Chapter 5 Quantum Theory and Atomic Structure

5-1 The Schrödinger Equation

Besides not working with any other atom there is an additional problem with the Bohr model. In the Bohr model the electron is in a well defined circular orbital, much like a planet in an orbit around the sun. In such a model we should be able to know just exactly where the electron is and how fast it is moving, just like we know all the orbits of all the planets around the sun.

But about the same time the Bohr model is being developed a new principle is being developed called the Heisenberg uncertainty principle. This principle states that you can’t know both the position and the momentum \( p = mv \), hence \( v \) of any object beyond a certain limit.

\[
(\Delta x)(\Delta p) \geq \frac{H}{4\pi}
\]

Why? To know where something is you have to interact with it is some way with photons. As the photons interact with the thing they change its momentum and velocity, so that changes the very thing you are trying to measure!

I won’t make you do an uncertainty calculation, but the example given in the book is a nice illustration of the problem. In this problem you try to know the position of an electron in an atom to within a few % of the atom’s size. If you know an electron’s position to this accuracy, this results in having an 20% uncertainty in knowing the velocity of the electron.

Bottom line - We really can’t put electrons into nice well-defined orbitals!

So a new theory was developed around the Schrödinger equation, and equation that incorporates both wave and particle properties and the uncertainty principle. That equation is too complicated to be presented here, so we will only deal with the results.

The first results is that when we solve Schrödinger’s equation for the H atom, we get the same sets of discrete energy levels that we got with the Bohr model.

These solutions, however, don’t give us nice circular electron orbitals. Instead it gives us a three dimensional equation called the \( \psi \) function or wave function associated with each energy level.

\( \psi = \psi(x,y,z) \) so it depends on where you are around the nucleus

\( \psi^2(x,y,z) \) is called the probability density because it tells the probability of finding an electron at any \( x,y,z \) position.
When we talk about an **atomic orbital**, what we are really referring to is a wave function that solves the Schrödinger equation and results in a particular energy level.

Since this equation is both quantitized and three-dimensional, we find that there are three different quantum numbers imbedded within it: \( n \), \( l \), and \( m \).

We will discuss each, one at a time.

**Key Concept:**

- \( n \) is called the **principal quantum number**
  - Determines the energy of the electron in the hydrogen atom
  - Also gives the overall size of the orbital
  - \( n \) can have values of integers > 0 (1, 2, ...)
  - Corresponds to the ‘shells’ we were describing earlier

\( n = 1 \) is the lowest level
- hence called the **ground state**
- when \( n = 1 \) orbital is spherically symmetric
  - (Depends only on \( r \))
  - Sometimes denoted \( \psi_{1s} \)
  - Figures 5.2, 5.3, and 5.4

### 5-2 Shape and the second quantum number

**Key Concept:**

- The second quantum number is: **azimuthal quantum number** (Angular momentum number) = \( l \)
  - Has values between 0 and \( n-1 \)
  - Thus depends on previous quantum number
  - Determines shape of orbital
  - Historical reasons: 0 = s, 1 = p, 2 = d, 3 = f, 4 = g
  - Called subshells
    - s - sharp
    - p principal
    - d diffuse
    - f fundamental
  - Designation had to do with atomic emission lines

A couple of years ago a student gave this interpretation
- s - spherical
- p peanut
- d double peanut
- f fricken crazy
- g Gawd No!
For hydrogen there are two orbitals with n=2: 2s & 2p
- The both have the same energy.
- When two different orbitals have the same energy they are called **degenerate**

For hydrogen there are three degenerate orbitals with n=3, 3s,3p, & 3d

How are the 1s,2s, and 2s orbitals different?
- Size and energy
  - **Figure 5.5 & 5.6**
  - The radius that encloses 99% of electrons is 200 pm in 1s, 600 pm in 2s, and 1300 pm in 3s!
  - Also note the **nodal surfaces** regions where electron density for to 0!

Now how is s different from p (won’t do d yet)
- p is cylindrically symmetric
- Has an axis
- Also - peanut shape)
  - **Figure 5.7 & 5.8**

### 5-3 Orientation and the magnetic quantum number
**Key Concept:**
- Third quantum number is called magnetic quantum number (M_i)
  - determines orientation of orbital
  - has integer values from -l to +l
  - Thus depends on the previous quantum number

Going back to previous 2p orbital
- p corresponds to l=2, so m_i can = -1,0,+1
- so there are three 2p orbitals, one oriented along each axis, x, y, and z designated p_x, p_y, and p_z
  - **Figure 5.9, but the powerpoint doesn’t work**

We haven’t looked at the n=3,l=2, m_i = -2,-1,0,+2,+2
- (The five 3d orbitals)
  - **Figure 5.10**
  - Remember my student’s designation of double peanut?

What do the seven G orbitals look like?
- I won’t show them! Remember my student designation of Gawd NO!

Let’s put this all together in a single table
- **Table 5.2 on board**

**Clicker question: identify some incorrect and correct set of quantum #**
5-4 **Electron spin quantum number**

The Schrödinger solution model with 3 quantum numbers is consistent with lots of experimental data, but there were still some experiments that it didn’t explain.

So the theory had to be expanded a bit to include one additional effect. **Intrinsic electron spin**

The classical analogy is this. When a charged particle, like an electron moves in a circle it induces a magnetic field. If they spin in one direction, the field points in one direction, if they spin in the other direction the magnetic field is reversed.

Note this is a classical explanation. Since the Schrödinger equation is non-classical, wave-quantum theory, we have to add two states that arise due to relativistic effects.

**Key Concept:**

- **Spin quantum number** ($m_s$)
- Values of $+\frac{1}{2}$ or $-\frac{1}{2}$

5-5 **Energy state when there are 2 or more electrons**

Remember how I said that the orbitals in Hydrogen were degenerate? So all the $n=3$ orbitals 3s, 3p, and 3d had the same energy? Well that is true because H only has 1 electron.

What happens in other elements that have more than 1 electron? Things get complicated. All the electrons interact with each other so the different orbitals at a given $n$ number start to have different energies.

Believe it or not, you need to know this order because it will explain the periodic table to you. Trying to keep figure 5.11 in your head is pretty hard, so let me show you an easy to remember shortcut.

**Figure 5.12 on board**

5-6 **The Pauli exclusion Principle**

One last piece before I explain the periodic table.

**Key Concept:**

- No two electrons in a atom can have the same set of 4 quantum numbers.

First proposed by Pauli in 1926.

Bottom line - first three quantum numbers define the orbital. And each orbital can only contain two electrons, one with spin $+\frac{1}{2}$ one with spin $-\frac{1}{2}$.
Now we can expand our quantum table to.

Chemists use the term spin up for $+ \frac{1}{2}$ and spin down for $- \frac{1}{2}$

Materials will have different properties if all electrons are paired or if some are unpaired

Have a shorthand to designate pairing

$$\begin{array}{llllll}
1s & 2s & 2p \\
\end{array}$$

5-7 Electron Configurations

Now let’s start looking at the ground state (lowest energy state) of our elements.

The arrangement of electrons in orbitals is called the **electron configuration**

He

$$\begin{array}{c}
1s \quad \text{or} \quad 1s^2 \\
\end{array}$$

Li, well I can’t put three electrons in one orbital, So

$$\begin{array}{c}
1s & 2s \quad \text{or} \quad 1s^2 2s^1 \\
\end{array}$$

Note: the 2s orbital could be either $+ \frac{1}{2}$ or $- \frac{1}{2}$ spin. Standard convention says $+ \frac{1}{2}$ on left

Note that $1s^2 2s^1$ is the same as the Li· or [He]· designation we used earlier so the 1s is the core and the 2s is the valence electron in this example

Be

$$\begin{array}{c}
1s & 2s & 1s^22s^2 \quad [\text{He}]: \\
\end{array}$$

B

$$\begin{array}{c}
1s & 2s & 2p & 1s^22s^22p^1 \\
\end{array}$$

(Note: The 2p orbitals are degenerate, so electron could go in any of the three, but by convention we start with the first one)

Practice problems:

What are electron configurations for:

B⁺

$$\begin{array}{c}
1s & 2s & 2p & 1s^22s^2 \\
\end{array}$$

C⁺

$$\begin{array}{c}
1s & 2s & 2p & 1s^22s^22p^1 \\
\end{array}$$

F⁻

$$\begin{array}{c}
1s & 2s & 2p & 1s^22s^23p^6 \\
\end{array}$$
Key Concept:
 Isoelectronic: atoms or ions with the same ground state electron configuration

In the above example B⁺ is isoelectronic with Be, C⁺ with B, and F⁻ with Ne

5-8 Hund’s Rule
With the ground state of C we have three possible electron configurations all designated 1s²2s²2p²

1s 2s 2p
↑ ↓ ↑ ↓
↑ ↓ ↑ ↑
↑ ↑ ↑ ↓

In the first case we have two electrons forced to occupy the same orbital, so this is actually a higher energy that the second two cases. This does not happen.

For the last two, it has been determined experimentally that the lower energy occurs when the electrons have parallel spin. So ↑ ↑ ↑ ↑ is the lowest energy configuration

This leads to Hund’s rule:

Key Concept:
 For any subshell the ground state is found by placing as many electrons as possible in different orbitals with parallel spins

Practice problems:
Give the electron configuration for:

N  ↑ ↓ ↑ ↓ ↑ ↑ 1s²2s²2p₁²p₁²p₂¹ or 1s²2s²2p³
O  ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓ 1s²2s²2p₁²p₂¹²p₂¹ or 1s²2s²2p⁴

5-9 Absorption of light
When light is absorbed an electron is moved from a low energy orbital to a higher energy orbital

For instance when lithium absorbs 671 nm light we have the equation

Li(1s²2s¹) + hv → Li⁺(1s²2p¹)

Key Concept:
 We call the transition of the highest energy ground state electron to the next available orbital the **first excited state**
Once you get into the third row elements, writing the electron configurations can become a real pain. So let’s do the same thing we were doing in the Lewis diagrams

Na\(^-\) = [Ne] \ 1s^2 2s^2 2p^6 3s^1 = [Ne] 3s^1

Notice how this really focuses you on the difference between the core (a filled shell of electrons) and the valence electrons (outer unfilled shell)

Practice problems
Write the electron configurations of

Al \ [Ne]3s^2 3p^1
Al^{3+} \ [Ne]
Cl \ [Ne]3s^2 3p^5
Cl^{-} \ [Ne]3s^2 3p^5 or [Ar]

Clicker question: electron configuration for some other group 1-18 elements

5-10 Atom families and valence shell configurations
Now, at last, we can start to explain the periodic table

If your write the electron configuration of all the element in group 1 you will find they all have the same s\(^1\) valence configuration. That is why they have the same chemical reactivity

Similarly group 2 are s\(^2\) valence electrons

group 16 p\(^4\), 17 p\(^5\) and 18 p\(^6\) or closed shell (hence non reactive!)

So not only did Schrödingers equation properly expand our understanding of electron orbitals in atoms beyond H, but it also explains the periodic table!
5-11 Transition metals
With the transition metals we begin to fill in the d orbitals. Remember that with Sc, even though we are in the 4\textsuperscript{th} row, we are filling in 3d orbitals because this is the point where the orbital energy overlap starts making things go crazy.

Practice Problems
What is the electron configuration of
- Sc: [Ar]4s\textsuperscript{2}3d\textsuperscript{1}
- V: [Ar]4s\textsuperscript{2}3d\textsuperscript{3}
- Cr: [Ar]4s\textsuperscript{2}3d\textsuperscript{5}
- Cu: [Ar]4s\textsuperscript{2}3d\textsuperscript{9}

Correction!!!
What you just did for Cr and Cu is actually wrong! Since the energy levels of the 4s and 3d orbital are so close what you actually get are:
- Cr: [Ar]4s\textsuperscript{1}3d\textsuperscript{5}
- Cu: [Ar]4s\textsuperscript{1}3d\textsuperscript{10}

As you get further down the table, there are a few more gotcha’s like this. These are the only two I expect you to remember.

Figure 5.15
In row 6 we start with 6s\textsuperscript{2} but then start filling in the fourteen 5p electrons. Again there are some exceptions to the filling order, but you don’t have to worry about them.

And so it goes until you have the entire table.
Review table and orbitals

Clicker question: electron configuration of some harder elements

5-12 Periodic Properties
Let’s put two physical properties into the context of the periodic table, size and ionization energy.

Size
Size of atom is hard to define. Just saw that the \( \psi \) function is never zero, so there is no cut off that says ‘the atom stops here’

Atomic radii are based on models. The model we use is \( \frac{1}{2} \) the distance between atoms in a simple crystal array of atoms. Called crystallographic radii.

Crystallographic radii shown in figure 5.19

As you can see Radius large as go down
Smaller as go up
smaller as go to right

Up and down makes sense. As go down more electrons, higher quantum numbers higher q # means larger size

But why smaller to right?
As go to right, more charge in nucleus pulling electrons in closer!

Ionization E
Figure 4.1
Lowest E, easiest to ionize is bottom left, just like largest size
largest size furthest from nucleus easiest to pull off
As go up or to right, get closer to charge of nucleus so harder to pull off for ionization E

Clicker question on relative size and ionization E of some elements.