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, lambda, and amplitude, A.
- The frequency, nu, of a wave is the number of cycles that pass a point in one second.
  - The units of \( \nu \) 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 \( c = \) .
  - 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.

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1 Figure 6.2 from Transparency Pack
2 Figure 6.4 from Transparency Pack
3 “Electromagnetic Spectrum” Activity from Instructor’s Resource CD/DVD
4 Table 6.1 from Transparency Pack
5 “Blackbody Radiation” VCL Simulation from Instructor’s Resource CD/DVD
• 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 \( \times \) 10\(^{-34}\) J·s).
  • To understand quantization, consider the notes produced by a violin (continuous) and 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 \( E = h \nu \).
  • 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.

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6 **September 2004** issue of *Scientific American* from Further Readings
7 “Photoelectric Effect” VCL Simulation from Instructor’s Resource CD/DVD
8 “Photoelectric Effect” Animation from Instructor’s Resource CD/DVD
9 Figure 6.7 from Transparency Pack
10 “Put Body to Them!” from Further Readings
11 Figure 6.10 from Transparency Pack
12 “Flame Tests for Metals” Movie from Instructor’s Resource CD/DVD
13 “The Rydberg Equation” VCL Simulation from Instructor’s Resource CD/DVD
14 “Atomic Emission Spectra” VCL Simulation from Instructor’s Resource CD/DVD
15 Figure 6.12 from Transparency Pack
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**\(^{16,17}\)

- 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**\(^{18,19,20}\)

- 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
  - where \( n \) is the principal quantum number (i.e., \( n = 1, 2, 3, \ldots \) ) and \( R_H \) is the Rydberg constant.
    - The product \( hcR_H = 2.18 \times 10^{-18} \) 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 (\( E = h \)).
  - 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

**Limitations of the Bohr Model**\(^{21,22}\)

- The Bohr Model \( E = E_f - E_i = h\nu = 2.18 \times 10^{-18} \) J \( \frac{1}{n_f^2} - \frac{1}{n_i^2} \) has several limitations:

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\(^{16}\) “Presenting the Bohr Atom” from Further Readings

\(^{17}\) “Bohr Model” Activity from Instructor’s Resource CD/DVD

\(^{18}\) “Getting the Numbers Right—The Lonely Struggle of Rydberg” from Further Readings

\(^{19}\) Figure 6.13 from Transparency Pack

\(^{20}\) “Suitable Light Sources and Spectroscopes for Student Observation of Emission Spectra in Lecture Halls” from Further Readings

\(^{21}\) “Neils Bohr” from Further Readings

\(^{22}\) “100 Years of Quantum Mysteries” from Further Readings
• 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 de Broglie.
• Using Einstein’s and Planck’s equations, de Broglie derived: \[ \frac{h}{m} \]
• The momentum, \( m \) is a particle property, whereas \( \frac{h}{m} \) is a wave property.
• Matter waves is the term used to describe wave characteristics of material particles.
• Therefore, in one equation de Broglie summarized the concepts of waves and particles as they apply to low-mass, high-speed objects.
• As a consequence of de Broglie’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.
• The wave function describes the electron’s matter wave.
• The square of the wave function, \( \psi^2 \), gives the probability of finding the electron.
• That is, \( \psi^2 \) gives the electron density for the atom.
• \( \psi^2 \) 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

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23 “On a Relation between the Heisenberg and de Broglie Principles” from Further Readings
24 “Heisenberg Uncertainty Principle” VCL Simulation from Instructor’s Resource CD/DVD
25 “Introducing the Uncertainty Principle Using Diffraction of Light Waves” from Further Readings
26 “Perspectives on the Uncertainty Principle and Quantum Reality” from Further Readings
27 Figure 6.16 from Transparency Pack
28 “A Student’s Travels, Close Dancing, Bathtubs, and the Shopping Mall: More Analogies in Teaching Introductory Chemistry” from Further Readings
29 “The Mole, the Periodic Table and Quantum Numbers: An Introductory Trio” from Further Readings
30 “Quantum Numbers” Activity from Instructor’s Resource CD/DVD
If we solve the Schrödinger equation we get wave functions and energies for the wave functions.

We call 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, \( 3p \) orbitals have \( n = 3 \) and \( l = 1 \).

Orbitals can be ranked in terms of energy to yield an Aufbau diagram.

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.
  - \( \psi = 0 \) 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 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 $n \geq 2$, 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 $= \frac{1}{2}$.
• 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 \( m_s = +\frac{1}{2} \) (spin up).
  - An arrow pointing downwards has \( m_s = -\frac{1}{2} \) (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 \( 1s^22s^22p^63s^23p^3 \).
    - but Ne is \( 1s^22s^22p^6 \).

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45 “The Magnetic Eye” from Further Readings
46 “Demystifying Introductory Chemistry; Part 1. Electron Configurations from Experiment” from Further Readings
47 “Quantum Analogies on Campus” from Further Readings
48 “Housing Electrons: Relating Quantum Numbers, Energy Levels, and Electron Configurations” from Further Readings
49 “Pictorial Analogies VII: Quantum Numbers and Orbitals” from Further Readings
50 “The Quantum Shoe Store and Electron Structure” from Further Readings
51 Table 6.3 from Transparency Pack
52 “Electron Configuration” Activity from Instructor’s Resource CD/DVD
53 “Some Analogies for Teaching Atomic Structure at the High School Level” from Further Readings
54 “Ionization Energies, Parallel Spins, and the Stability of Half-Filled Shells” from Further Readings
55 “The Noble Gas Configuration—Not the Driving Force but the Rule of the Game in Chemistry” from Further Readings
Therefore, P is [Ne]3s^23p^3.

Transition Metals
• After Ar the d orbitals begin to fill.
• After the 3d orbitals are full the 4p orbitals begin to fill.
• The ten elements between Ti and Zn are called the transition metals, or transition elements.
• The 4f orbitals begin to fill with Ce.
  • Note: The electron configuration of La is [Xe]6s^25d^1.
• The 4f orbitals are filled for the elements Ce – Lu, which are called lanthanide elements (or rare earth elements).
• The 5f 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 3d orbitals fill after the 4s orbital. Similarly, the 4f orbitals fill after the 5d orbitals.

Anomalous Electron Configurations
• There are many elements that appear to violate the electron configuration guidelines.
  • Examples:
    • Chromium is [Ar]3d^54s^1 instead of [Ar]3d^44s^2.
    • Copper is [Ar]3d^104s^1 instead of [Ar]3d^94s^2.

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56 Figure 6.29 from Transparency Pack
57 “The Periodic Table as a Mnemonic Device for Writing Electronic Configurations” from Further Readings
58 “The Periodic Table and Electron Configurations” from Further Readings
59 Figure 6.30 from Transparency Pack
60 “Periodic Table” Activity from Instructor’s Resource CD/DVD
Further Readings:

2. The September 2004 issue of *Scientific American* is a special issue with numerous articles dealing with how Einstein’s ideas reshaped the world.


Live Demonstrations


\[ E = E_i + \Delta E, \Delta E = h\nu \]

\[ 2.18 \times 10^{-18} \text{ J} \]

\[ \frac{1}{n^2} \]

\[ \frac{1}{n^2} \]