Chapter 7

The Quantum Mechanical Atom

Characteristics of Atoms

• Atoms:
  – possess mass
  – contain positive nuclei
  – contain electrons
  – occupy volume
  – have various properties
  – attract one another
  – combine to form molecules
• How do we study atoms?

7.1 Electromagnetic Radiation

• We use electromagnetic radiation to study atoms.
• What we call light is just one form of electromagnetic radiation.
• It is important to know the properties of light in order to understand how atomic structure is revealed by electromagnetic radiation.
• Energy can be transported by electromagnetic radiation.
Light is wave-like

- **Wavelength** \((\lambda)\) - the distance between two successive crests (units: meters or nanometers)
- **Frequency** \((\nu)\) - the number of waves passing a certain point over a unit of time (units: \(s^{-1} = \text{Hz}\))
- **Amplitude** - height of the wave measured from the axis of propagation, a measure of intensity

\[
\lambda \times \nu = c
\]

Where \(c\) is the speed of light
\(c = 3.00 \times 10^8 \, \text{m/s}\)

*Mycobacterium tuberculosis*, the organism that causes tuberculosis, can be completely destroyed by irradiation of UV light with a wavelength of 254 nm. What is the frequency of this radiation?
Light and energy

- How is it that your car heats up in the summer?
- Light is wave-like and... has energy.

- Max Planck – electromagnetic radiation can be viewed as a stream of tiny packets of energy called photons.

- The energy of a photon is dependent on the radiation’s frequency.

Einstein and Planck

- Light has two properties
  - Wave-like
  - Particle-like

- The “particles” are called photons, which are packets of energy.
The relationship…

\[ E_{\text{photon}} = h \nu_{\text{photon}} \]

Planck’s Constant: \( h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \)

Intensity and Energy

- Intensity and energy are two different measurements.
- Energy is related to the frequency of a photon.
- Intensity is related to the number of photons.

Calculate the energy of a mole of photons of blue light (4.00 \( \times \) 10\(^2\) nm)
7.2 Atomic Line Spectra

- **Continuous spectrum**: a continuous, unbroken distribution of light of all colors
  - A rainbow after summer shower
  - Light reflecting off of water droplets
- **Atomic emission spectrum**: a series of individual lines that are observed when a specific element is excited using an electric discharge. (AKA: line spectrum)

**Energy and Atoms**

- **Ground state**: lowest energy state of an atom.
- **Excited state**: when an atom *absorbs* a photon
- **Energy level diagram**: depicts the changes in energy of an atom
- When an atom *emits* a photon (or radiates heat), it returns to the ground state.
- $\Delta E = \pm \hbar \nu_{\text{photon}}$
Emission Spectra

- Where are the lines coming from?
- Excited atoms are emitting photons to relax back to the ground state.
- When excited atoms emit photons, the frequencies of the photon are specific.
- An emission spectrum plots the intensity of light as a function of frequency.

Quantized Energy

- It turns out that atoms can only absorb and emit radiation of specific energies (frequencies).
- Because the values are restricted, the energy is said to be quantized → only specific values are allowed.
- WHY?
- Because when photons are absorbed (or emitted), the electrons in an atom are absorbing (or emitting) the energy.
• An electron can only have energy that corresponds to the energy levels in an atom.
• Therefore, the energy of the electron is quantized, discrete.

7.3 Electrons have properties of both particles and waves
• Each electron has the same mass and charge
• But, inside an atom, electrons also behave as waves.
• DeBroglie proposed a relationship between the electron as a particle and the electron as a wave.

\[ \lambda_{\text{particle}} = \frac{h}{mv} \]

Where \( m \) is mass and \( v \) is velocity
• Suggests that every moving thing has a wavelength associated with it.

So, every moving object is like a particle and like a wave?
• Yes, but heavy objects (like your book) have extremely short wavelengths.
• The waves of radiation that are emitted are so close together that they go unnoticed.
• But, small light particles (like electrons) have much longer wavelengths, therefore their wave-like properties become important.
How do we give the position of an electron if it is wave-like?

1. A particle occupies a particular location, but a wave has no exact position.
2. Because of their wave-like properties, electrons are always spread out in space.
3. As a result, the position of an electron cannot be precisely defined.
4. Therefore, electrons are delocalized, rather than pinpointed.

The Heisenberg Uncertainty Principle – the more accurately we know position, the more uncertain we are about motion, and vice versa.

Quantum Numbers

• Schrödinger (1926) developed an equation that describes the wave-like properties of electrons in atoms.

• Solutions to the equation identify a “probable location” of the electrons in an atom, not an exact one.

• Remember you can’t pinpoint it because the electron is constantly moving.

Quantum Numbers

• The cloud of electrons that orbits the nucleus are referred to as orbitals.

• Each orbital is given a number and a letter designation.

• The number is called the principal energy level, the higher the number, the higher in energy the orbital. The number tells the energy level, the size of the orbital and the distance from the nucleus.

• The letter tells us what the orbital looks like, its shape: s, p, d or f.
Principal Quantum Number

- \( n = 1, 2, 3 \ldots \) to infinity
- Describes the energy of the electron and the average distance from the nucleus.
- As \( n \) increases, so does the energy of the electron, and the average distance from the nucleus.
- All orbitals that have the same value of \( n \) are said to be in the same shell.

Secondary Quantum Number

- Divides the orbitals into subshells.
- \( l = 0, 1, 2, 3, \ldots, (n-1) \)
- The value of \( l \) corresponds to an orbital shape
- If \( n = 2 \) and \( l = 1 \), we represent it by writing 2p
- What happens if \( l > 3 \)?

<table>
<thead>
<tr>
<th>Value of ( l )</th>
<th>Subshell Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
</tr>
<tr>
<td>1</td>
<td>p</td>
</tr>
<tr>
<td>2</td>
<td>d</td>
</tr>
<tr>
<td>3</td>
<td>f</td>
</tr>
</tbody>
</table>

Magnetic Quantum Number

- Orbitals described by \( l \) can have direction (see picture)
- Therefore, orbitals must have their orientation described
- Which direction are they facing?
- It affects where the electron is probably located.
- \( m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l \)
7.4 Electron spin: spin quantum number

- An electron also has magnetism associated with a property called spin.
- Just as magnetism is directional, so is spin.
- Electron spins have two orientations
- Possible values: $m_s = +\frac{1}{2}$ (up, clockwise) and $-\frac{1}{2}$ (down, counterclockwise)

When $n = 3$, list all valid sets of quantum numbers.

For a 4s orbital, what are the possible values of $n$, $l$, $m_l$, and $m_s$?
For a 4f orbital, what are the possible values of \( n \), \( l \), \( m_l \) and \( m_s \)?

State which of the following cannot exist according to the quantum theory and explain why: 2s, 2d, 3p, 3f, 4f, and 5s

<table>
<thead>
<tr>
<th>Value of ( n )</th>
<th>Value of ( l )</th>
<th>Values of ( m_l )</th>
<th>Subshell</th>
<th>Number of Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1s</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>(-1, 0, 1)</td>
<td>2s</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>(-1, 0, 1)</td>
<td>3s</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>(-1, 0, 1)</td>
<td>(-1, 0, 1)</td>
<td>4s</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>(-1, 0, 1)</td>
<td>4p</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(-1, 0, 1)</td>
<td>4d</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>(-1, 0, 1)</td>
<td>4f</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>(-1, 0, 1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.7 Shapes and Sizes of Orbitals

- Orbitals get larger as the principle quantum number $n$ increases.
- Nodes, or regions of zero electron density, appear beginning with the 2s orbital.

$p$-orbitals

- $p$ orbitals are quite different from $s$ orbitals
- They possess a nodal plane which includes the nucleus and separates the “lobes” of high probability.

$d$ orbitals

- The shape and orientation of $d$ orbitals are more complicated than for $p$ orbitals
- Shape and directional properties of the five $d$ orbitals in a $d$ subshell.
- The $f$ orbitals are even more complex than the $d$ orbitals
7.5 Electron Configurations

- **Electron configuration** – the most stable distribution of electrons among the orbitals of an atom
- Also called electronic structure.
- Two methods for representing electrons in an atom:
  - Orbital Diagrams (draw pictures)
  - Electron configuration (use numbers and letters)
- How do we place the electrons?

Pauli Exclusion Principle

- In general, most systems in nature tend to form a stable state.
- So, we might expect all electrons to be in the most stable orbital.
- NOT the case! Why?
- **Pauli Exclusion Principle:** no two electrons in the same atom can have identical values for all four of their quantum numbers ($n, l, m_l$, and $m_s$)
- So, this means the maximum number of electrons in any orbital is two and they must have opposite spin.
- Electrons in the same orbital with opposite spin are said to be **paired**.

The Aufbau Principle

- But, we still want the electrons in the most stable state possible.
- Most stable --- electrons occupy lowest energy orbitals possible.
- The _ground state_ of an atom is the most stable arrangement of its electrons.
- **Aufbau principle:** we place electrons in orbitals starting with the lowest energy orbital following Pauli Exclusion Principle.
Rules of Ground-State Electron Configuration

1. Each electron in an atom occupies the most stable available orbital. (Aufbau)
2. No two electrons can have identical quantum numbers. (Pauli)
3. Orbital capacities are as follows:
   - $s$: 2 electrons, $p$: 6 electrons
   - $d$: 10 electrons, $f$: 14 electrons
4. The higher the values of $n$, the less stable the orbital.
5. For equal $n$, the higher the value of $l$, the less stable the orbital.

Hund’s Rule

- All three are possible, but are they probable?
- **Hund’s Rule**: The most stable configuration is the one with the maximum number of unpaired electrons.
Electrons and Magnets

- Remember, electrons behave as magnets.

- Substances with unpaired electrons are slightly attracted to a magnet and are called **paramagnetic**.

- Substances in which all electrons are paired are called **diamagnetic**.

The periodic table is our friend!
(7.6 Electron configurations explain the periodic table.)
Write the electron configurations for the following atoms:

- C
- F
- S
- Kr
- Ti
- Zn

Electron Accessibility

- The chemical properties of an atom are determined by the electrons that are easily accessible to other atoms.
- An electron is spatially accessible when it occupies one of the largest orbitals of an atom.
- An electron is energetically accessible when it occupies one of the least stable occupied orbitals of the atom.
- Accessible electrons are called valence electrons.
Chapter 7

Valence Electrons vs. Core Electrons

• Valence electrons participate in chemical reactions.
• Core electrons do not.
• *Valence electrons are the ones in the orbitals with the largest value of n plus those in partially filled d and f orbitals.*
• Electrons with lower n values are core electrons.
• How can you quickly determine the number of valence electrons?

Noble Gas Configuration

• As the atomic number increases, so does the number of electrons.
• The electron configuration can get quite lengthy….how can we make it more compact?
• Noble Gas Configuration — specify the noble gas before the element and then build the remaining portion of the electron configuration according to Aufbau.

– Na: 1s²2s²2p⁶3s¹
– Na: [Ne]3s¹

Exceptions…

• Orbitals are filled according to the periodic table.
• However, some elements are bound to have configurations that don’t match the regular progression.
• In the first 40 elements, there are only two exceptions: Cr and Cu
• What would you expect them to look like?
What is the cause?

- **Near-Degenerate Orbitals:** orbitals with nearly the same energy.
- Because the orbitals are so close in energy, it is possible for an electron to be “borrowed” and promoted to the higher energy orbital.
- More common above 40 as energy levels are closer together.

---

Depict the electron configuration and noble gas configuration for the following atoms or ions. Identify the number of valence electrons and determine whether they are paramagnetic or diamagnetic.

- Mg
- Cu
- Se
- Ga
- Mn
- I
- Fe
Defense in Basketball

- What is the purpose?

- Which is a better situation for the offense?
  - A one-on-one fast break
  - A one-on-four fast break

- Electrons do a similar thing.

- The core electrons “defend the nucleus” from the valence electrons.

- In chemistry, we call this screening/shielding (not defense—that would be too simple).

Effective Nuclear Charge, $Z_{\text{eff}}$

- The nuclear charge experienced by a particular electron in a multi-electron atom. (the pull towards the nucleus)

- What does this mean?
  - The charge an electron feels is dependent on the distance from the nucleus and the presence of core electrons(screening).
  - $Z_{\text{eff}}$ just gives it a number.

- $Z_{\text{eff}}$ decreases as you increases $n$
  - Electrons further away from the nucleus have a lower $Z_{\text{eff}}$.

Atomic Properties and Trends

- Atomic Size
  - Distance between center of nucleus and outer electron shell

- Ionization Energy
  - Energy required to remove an electron from an atom or ion in the gas phase
Atomic Size

- For the main group elements, the atomic radius of atoms increases going to the left and down on the periodic table.
  - Going down a group, n increases
    - so adding extra shells, thus the atoms are larger
  - Going across a period, n is constant, adding electrons, protons and neutrons, result is an increase in $Z_{\text{eff}}$
    - Nucleus has stronger pull on the outer electrons, thus the atoms are smaller

Ion Sizes

- Similar to atomic radii, ions also follow trends
  - Follow similar trend as atomic, except:
    - The radius of an anion is always larger than the corresponding atom $F^- > F$
    - The radius of a cation is always smaller than the corresponding atom $Li^+ < Li$
Practice Problem

• Predict which is larger: Si or Cl, S or Se, Mo or Ag, Cl or Cl⁻

Ionization Energy

• For the main group elements, the IE increases going up and across to the right of the periodic table.
  – Going down a group, n increases
    • so adding extra shells, thus the atoms are larger, easier to remove an electron, thus IE decreases
  – Going across a period, n is constant, adding electrons in the same shell, but also adding protons, result is an increase in Z_{eff}
    • Nucleus has stronger pull on the outer electrons, harder to remove
Let’s do another problem…

- Place in order of increasing ionization energy

   C
   O
   Si