

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.

$$\Delta X * \Delta(mV) \geq \frac{h}{4\pi}$$

Do a calculation.

$$\Delta X \geq \frac{h}{4\pi m \Delta V} = \frac{6.626 \times 10^{-34} \text{ js}}{4\pi \cdot 9.11 \times 10^{-31} \text{ kg} \cdot \Delta V} = \frac{5.8 \times 10^{-5}}{\Delta V} \text{ meters}$$

$$\Delta V = 1\% \text{ error in velocity} = 5 \times 10^4 \text{ m/s}$$

$$\Delta X = 1 \times 10^{-9} \text{ m or } 10 \text{ \AA}$$

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**.

Show computer animation

- 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.

Dorm Room Analogy

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.**
- **Angular momentum 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).
Usually we refer to the s , p , d and f orbitals.
- **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 $+l$.
- There are $(2l+1)$ possible values of m_l . • For example, for $l = 1$, there

are $(2 \times 1 + 1) = 3$ values of m_l : 0, +1, and -1.

- Consequently, for $l = 1$, there are 3 orbitals: p_x , p_y and p_z .

- 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**.

- There are n^2 orbitals in a shell described by a the n value.

- For example, for $n = 3$, there are $3^2 = 9$ orbitals.

- 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 $l = 1$.

- There are n types of subshells in a shell described by a the n value.

- For example, for $n = 3$, there are 3 subshells: $3s$, $3p$ and $3d$.

- 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.

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 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.

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**.

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 $m_s = \text{spin magnetic quantum number} = \pm 1/2$.
- **Pauli's exclusion principle** states that no two electrons can have the same set of 4 quantum numbers. • Therefore, two electrons in the same orbital must have opposite spins.

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 $m_s = + 1/2$ (spin up).
 - An arrow pointing downwards has $m_s = - 1/2$ (spin down).
- **Hund's**
 - **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 $1s^2 2s^2 2p^6 3s^2 3p^3$,
- but Ne is $1s^2 2s^2 2p^6$.
- Therefore, P is $[\text{Ne}]3s^2 3p^3$.
- **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 Lanthanides and Actinides**
- The $4f$ orbitals begin to fill with Ce. • Note: The electron configuration of La is $[\text{Xe}]6s^2 5d^1$.
- 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**.
- The actinide elements are radioactive and most are not found in nature.

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.
- In general, for representative elements we do not consider the electrons in completely filled d or f subshells to be valence electrons. ⁵⁵ Figure 6.30 from Transparency Pack ⁵⁶ “The Periodic Table as a Mnemonic Device for Writing Electronic Configurations” from Further Readings ⁵⁷ “The Periodic Table and Electron Configurations” from Further Readings ⁵⁸ Figure 6.31 from Transparency Pack ⁵⁹ “Periodic Table” Activity from Instructor’s Resource CD/DVD

Anomalous Electron Configurations

- There are many elements that appear to violate the electron configuration guidelines.
- Examples:
 - Chromium is $[\text{Ar}]3d^54s^1$ instead of $[\text{Ar}]3d^44s^2$.
 - Copper is $[\text{Ar}]3d^{10}4s^1$ instead of $[\text{Ar}]3d^94s^2$.
- Half-full (d^5) and full (d^{10}) d subshells are particularly stable.