

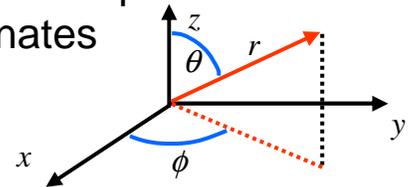
Chapter 9: Atoms

- Although we won't solve the equations which lead to the energy levels of hydrogen (or any other atom) we can use some of what we have learned to make some qualitative statements about the wave functions for energy levels and the behavior of atom.
- Warnings:
 - This chapter is very qualitative
 - In many cases we will state a principle without justification...maybe we will make a *plausible* argument but by no means will we prove anything. Much of this will need to wait for a later quantum mechanics course.

Radial and Angular Wave Functions

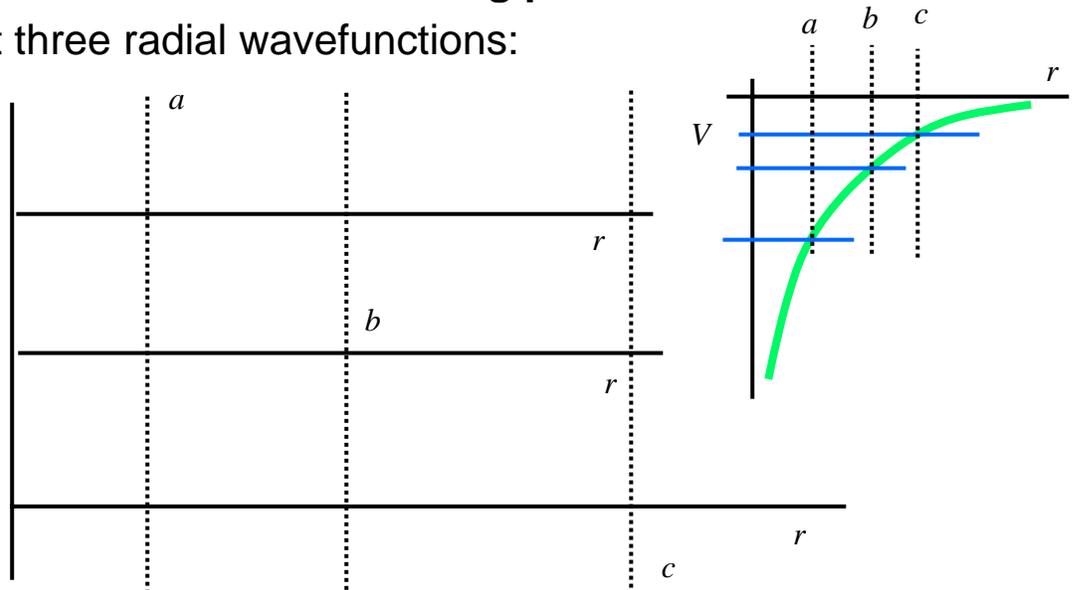
- One of the obvious shortcomings of the Bohr model is that it demands the electrons are in circular orbits
 - It does not allow for any radial motion of the electron
 - If we perform a fully quantum mechanical treatment of hydrogen we find that electrons are not in circular orbits and can spread out in the radial direction.
 - The hydrogen atom is clearly a 3-dimensional problem. Let's break it down into spherical coordinates

□ (r, ϕ, θ)



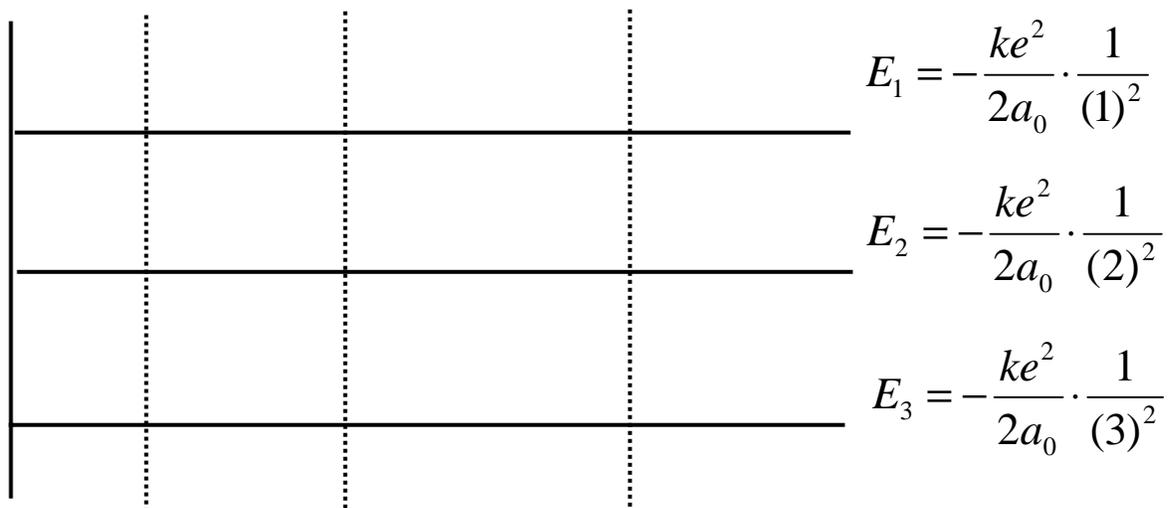
- Consider only the *radial direction*

- This is clearly suspect but it turns out that there are *some* energy eigenfunctions which do not depend of ϕ and θ and therefore only depend on r .
- Plausible Statement: **The lowest energy state that depends only on r will fit a “half a wavelength” between the classical turning points.**
- First three radial wavefunctions:



Radial Wavefunctions

- Properties of the radial wave functions
 - At the classical turning point at large r , the wavefunction is an exponential decay in the classically forbidden region. (More on this in Chapter 11)
 - $R=0$ is the other “classical turning point”...the wave function goes to zero at $r=0$. This implies that the electron won't be found in near the nucleus.
- If we take the absolute square of the radial wave functions we get:



- Notice that for these energy levels “ n ” is the number of “radial bumps”...not the number of full wavelengths **around** the atom as in the case in the Bohr Model.
 - To distinguish this let's label these “ n_r ”
 - Also remember we were considering wavefunctions that had no dependence on ϕ and θ ...no for these there are NO bumps in the wavefunction “around” the atom.

Radial+Angular Dependence

- It's not that Bohr got it completely wrong. We can still have a dependence as we go "around" the atom.
 - We still must demand that the wavefunction matches as it makes a complete revolution.
 - Must still be an integer number of wavelengths.

- As we saw when we discussed spectral lines we saw that the number (ℓ) of wavelengths was related to the angular momentum:

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

Note: This is not quite right...real answer is $\sqrt{\ell(\ell+1)}\hbar$

- If we think about the absolute square of the wave function, the number of "bumps" as we go around the atom is 2ℓ
- Now we can combine the angular and radial parts. It turns out that the "n" we use for the energy determination is given by

- This implies that we can "trade-off" radial "bumps" for angular "bumps" (1 radial = 2-angular).



- How did Bohr get this right?? The Bohr levels are basically $n_r=1$ and maximum ℓ but since these are degenerate with the others Bohr predicted all the levels.

Example Wave Functions

Quantum Numbers

- A model has started to emerge where we can define the electron state by a set of numbers that we call the **quantum numbers**:
 - (1) n : principle quantum number (defines Energy)
 - (2) ℓ : angular momentum quantum number. Note: $n = n_r + \ell$ (Note: n_r must be at least 1, so the number of possible values of ℓ for a given n is $n - 1 + 1 = n$...the "+1" is including the $\ell = 0$.)
 - (3) m : This gives the spin projection along the z-axis. For a given value of ℓ there are $2\ell + 1$ possible projections along the z-axis.
 - (4) m_s : The spin projection along the z-axis...for electrons, which have spin $S = \frac{1}{2}$ there are two possible values $+\frac{1}{2}$ and $-\frac{1}{2}$.
- Let's consider some possible states for the electron in hydrogen:

n	ℓ	m	m_s	E (eV)
1	0	0	$\frac{1}{2}$	-13.6
1	0	0	$-\frac{1}{2}$	-13.6
2	0	0	$\frac{1}{2}$	-13.6/4
2	0	0	$-\frac{1}{2}$	
2	1	-1	$\frac{1}{2}$	
2	1	-1	$-\frac{1}{2}$	
2	1	0	$\frac{1}{2}$	
2	1	0	$-\frac{1}{2}$	
2	1	+1	$\frac{1}{2}$	
2	1	+1	$-\frac{1}{2}$	

Periodic Table

- Based on the concepts we have learned we can understand some of the properties that lead to the structure (Chemistry) of the period table.
 - The structure (trends) in the periodic table can be traced to how the electron shells are filled.
 - The order in which shells are filled is dictated by the energy levels of the shells...filling lowest energy shells...this is the most stable situation.
 - The Pauli Exclusion principle also plays a HUGE role.
 - ❑ If it were not true all the electrons would fall into the lowest energy shell.
- Is there any way that we can make some qualitative predictions about the energy levels of multi-electron atoms?
 - When we put the first electron on the atom, the energy levels should look like hydrogen except the levels will be lower because of the larger charge of the nucleus

$$E_n = -\frac{Zke^2}{2a_o} \cdot \frac{1}{n^2}$$

Note: a_o has a dependence on Z in it.

- As soon as we put more electrons onto the atom the energy levels will become modified.
- However, imagine will fill up all the shells at a given “n” (principle quantum number). This means the all the possible values of ℓ , m , m_s are filled. The charge density of these is spherical and shield the nucleus.

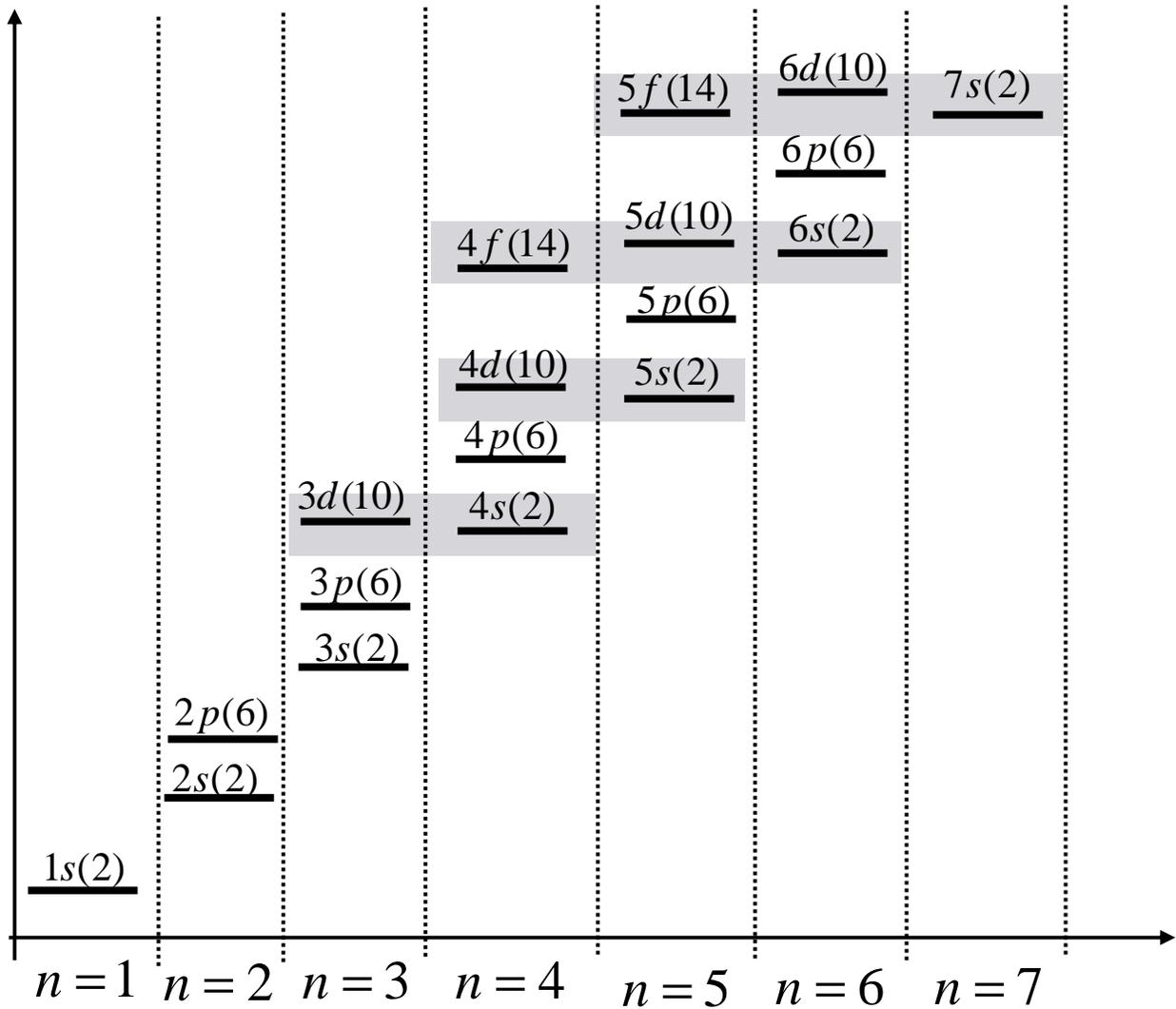
Periodic Table

- Now, if we add an electron to the atom, the energy levels should be “hydrogen-like”
 -
 -

- Look back at the shape of the wavefunctions for the $n=3$ case.
 - For lower l , the wavefunction has more peaks in close to the nucleus than higher l .
 - This implies that for smaller l , less of the nucleus will be shielded and the energy level of this shell will be lowered relative to the other shells at the same “ n ” but different l
 - This leads to a partial breaking of the degeneracy of the energy levels for fixed “ n ”
 - l
 -

- The next page shows the rough energy levels of multi-electron atoms is shown on the next page:
 - The levels in the grey bands are very close together and the exact ordering of these levels can change depending on the atom.

Multi-electron Energy Levels



Spectroscopic Notation

$$nX^y$$

n =principle quantum number

X = "s", "p", "d", "f" for $l = 0, 1, 2, 3$

y (not used above) is number of electrons in that shell.

Properties of the Periodic Table

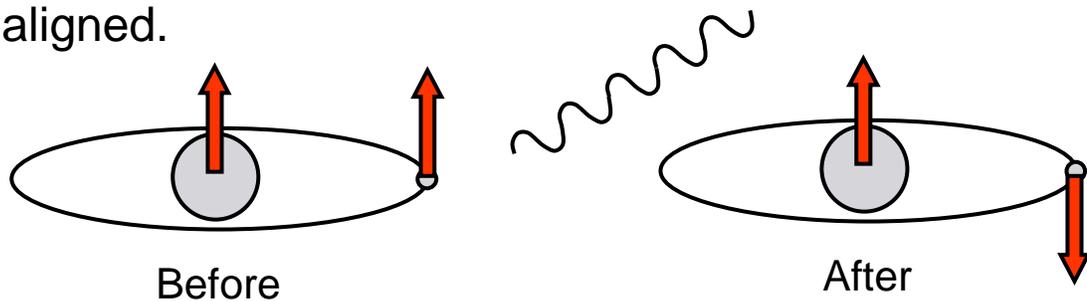
- Using the energy level diagram let's predict a few of the general properties of the Periodic Table.
- (1) Helium is fairly inactive. This is because it has two electrons which can both fit down into the 1s state (two spin directions). In addition, the energy gap to the 2s state is fairly large.
 - Other Noble gases share this same property where a set of levels are full and the energy jump to the next level is somewhat large
 - Ne ($n_{\text{electron}} = 10$1s, 2s, and 2p are full)
 - Ar ($n_{\text{electron}} = 18$1s, 2s, 2p, 3s, and 3p are full)
- (2) Lithium ($n_{\text{electron}} = 3$)
- (3) Beryllium ($n_{\text{electron}} = 4$)
- .
- (4) Sodium ($n_{\text{electron}} = 11$)
- .
- These trends continue where elements that have similar chemical activity have a similar population in their outer electron shells. The chemical activity is to a great extent determined by the energy levels.

Selection Rules

- We also can consider the emission of photons between energy levels in atoms. We saw that spectral lines were the results of emitting photons as an electron made a transition between energy levels of an atom.



- Recall the discussion of 21-cm hydrogen line. The photon for this line was emitted in a transition between the 1s states where the spin of the electron is aligned with the proton spin, to a state where the spin is antialigned.



- Both before and after the emission of the photon, the electron is in a $n=1$ and $l=0$ state. So the orbital angular momentum has not changed. However, the spin angular momentum has decreased by $2\left(\frac{\hbar}{2}\right) = \hbar$. So the *total* angular momentum of the atom has changed by \hbar . Since angular momentum is conserved, the photon must have taken \hbar worth of momentum away. This means that the photon is a **boson** of spin at least equal to $1\hbar$ (in fact it is 1).

Selection Rule

- Because the photon carries away angular momentum, we must have transitions of the atom which change the angular momentum by +/- 1 unit of h-bar
- There are a couple of features to this, which we will not prove, but state



- This leads to a selection rule (which is not **always** obeyed.)

$$\Delta \ell = \pm 1$$

- One of the interesting consequences of this in conjunction with the Pauli Exclusion principle, is the existence of *metastable* states. For example, say that we excited an electron in hydrogen from the 1s state to the 2s state. The transition back down into the 1s would violate our selection rule. It will eventually happen but the H atom will exist in this state for an extended time...it is *metastable*.
- This is the principle behind glowing toys and is also used in the construction of lasers (Read Section 9.4)