Chapter 6. Electronic Structure of Atoms

Lecture Outline

6.1 The Wave Nature of Light

- The **electronic structure** of an atom refers to the arrangement of electrons.
- Visible light is a form of **electromagnetic radiation**, or *radiant energy*.
- Radiation carries energy through space.
- Electromagnetic radiation is characterized by its wave nature.
- All waves have a characteristic **wavelength**, $\subseteq$(lambda), and amplitude, *A*.
- The **frequency**, $\not\in$ (nu), of a wave is the number of cycles that pass a point in one second.
  - The units of $\not\in$ are Hertz (1 Hz = 1 s^{-1}).
- The speed of a wave is given by its frequency multiplied by its wavelength.
  - For light, speed is $c = \subseteq\not\in$.
  - Electromagnetic radiation moves through a vacuum with a speed of 3.00 x 10^8 m/s.
- Electromagnetic waves have characteristic wavelengths and frequencies.
- The *electromagnetic spectrum* is a display of the various types of electromagnetic radiation arranged in order of increasing wavelength.
  - Example: visible radiation has wavelengths between 400 nm (violet) and 750 nm (red).

6.2 Quantized Energy and Photons

- Some phenomena cannot be explained using a wave model of light.
  - *Blackbody radiation* is the emission of light from hot objects.
  - The *photoelectric effect* is the emission of electrons from metal surfaces on which light shines.
  - *Emission spectra* are the emissions of light from electronically excited gas atoms.

Hot Objects and the Quantization of Energy

- Heated solids emit radiation (blackbody radiation)
  - The wavelength distribution depends on the temperature (i.e., "red hot" objects are cooler than "white hot" objects).
- Planck investigated black body radiation.
  - He proposed that energy can only be absorbed or released from atoms in certain amounts.
  - These amounts are called quanta.
  - A **quantum** is the smallest amount of energy that can be emitted or absorbed as electromagnetic radiation.
  - The relationship between energy and frequency is:

$$E = h\nu$$

    - where *h* is **Planck's constant** (6.626 x 10^{-34} J-s).
- To understand quantization, consider the notes produced by a violin (continuous) and a piano (quantized).
  - A violin can produce any note when the fingers are placed at an appropriate spot on the bridge.
  - A piano can only produce notes corresponding to the keys on the keyboard.

The Photoelectric Effect and Photons

- The **photoelectric effect** provides evidence for the particle nature of light.
  - It also provides evidence for quantization.
- Einstein assumed that light traveled in energy packets called **photons**.
  - The energy of one photon is $E = h\not\in$.
- Light shining on the surface of a metal can cause electrons to be ejected from the metal.
  - The electrons will only be ejected if the photons have sufficient energy (*work function*):

    - Below the threshold frequency no electrons are ejected.
    - Above the threshold frequency, the excess energy appears as the kinetic energy of the ejected electrons.
- Light has wave-like AND particle-like properties.

6.3 Line Spectra and the Bohr Model

Line Spectra

- Radiation composed of only one wavelength is called *monochromatic*.
- Radiation that spans a whole array of different wavelengths is called *continuous*.
- When radiation from a light source, such as a light bulb, is separated into its different wavelength components, a **spectrum** is produced.
  - White light can be separated into a **continuous spectrum** of colors.
    - A rainbow is a continuous spectrum of light produced by the dispersal of sunlight by raindrops or mist.
  - Note that on the continuous spectrum there are no dark spots, which would correspond to different lines.
- Not all radiation is continuous.
  - A gas placed in a partially evacuated tube and subjected to a high voltage produces single colors of light.
  - The spectrum that we see contains radiation of only specific wavelengths; this is called a **line spectrum**.

Bohr's Model

- Rutherford assumed that electrons orbited the nucleus analogous to planets orbiting the sun.
  - However, a charged particle moving in a circular path should lose energy.
  - This means that the atom should be unstable according to Rutherford's theory.
- Bohr noted the line spectra of certain elements and assumed that electrons were confined to specific energy states. These were called orbits.
- Bohr's model is based on three postulates:
  - Only orbits of specific radii, corresponding to certain definite energies, are permitted for electrons in an atom.
  - An electron in a permitted orbit has a specific energy and is an "allowed" energy state.
  - Energy is only emitted or absorbed by an electron as it moves from one allowed energy state to another.
    - The energy is gained or lost as a photon.

The Energy States of the Hydrogen Atom

- Colors from excited gases arise because electrons move between energy states in the atom.
- Since the energy states are quantized, the light emitted from excited atoms must be quantized and appear as line spectra.
- Bohr showed mathematically that

$$E = -(hcR_{\mathrm{H}})\left(\frac{1}{n^2}\right) = (-2.18x10^{-18}\,J)\left(\frac{1}{n^2}\right)$$

  - where n is the *principal quantum number* (i.e., n = 1, 2, 3, …. …) and R_{H} is the Rydberg constant.
  - The product $hcR_{\mathrm{H}} = 2.18 \times 10^{-18}$ J.
- The first orbit in the Bohr model has n = 1 and is closest to the nucleus.
- The furthest orbit in the Bohr model has n □ … and corresponds to E = 0.
- Electrons in the Bohr model can only move between orbits by absorbing and emitting energy in quanta ($E = h\nu$).
  - The **ground state** = the lowest energy state.

  - An electron in a higher energy state is said to be in an **excited state**.
- The amount of energy absorbed or emitted by moving between states is given by

$$\Delta E = E_{\mathrm{f}} - E_{\mathrm{i}} = h\nu = 2.18x10^{-18}\,J\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Limitations of the Bohr Model

- The Bohr Model has several limitations:
  - It cannot explain the spectra of atoms other than hydrogen.
  - Electrons do not move about the nucleus in circular orbits.
- However, the model introduces two important ideas:
  - The energy of an electron is quantized: electrons exist only in certain energy levels described by quantum numbers.
  - Energy gain or loss is involved in moving an electron from one energy level to another.

6.4 The Wave Behavior of Matter

- Knowing that light has a particle nature, it seems reasonable to ask whether matter has a wave nature.
- This question was answered by Louis deBroglie.
- Using Einstein's and Planck's equations, deBroglie derived:

$$\lambda = h/mv$$

- The **momentum**, mv, is a particle property, whereas λ is a wave property.
  - **Matter waves** is the term used to describe wave characteristics of material particles.
  - Therefore, in one equation deBroglie summarized the concepts of waves and particles as they apply to low-mass, high-speed objects.
  - As a consequence of deBroglie's discovery, we now have techniques such as X-ray diffraction and electron microscopy to study small objects.

The Uncertainty Principle

- **Heisenberg's uncertainty principle**: we cannot determine the *exact* position, direction of motion, and speed of subatomic particles simultaneously.
- For electrons: we cannot determine their momentum and position simultaneously.

6.5 Quantum Mechanics and Atomic Orbitals

- Schrödinger proposed an equation containing both wave and particle terms.
- Solving the equation leads to **wave functions**, ψ
- The wave function describes the electron's matter wave.
  - The square of the wave function, ψ^2, gives the probability of finding the electron.
  - That is, ψ^2 gives the electron density for the atom.
    - ψ^2 is called the **probability density**.
- **Electron density** is another way of expressing probability.
  - A region of high electron density is one where there is a high probability of finding an electron.

Orbitals and Quantum Numbers

- If we solve the Schrödinger equation we get wave functions and energies for the wave functions.
- We call ψ **orbitals**.
- Schrödinger's equation requires three quantum numbers:
- *Principal quantum number, n*. This is the same as Bohr's *n*.

  - As *n* becomes larger, the atom becomes larger and the electron is further from the nucleus.
- *Azimuthal quantum number, l*. This quantum number depends on the value of *n*.

  - The values of l begin at 0 and increase to $n - 1$.
  - We usually use letters for l (*s*, *p*, *d* and *f* for $l = 0$, 1, 2, and 3).
  - This quantum number defines the shape of the orbital.
- Magnetic quantum number, m_l.
  - This quantum number depends on l.
  - The magnetic quantum number has integer values between $-l$ and $+l$.
  - Magnetic quantum numbers give the three-dimensional orientation of each orbital.
- A collection of orbitals with the same value of n is called an **electron shell**.
  - A set of orbitals with the same n and l is called a **subshell**.
    - Each subshell is designated by a number and a letter.
    - For example, 3*p* orbitals have $n = 3$ and $l = 1$.
- Orbitals can be ranked in terms of energy to yield an Aufbau diagram.
  - Note that this Aufbau diagram is for a single electron system.
- As n increases note that the spacing between energy levels becomes smaller.

6.6 Representations of Orbitals

The *s* Orbitals

- All *s* orbitals are spherical.
- As n increases, the *s* orbitals get larger.
- As n increases, the number of **nodes** increases.
  - A node is a region in space where the probability of finding an electron is zero.
    - $\psi^2 = 0$ at a node.
  - For an *s* orbital the number of nodes is given by $n - 1$.
- We can plot a curve of *radial probability density* vs. distance (r) from the nucleus.
  - This curve is the **radial probability function** for the orbital.

The *p* Orbitals

- There are three *p* orbitals: p_x, p_y and p_z.
  - The three *p* orbitals lie along the *x*-, *y*-, and *z*-axes of a Cartesian system.
  - The letters correspond to allowed the values of m_l of -1, 0, and $+1$.
- The orbitals are dumbbell shaped; each has two *lobes*.
- As n increases, the *p* orbitals get larger.
- All *p* orbitals have a node at the nucleus.

The *d* and *f* Orbitals

- There are five *d* and seven f orbitals.
  - Three of the *d* orbitals lie in a plane bisecting the *x*-, *y*-, and *z*-axes.
  - Two of the *d* orbitals lie in a plane aligned along the *x*-, *y*-, and *z*-axes.
  - Four of the *d* orbitals have four lobes each.
  - One *d* orbital has two lobes and a collar.

6.7 Many-Electron Atoms

Orbitals and Their Energies

- In a many-electron atom, for a given value of n,
  - the energy of an orbital increases with increasing value of l.
- Orbitals of the same energy are said to be **degenerate**.
- For n □ 2, the *s* and *p* orbitals are no longer degenerate.
- Therefore, the Aufbau diagram looks slightly different for many-electron systems.

Electron Spin and the Pauli Exclusion Principle

- Line spectra of many-electron atoms show each line as a closely spaced pair of lines.

- Stern and Gerlach designed an experiment to determine why.
  - A beam of atoms was passed through a slit and into a magnetic field and the atoms were then detected.
  - Two spots were found: one with the electrons spinning in one direction and one with the electrons spinning in the opposite direction.
- Since **electron spin** (electron as a tiny sphere spinning on its own axis) is quantized,
  - we define m_s = **spin magnetic quantum number** = ± ½.
- **Pauli's exclusion principle** states that no two electrons can have the same set of four quantum numbers.
  - Therefore, two electrons in the same orbital must have opposite spins.

6.8 Electron Configurations

- **Electron configurations** tell us how the electrons are distributed among the various orbitals of an atom.
- The most stable configuration, or ground state, is that in which the electrons are in the lowest possible energy state.
- When writing ground-state electronic configurations:
  - electrons fill orbitals in order of increasing energy with no more than two electrons per orbital.
  - no two electrons can fill one orbital with the same spin (Pauli).
  - for degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron.
  - How do we show spin?
    - An arrow pointing upwards has m_s = + ½ (spin up).
    - An arrow pointing downwards has m_s = – ½ (spin down).

Hund's Rule

- **Hund's rule**: for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.
  - Thus, electrons fill each orbital singly with their spins parallel before any orbital gets a second electron.
  - By placing electrons in different orbitals, electron-electron repulsions are minimized.

Condensed Electron Configurations

- Electron configurations may be written using a shorthand notation (*condensed electron configuration*):
  - Write the **valence electrons** explicitly.
    - **Valence electrons** are electrons in the outer shell.
      - These electrons are gained and lost in reactions.
  - Write the **core electrons** corresponding to the filled noble gas in square brackets.
    - Core electrons are electrons in the inner shells.
      - These are generally not involved in bonding.
  - Example:
    - P is $\mathbf{1s^2 2s^2 2p^6} 3s^2 3p^3$,
    - but **Ne** is $\mathbf{1s^2 2s^2 2p^6}$.
    - Therefore, P is **[Ne]**$3s^2 3p^3$.

Transition Metals

- After Ar the *d* orbitals begin to fill.
- After the 3*d* orbitals are full the 4*p* orbitals begin to fill.
- The ten elements between Ti and Zn are called the **transition metals**, or **transition elements**.
- The 4*f* orbitals begin to fill with Ce.
  - Note: The electron configuration of La is $[Xe]6s^2 5d^1$.

- The 4*f* orbitals are filled for the elements Ce – Lu, which are called **lanthanide elements** (or rare earth elements).
- The 5*f* orbitals are filled for the elements Th – Lr, which are called **actinide elements**.
  - Most actinides are not found in nature.

6.9 Electron Configurations and the Periodic Table

- The periodic table can be used as a guide for electron configurations.
- The period number is the value of *n*.
- Groups 1A and 2A have their *s* orbitals being filled.
- Groups 3A – 8A have their *p* orbitals being filled.
- The *s*-block and *p*-block of the periodic table contain the representative, or main-group, elements.
- Groups 3B – 2B have their *d* orbitals being filled.
- The lanthanides and actinides have their *f* orbitals being filled.
  - The actinides and lanthanide elements are collectively referred to as the ***f*-block metals**.
- Note that the 3*d* orbitals fill after the 4*s* orbital. Similarly, the 4*f* orbitals fill after the 5*d* orbitals.

Anomalous Electron Configurations

- There are many elements that appear to violate the electron configuration guidelines.
  - Examples:
    - Chromium is $[Ar]3d^5 4s^1$ instead of $[Ar]3d^4 4s^2$.
    - Copper is $[Ar]3d^{10} 4s^1$ instead of $[Ar]3d^9 4s^2$.