

# Fundamentals of Nanoelectronics

ECE495 - Session 10, Sept 16, 2009

## Atomic Energy Levels

Ref: Chapters 2.3 and 3.1

## Professor Supriyo Datta

Class notes taken by: Mehdi Salmani

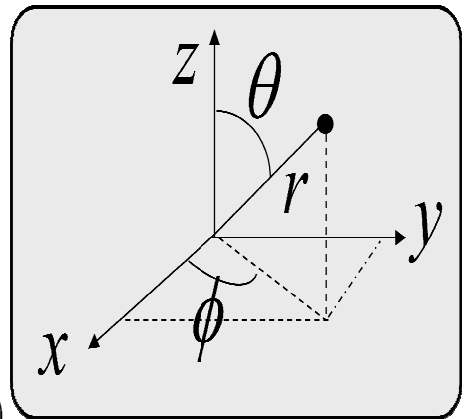
### Review

3-D Schrödinger equation is:  $E\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + U(\vec{r})\Psi$

In spherical coordinates the variables are:

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ In Cartesian Coordinate}$$

$$\nabla^2 \equiv \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$



In Spherical Coordinate

### Spherical Coordinate

The potential in spherical coordinates depends only on "r" and it is separable. It can be written as 3 function of r,  $\Theta$  and  $\Phi$  where the function of  $\Theta$  and  $\Phi$  are basically zero. The hard thing about this coordinate system is that the operators are much more complicate; hence more complicated to work with.

For potentials that are symmetric in "r" and do not depend on  $\Theta$  and  $\Phi$  one can write the solutions to the Schrödinger equation as:

$$\boxed{U(\vec{r}) = -\frac{q^2}{4\pi\epsilon_0 r}} \quad \Psi(r, \theta, \phi) = \underbrace{\psi(r)}_{\text{Radial}} \underbrace{Y_l^m(\theta, \phi)}_{\text{Angular}}$$

The angular part is already known for any atom whose potential does not depend on  $\Theta$  and  $\Phi$ . One only has to find the radial part. The  $Y(l,m)$  are called **spherical harmonics**. Let's discuss them more.

### Spherical Harmonics

$$\nabla^2 \equiv \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \overbrace{\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)}^L$$

If we act operator "L" on  $Y(l,m)$ 's we get:  $L(\theta, \phi)Y_l^m = -l(l+1)Y_l^m$

We see that the operator acts on the function and generates the same function with a multiplicative constant. In such cases the functions are called to be the eigenfunctions of the operator. The property of  $Y(l,m)$ 's is that they are eigenfunctions of "L".

The simplest  $Y(l,m)$  is  $Y(0,0)$  and is just a constant:  $Y(0,0)=1$ .

So : if  $l = 1$  then  $m = -1, 0, 1$  and the  $Y(l,m)$ 's are:

$$Y_0^0 = 1$$

$$Y_1^0 = \cos(\theta)$$

$$Y_1^{\pm 1} = \sin(\theta)e^{\pm i\phi}$$

The general rule is:

**If  $l = n$**

**Then  $m = -n, -(n-1), ..0, 1, 2, n-1, n$**

**$n = 0, 1, 2, ...$**

Let's see if  $Y(1,0)$  is an eigenfunction of the operator "L"

$$LY_1^0 = (\text{some constant}) \times Y_1^0 \quad ?$$

$$L = \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$$\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} (\cos \theta) = 0 \quad (I) \text{ and}$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) (\cos \theta) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \cdot -\sin \theta) = \frac{1}{\sin \theta} (-2 \sin \theta \cos \theta) = -2 \cos \theta \quad (II)$$

$$(I) \& (II) \Rightarrow LY_1^0 = -2 \times Y_1^0 \quad \text{where } -l(l+1) = -1(1+1) = -2$$

## Radial Part of Schrödinger Equation

Back to the solution of Schrödinger equation. Consider the function:  $\Psi(r, \theta, \phi) = \psi Y_l^m(\theta, \phi)$

Putting this answer into the Schrödinger equation,  $E\Psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right) \Psi$  we get:

$$E\psi Y_l^m = \left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + U(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right] \psi Y_l^m$$

we can drop easily  $Y_l^m$  part because the

operator is not dependent to  $\Theta$  and  $\Phi$ .  $E\psi = \left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + U(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right] \psi$

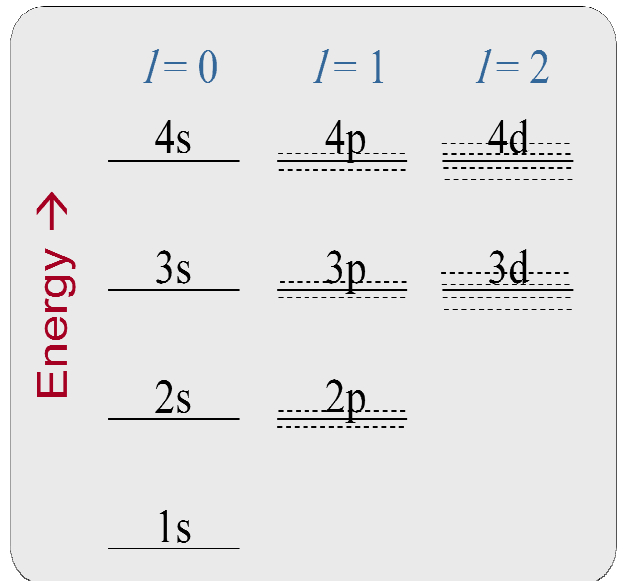
We want to drop this term  $\frac{2}{r} \frac{d}{dr}$ . We will assume  $\psi \equiv \frac{f(r)}{r}$  then

$$Ef(r) = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + U(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right) f(r)$$

### Atomic Energy Levels

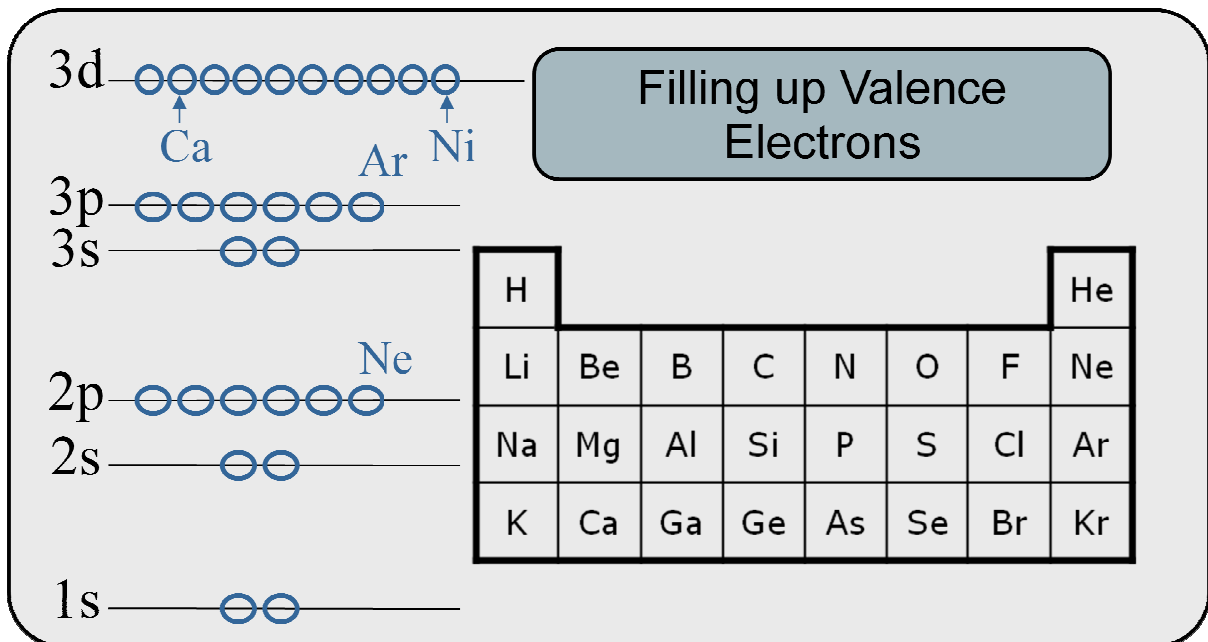
We can now talk about energy levels in Hydrogen atom. Since the potential in Hydrogen atom has the form of  $1/r$ , the levels 2s and 2p are at the same energy. This does not have to be the case for other atoms. Also note that for each value of "l", there are 2l+1 values of "m" that have the same energy. So when l=1, m=-1,0,1 and the levels comes in triplets. When l=2, there will be 5 degenerate levels.

There is spin concept; each level is coming in pairs.



### Energy Levels and Periodic Table

As one goes through the periodic table energy levels of atoms get filled by electrons. As we go down the rows the valence levels fill. As a level fills, going along left to right, energy levels become more negative.



Electrical and optical properties are all about the valence electrons! Not concerned with core electrons. Although, core electrons are valuable for diagnostic purposes (e.g. knowing what impurities are present in silicon) Note that core electrons do not get affected by the surroundings.

Based on **photoemission** and **spectroscopy**, scientists can determine the energy levels experimentally.

The energy level for Hydrogen is -13.6eV. For Helium (He),  $U(r) = \frac{-2q^2}{4\pi\epsilon_0 r}$ . Solving for He 1s level we get -54.4eV. But the experimental value is measured to be -23.4eV!?

The difference is due to He has another electron and  $U(r) = \frac{-2q^2}{4\pi\epsilon_0 r} + U_{ee}(r)$ . If we kick out one electron we will need 54.4eV for next electron.