Chapter 7
Many-Electron Atoms
(We only have 2 days for chapter 7!)

7.1 Electron Spin

Electron spin is the cause of the fine structure in spectral lines, and the anomalous Zeeman effect ("extra" and "missing" splittings of spectral lines in the presence of magnetic fields). Electron spin is also important in magnetism.

Spectral lines are due to photons emitted when electrons change their energy state.

Changes in the principal quantum number n cause the most noticeable changes. However, changes in other quantum numbers also give rise to changes in electron energies. Such changes typically involve less energy, and result in a "splitting" of the primary lines.

Not all splittings can be explained by the quantum theory developed in chapter 6. It turns out we need another quantum number -- spin.

The Stern-Gerlach experiment is a famous experiment which demonstrated electron spin. I might ask a test or quiz question on it.

Sometimes we visualize electron spin by imagining a charged sphere spinning on its axis.

That's the classical picture of electron spin.

It gives rise to an intrinsic angular momentum, associated with the spin and independent of the orbital angular momentum. It also gives rise to the intrinsic magnetic moment of an electron.

Such a classical picture of the electron doesn't work. See Beiser. I may also ask a test/quiz question on this. But the classical picture can be used to give you insight.

The spin quantum number $s$ which describes the spin angular momentum of an electron has a single value, $s=\frac{1}{2}$.

Just as is the case with the orbital quantum number $l$ and orbital angular momentum $L$, the spin angular momentum is given by

$$S = \sqrt{s(s + 1)}\hbar = \frac{\sqrt{3}}{2}\hbar.$$ 

The existence of the spin quantum number requires still another quantum number, $m_s$.

Just as the space quantization of the orbital angular momentum is specified by $m_l$, the space quantization of the spin angular momentum is described by $m_s$.

The equation
\[ S_z = m_s \hbar = \pm \frac{1}{2} \hbar \]

gives the \( z \) component of the spin angular momentum.

See figure 7.2 for the two possible orientations of the spin angular momentum vector in a magnetic field.

You can also calculate the spin magnetic moment of an electron, and its \( z \) component. Since we skipped corresponding section on magnetism in Chapter 6, we will not go into further detail here, and I will not hold you responsible for it on exams or quizzes.

### 7.2 Exclusion Principle

This is a very brief, but very important section.

Wolfgang Pauli postulated the (Pauli) exclusion principle, which states that no two electrons can exist in the same atom (i.e., in the same potential) in the same quantum state.

"State" refers to the four quantum numbers \( n, l, m_l, m_s \). Obviously, all electrons have the same \( s \).

Another way of stating the exclusion principle is that no two electrons in an atom can have the same set of quantum numbers.

This is a very simple principle, but a very important one. We will come back to it many times in this course.

### 7.3 Symmetric and Antisymmetric Wave Functions

We will soon be investigating many-particle systems. It is important to understand the different kinds of wave functions such systems can have.

For a system of \( n \) noninteracting identical particles, the total wave function of the system can be written as

\[
\psi(1,2,3,\ldots,n) = \psi(1)\psi(2)\psi(3)\ldots\psi(n).
\]

In other words, the total wave function can be written as a product of individual wave functions.

Right now you should be asking yourself, what does this "noninteracting" mean, and how restrictive is it? If we don't come back to this question, you should bring it up as appropriate.

If the particles are identical, it shouldn't make a difference to our measurements if we exchange any two (or more) of them.

For a two particle system, we express this mathematically as
Keep in mind that it is the magnitude of the wave function squared that is related to what we measure.

That last equation implies

\[ \psi(2,1) = \psi(1,2) \quad \text{or} \quad \psi(2,1) = -\psi(1,2). \]

If the wave function does not change sign upon exchange of particles, it is said to be symmetric. If it does change sign, it is said to be antisymmetric.

Remember, we can't directly measure the wave function, so we don't know what its sign is, although, as you will see, we can tell if it changes sign upon exchange of particles.

This discussion can be extended to any number of particles. If the total wave function doesn't change sign upon exchange of particles, it is symmetric. If it does change sign, it is antisymmetric.

Now let's take these ideas a step further, and consider identical particles which may exist in two states, a and b.

If particle 1 is in state a
particle 2 is in state b
then \( \psi_1 = \psi_a(1)\psi_b(2) \) is the wave function of the system.

If particle 2 is in state a
particle 1 is in state b
then \( \psi_2 = \psi_a(2)\psi_b(1) \) is the wave function of the system.

But we can't tell 1 and 2 apart (remember, I said they are identical), so we can't tell \( \psi_1 \) and \( \psi_2 \) apart; i.e., both are equally likely to describe our system.

Our system's wave function should therefore be constructed of equal parts \( \psi_1 \) and \( \psi_2 \). Or, as the book puts it, the system spends half of its time in state I and half in state II.

There are two ways to construct our system's total wave function \( \psi_1 \):

Symmetric

\[ \psi_\text{sym} = \frac{1}{\sqrt{2}} \left[ \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \right]. \]
Antisymmetric

\[ \psi_s = \frac{1}{\sqrt{2}} \left[ \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \right] \]

Exchanging 1 and 2 changes the sign of \( \psi_A \) but not of \( \psi_S \).

What's important here is that if individual particle wave functions are antisymmetric, then if we try to put both particles in the same state, we get \( \psi_A = 0 \).

There is zero probability of finding the system in such a state.

The system simply cannot exist in such a state.

This ought to sound like the Pauli exclusion principle. In fact, electrons obey the Pauli exclusion principle because their wave functions in a system are antisymmetric.

Half integral spin particles (s=1/2, 3/2, etc.) have antisymmetric \( \psi \)'s and are called fermions.

Electrons are described by antisymmetric \( \psi \)'s which change sign upon exchange of pairs of them.

Other examples are neutrons (neutrons??--you should ask how they can have a spin) and protons. They are also fermions.

Integral spin particles (s=0,1,2, etc) have symmetric wave functions, and are called bosons.

Examples are photons, alpha particles, etc.

There is no restriction on how many of them in the same system can have the same set of quantum numbers.

7.4 Periodic Table

Refer to the periodic table in room 102 and call attention to the following:

- period
- group
- metals
- nonmetals
- transition elements
- rare earths
- actinides
- most active metal (why?)
- most active nonmetal (why?)
7.5 Atomic Structures

Electronic structures of the elements are based on the following principles:
- Total energy is minimized.
- Electrons obey the Pauli exclusion principle.

Electrons having the same n are roughly the same average distance from the nucleus, and have roughly the same energies.

We talk about atomic shells corresponding to different n's, and label them as follows:

\[
\begin{array}{cccccc}
\text{n} & 1 & 2 & 3 & 4 & 5 \\
\text{K} & \text{L} & \text{M} & \text{N} & \text{O} \\
\end{array}
\]

Electrons within a shell generally have lower total energies (bigger negative energies, and therefore larger binding energies) when they have lower \( l \).

Electrons having the same \( l \) are said to occupy the same subshell.

We write electronic configurations showing shells and subshells. For example, magnesium has a \( 1s^22s^22p^63s^2 \) configuration.

The \( 2p^6 \) above, for example, means that for \( n=2, l=1 \), there are six electrons.

How many electrons can fit in a particular subshell?

Let's do the \( 2p \) subshell as an example.

\( 2p \) means \( n=2, l=1 \). The possible values of \( m_l \) are 0, \(\pm 1 \). That's three. But corresponding to each \( m_l \) are \( m_s=\pm 1/2 \). Thus, a total of 6 electrons can fit in the \( 2p \) subshell.

Let's do the \( 4f \) subshell as another example.

\( 4f \) means \( n=4, l=3 \). The possible values of \( m_l \) are 0, \(\pm 1, \pm 2, \pm 3 \). For each \( m_l \) the possible values of \( m_s \) are \( \pm 1/2 \). Thus \( 7\times 2=14 \) electrons can fit in the \( 4f \) subshell.

A maximum of \( 2n^2 \) electrons can fit in any shell.

7.6 Explaining the Periodic Table

Syllabus says skip this section. These notes are left over from a semester when we covered it.

Sometimes I show a transparency of pages 240-241.

Things to notice:
One or two electrons outside filled shell result in low ionization energies.

This is due to the shielding of protons in the nucleus by electrons of inner filled shells.

Elements with filled shells have highest ionization energies.

The largest atoms are the alkali elements, with a single s electron outside a filled shell.

The smallest elements are the inert gases, with filled shells.

Typical atomic dimensions are an angstrom or two. A good question is just exactly what is an atomic dimension? One criterion is interatomic spacing in close packed crystals.

Note how size actually decreases across, for example, transition elements. Adding more electrons doesn't necessarily make a bigger atom.

Note how higher-n subshells do not always fill before lower-n subshells. This starts as early as potassium.

Note why rare earth elements and actinides are so similar.

Hund's rule: electrons fill subshell with parallel spins.

This is a "rule of thumb," to which there are exceptions.

Hund's rule results in ferromagnetism of some transition metals.

It is (to me, anyway) counterintuitive. It arises because electrons with parallel spins tend to be farther apart in space, and therefore experience less repulsion, so that their energies are lowered.

7.7 Skip this section

7.8 Skip this section

7.9 X-ray Spectra

We skipped an introductory section on x-rays back in chapter 2.

Here's the idea of the section we skipped: suppose you zap a metal with high-energy electrons. You get off x-rays.

This is different than atomic spectra like we've been talking about lately, because the x-rays are high energy (much higher energy than visible light, for example).

Where do the x-rays come from?
If you hit an atom "hard" enough, you can completely knock out an inner (K) shell 1s electron. (It turns out it takes only a little more energy to completely knock the electron out of the atom than it does to promote it to a high-n energy level).

What are we left with? An atom with a missing n=1 electron.

Is this a tolerable situation? No.

What happens? An electron from another shell drops into place.

What does the electron do when it drops back in place? It emits a photon.

What is the photon energy? It can be large, i.e., an x-ray.

X-rays originating from an electron dropping into the K (n=1, the innermost) level are called "K" x-rays.

X-rays coming from an electron dropping into the K shell from the L shell (n=2) are called K\(\alpha\) x-rays.

X-rays coming from an electron dropping into the K shell from the M shell (n=3) are called K\(\beta\) x-rays.

See figure 7.20 for more kinds of x-rays.

Can anybody remind me what a K\(\alpha\) x-ray energy ought to be? What kind of voltages will I need to accelerate the electrons which knock the K-shell electron out of the atom?

Beiser calculates the frequency of a K\(\alpha\) x-ray photon (those last words are redundant, aren't they).

He uses our equations from chapter 4 for the energy of spectral lines. Those equations have to be modified to consider the charges involved.

Beiser assumes the nuclear charge seen from the L shell is reduced by one by the shielding due to the remaining s electron.

Beiser also assumes that the empty s state (into which the L shell electron falls) is also shielded by the remaining s electron.

The result for the frequency is

\[ f = \frac{3cR(Z - 1)^2}{4}, \]

and for the energy of the photon in eV
\[ E = (10.2\text{eV})(Z - 1)^2. \]

These equations come from replacing \( e^4 \) by \([ (Z-1)e^2 ]^2 \) in equations 4.15 and 4.18, and using \( n_i=2 \) and \( n_f=1 \) in equation 4.15.

Another different, but related, event can occur when we knock out an inner shell electron. This event does not involve the emission of a photon.

The Auger effect is a two-electron process. One outer shell electron drops down to fill the inner shell vacancy. But no photon is emitted.

How can this happen?

Energy must somehow be carried away. In this case, an electron with the extra energy is ejected from the atom.

The energy of the ejected electron is mostly the missing x-ray energy, but it is modified due to the chemical state of the atom.

We use Auger spectroscopy to learn what atoms are present in new materials. We can also learn the chemical state of the atoms; e.g., free carbon and carbon in an iron carbide compound give off different Auger electrons.