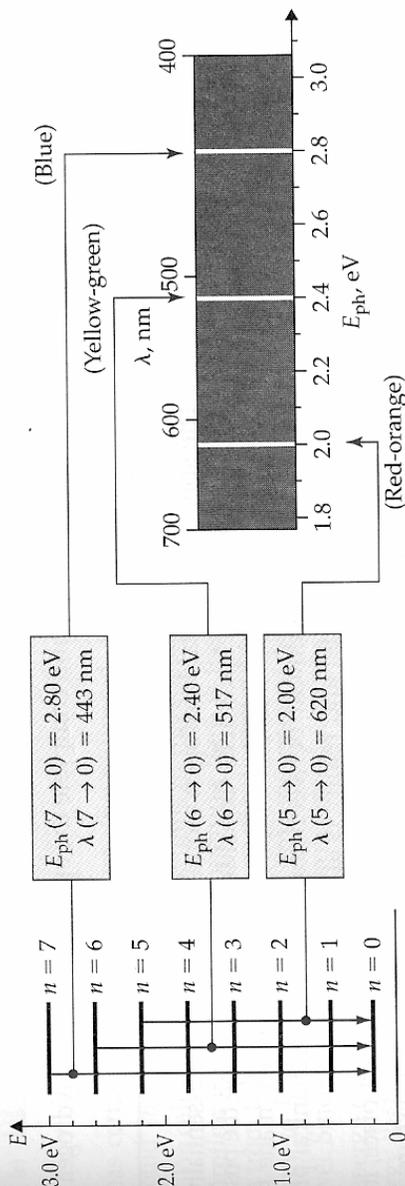
$$\lambda_{\text{box}} = \frac{8mc^2 L^2}{hc(n_i^2 - n_f^2)} \quad \lambda_H = \frac{2(hc)a_o}{ke^2} \left( \frac{n_i^2 n_f^2}{n_i^2 - n_f^2} \right)$$

# Example Spectra



**Figure Q8.2**

The transitions of an electron in a box 1.0 nm wide that give rise to visible photons. The spectrum shown on the right is what you would see if the light from a number of excited electrons were dispersed by a prism.

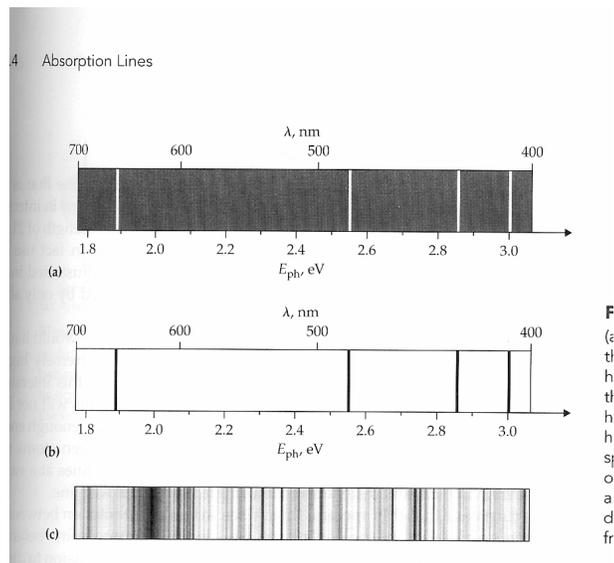


**Figure Q8.3**

Energy-level diagram and hypothetical spectral lines for a harmonic oscillator with  $\hbar\omega = 0.40$  eV. Note that all transitions with the same  $\Delta n$  will produce photons of the same wavelength: so the transitions  $8 \rightarrow 1, 9 \rightarrow 2$ , and so on therefore emit photons of the same wavelength as those emitted by the  $7 \rightarrow 0$  transition.

# Absorption Lines

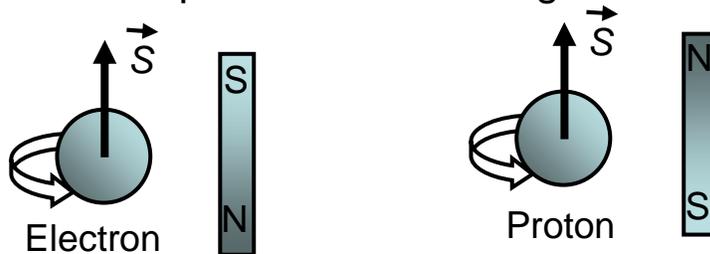
- The process of spectral emission can be reversed
  - Electrons can absorb a photon and jump from a lower energy level to a higher energy level.
  - As in the case with a spectral emission, only certain wavelengths of light can be absorbed by the electrons
    - ❑ Wavelengths that correspond to photon energies that equal the difference in the energy levels.
- If we shine white light on a gas the atoms in the gas will absorb some wavelengths of light leaving dark lines at the particular wavelengths absorbed.
  - The dark lines occur at the same wavelengths as the spectral emission lines for an atom.



- Absorption lines are an important tool for understand the composition of something from a distance.
  - For example, star light shines through a nebula toward earth. Based on the absorption lines we can understand the atomic composition of the nebula.

# Spin Revisited

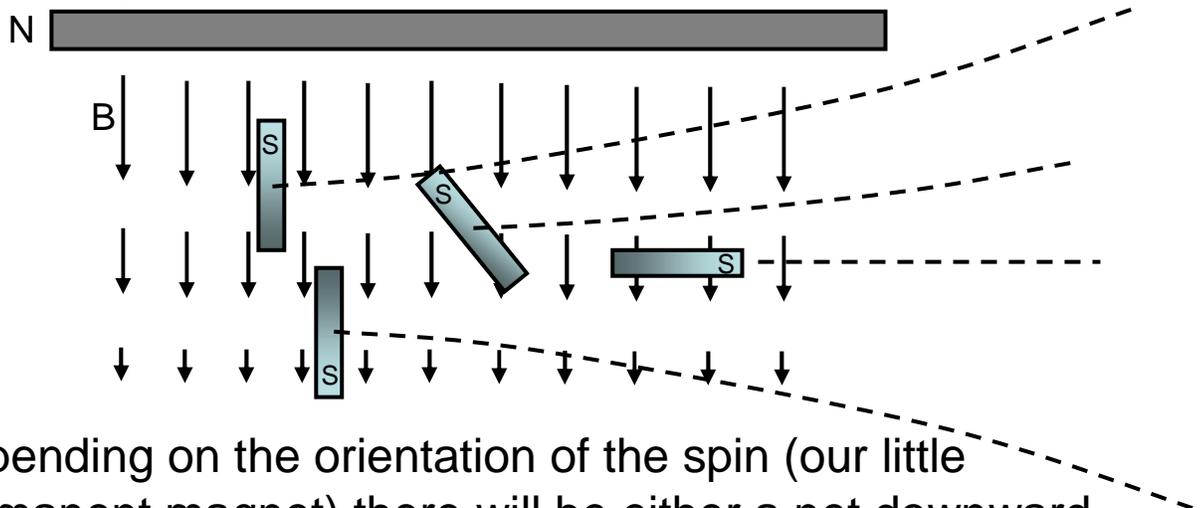
- We have talked about spin previously. Let's explore it in a little more detail because it has an interesting connection to spectral lines.
- First recall that spin is an *intrinsic quantity* much like mass or electric charge (although it is a vector not a scalar).
- Semiclassical Description of Spin:
  - IMPORTANT: This model cannot be correct...so do not take the analogy too far...it will fail you.
  - Imagine the electron and proton as spinning balls of charge.
    - Circulating charge (current) makes them look like little electromagnets with a “north” and “south” pole like permanent magnets.
  - We can use the “right-hand” rule to determine the direction the spin vector is rotating



- For the electron, because it is negatively charged, its “north pole” points the opposite direction of the spin.
- For protons, because it is positively charged, its “north pole” points in the same direction as the spin.

# Stern Gerlach Revisited

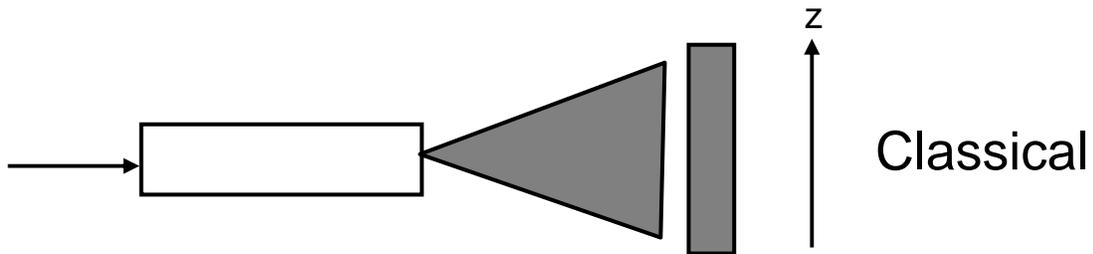
- The Stern-Gerlach Devices that we treated as black-boxes can now be explained in slight more detail (although not all the subtle details)
- Imagine these little magnets, which are the particles, passing through a magnetic field which points in the  $-z$  direction but is decreasing along  $-z$  (strongest at positive  $z$ )



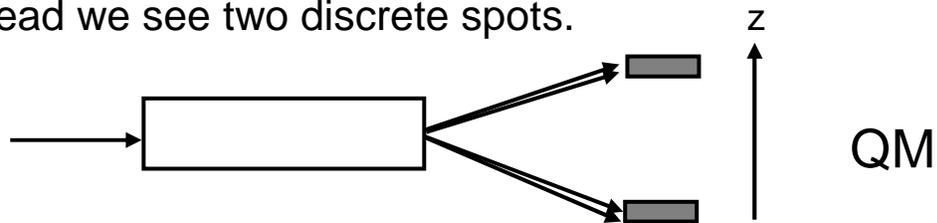
- Depending on the orientation of the spin (our little permanent magnet) there will be either a net downward or a net upward force.
  - The particle (magnet) with the south point directly up will feel a net upward force and deflect upward.
  - The particle (magnet) with the south pointing directly down will feel a net downward force and deflect downward.
  - The particle (magnet) that is horizontal will not feel any net force and will continue straight through.
  - The particle at an angle will feel a net upward but not as large as the one pointing directly upward.

# Stern-Gerlach

- This experiment can measure the spin projection along the z-axis.
  - Classically we would expect a range of values
  - Projecting the electrons onto a screen we would expect to see a full band from +1 to -1.



- But experimentally we don't see this continuous band instead we see two discrete spots.



- This corresponds to the feature of quantum mechanics that the spin projection is always completely aligned or completely antialigned along the axis of measurement.
  - ❑ So now we have a general idea about how a Stern-Gerlach device works.
  - ❑ Note: If we rotate the SG device so that the magnetic field points along the x-axis or y-axis, we still see that the spin projection we still see the two discrete spots on the screen.

# Absolute Magnitude of Orbital and Spin Angular Momentum

- The Stern-Gerlach measures the projection along certain axis. What about the absolute magnitude of the spin?
- First of all remember when we first introduced spin we said that it was related to angular momentum. When an electron is in an atom (e.g. H) it has two pieces of angular momentum
  - Orbit angular momentum:
    - Associated with the motion “orbit” around the proton.
  - Spin angular momentum:
    - Associated with the intrinsic spin of the object.
- In order to get some sense of the orbital angular momentum, let's return to the Bohr model of the atom
  - In the model the orbits are quantized.
  - The definition of angular momentum for a circular orbit is

$$L = mvr = pr = \frac{h}{\lambda} r = \frac{h}{2\pi\lambda} 2\pi r = \frac{\hbar}{\lambda} n\lambda = n\hbar$$

- So we expect the orbital angular momentum is quantized in units of h-bar.
- Although we won't prove it here, if we measure the projection of L along the z-axis, we only measure certain values:

$$L_z = +\ell\hbar, (\ell - 1)\hbar, \dots, 0, \dots, -(\ell - 1)\hbar, -\ell\hbar \quad \text{where } \ell = 0, 1, 2, \dots$$

# Magnitude of Spin (S) angular momentum

- The spin has a similar restriction on its possible values. Although we will not explore the exact reasons, spin has units of  $\frac{1}{2} \hbar$ . And its projection along the z-axis is given by:

$$S_z = +s\hbar, (s-1)\hbar, \dots, 0, \dots, -(s-1)\hbar, -s\hbar \quad \text{where } s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$$

- It turns out for many particles (e.g. electrons, protons, neutrons, leptons, quarks) that the total spin is  $s = \frac{1}{2}$ . This implies that they have two possible spin projections along the z-axis:

$$S_z = +\frac{\hbar}{2} \quad \text{or} \quad -\frac{\hbar}{2}$$

- Note: When we have talked about spin projection in the past we often just said “+1” and “-1”...this was just worrying about the coefficient in front of the absolute magnitude...but now we see that magnitude is a half unit of  $\hbar$ .

# Connection to Spectral Line

- When astronomers looked at spectral lines of cold Hydrogen gas in interstellar space they see an emission line at  $\lambda=21$  cm. This corresponds to an energy of  $\sim 6 \times 10^{-6}$  eV. It is a very prominent emission line
  - If we look at our energy level equation for hydrogen the only way to explain this small energy difference would be if it was a transition between very large “n” energy-levels.
  - However, it makes no sense that the cold interstellar Hydrogen would have many electrons up in these excited states.
- It turns out that this spectral line can be explained by an interactions between the spin of the electron and the spin of the proton.
  - If we define the proton spin direction as the +z axis, the electron spin is either aligned along +z or aligned along -z
  - It turns out that if the spins are antialigned, the electron is in a slightly lower energy state than if the spins are aligned.
    - ❑ In other words, the energy level at -13.6 eV in Hydrogen is actually **two** energy levels that are very close to one another (separated by about  $5.9 \times 10^{-6}$  eV)
    - ❑ A transition between these two close states leads to the 21 cm emission line from cold interstellar H.

# Pauli Exclusion Principle

- The study of spectral lines also led to the formation of an “*Exclusion Principle*” by Wolfgang Pauli in 1925.
- Physicists observed that in certain cases emission spectral lines were missing in multielectron atoms such as Helium (Hydrogen – single electron atom, didn’t suffer from this problem.)
- Pauli recognized the fact that the missing transitions corresponded to cases where two electrons would have to be sharing the same state (spin direction, orbital angular momentum, and energy (n-value)).
  - As long as one of these three were different among all the electrons, the emission line seem to be present.
- Pauli formed what is now known as the “Pauli Exclusion Principle”  
**“No two electrons can have the same quantum state”**
- He took this as and observational fact. There was no reason from the theory of quantum mechanics at the time why this needed to be true...although we could not live without it! (The Chemistry of life depends on atoms having their electrons in different shells...instead of all down in the lowest energy state.)
- In the 1950’s with the development of *Relativistic Quantum Mechanics* came the theoretical proof for the Pauli Exclusion principle.
  - It holds for all *fermions* (spin  $\frac{1}{2}$ ,  $\frac{3}{2}$ ,  $\frac{5}{2}$ , etc.)
  - It does **not** hold for *bosons* (spin 0, 1, 2, etc.)