Unit I

Atomic Structure and Periodic table

Introduction to Electronic Configuration

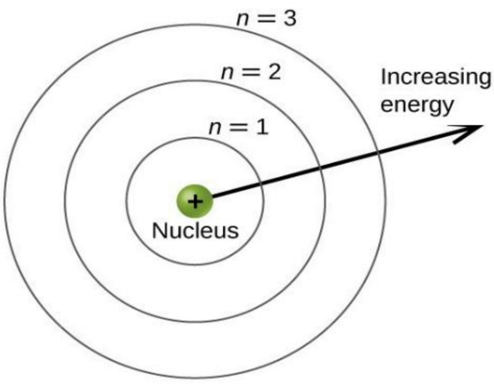
Understanding electronic configuration, the arrangement of electrons in atoms, is essential for unravelling atomic behavior and the nature of chemical reactions. This exploration, crucial in chemistry and physics, involves delving into foundational theories and principles that define how electrons are organized around the nucleus and how they dictate atomic interactions. Beginning with Bohr's model of quantized electron orbits, we venture into quantum mechanics, examining the dual wave-particle nature of electrons, the probabilistic approach introduced by the Heisenberg Uncertainty Principle, and the predictive power of the Schrödinger Equation. The journey encompasses the significance of wave functions and their normalization, detailing how electrons occupy specific orbitals and subshells as per Pauli's Exclusion Principle, Hund's Rule, and the Aufbau Principle. Each of these concepts collectively shapes our understanding of the atomic world, explaining the structure of atoms and the fundamentals of chemical properties and reactions.

1. Bohr Theory

Developed by Niels Bohr in 1913, the Bohr Theory represented a monumental leap in our understanding of atomic structure, bridging the gap between classical physics and the burgeoning field of quantum mechanics. This theory was revolutionary for its time, proposing a model of the atom that was both simple and radically different from the existing models.

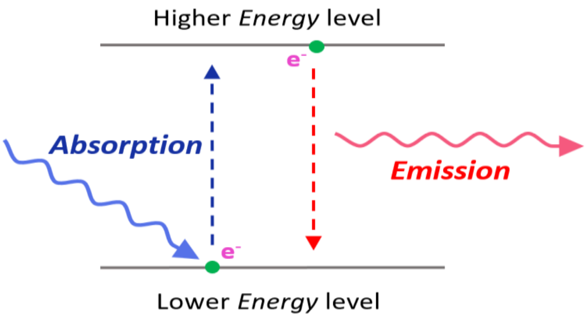
1.1 Core Concepts of Bohr's Theory

1. **Quantized Orbits**: Bohr postulated that electrons orbit the nucleus in specific, fixed paths or shells, each with a defined energy level. Unlike the classical view of electrons moving in any orbit, Bohr's model restricted electrons to these quantized orbits.



2. **Energy Absorption and Emission**: The theory also introduced the idea that electrons could 'jump' between these fixed orbits. When an electron moves to a higher-energy

orbit (further from the nucleus), it absorbs a discrete amount of energy. Conversely, when it returns to a lower-energy orbit, it emits energy, often in the form of light.



1.2 Key Equations

1. **Angular Momentum Quantization**:

$$L = n\left(\frac{h}{2\pi}\right)$$

In this equation, L represents the angular momentum of the electron, n is the principal quantum number (an integer), and h is Planck's constant. This equation implies that the angular momentum of an electron in a Bohr orbit is quantized.

2. **Radius of Electron Orbits**:

$$r_n = \frac{n^2h^2}{4\pi^2 kme^2}$$

r_n denotes the radius of the nth orbit, k is Coulomb's constant, m is the mass of the electron, and e is the electron charge. This formula shows that the orbit radius increases with the square of the principal quantum number.

3. **Energy of Electron Orbits**:

$$E_n = \frac{-2\pi^2k^2me^4}{h^2n^2}$$

This equation calculates the energy of an electron in the nth orbit. The negative sign indicates a bound state, meaning the electron is bound to the nucleus.

1.3 Limitations:

1. **Works Mainly for Hydrogen**: Bohr's theory accurately explains the hydrogen atom but fails to explain more complex atoms that have more than one electron.

2. **Ignores Electron-Electron Interactions**: It doesn't account for the repulsion between multiple electrons in atoms, which affects their behavior and energy levels.
3. **Not Align with Quantum Mechanics**: Bohr's model contradicts the uncertainty principle of quantum mechanics, which states you can't precisely know both the position and momentum of an electron.
4. **Fails to Explain Chemical Bonding**: The theory lacks the ability to describe how atoms bond together to form molecules, a key aspect of chemistry.

2. Dual nature of electrons:

The dual nature of electrons is a key concept in quantum mechanics, indicating that electrons possess both particle-like and wave-like properties. As particles, electrons have specific mass and charge, observable in phenomena like the photoelectric effect. As waves, they show interference and diffraction, evident in experiments like the double-slit experiment.

2.1 Particle Nature of Electrons

Electrons, when viewed as particles, are distinct entities with mass (m) and charge (e). In classical atomic models like Rutherford's and Bohr's, electrons orbit the nucleus similarly to how planets orbit the sun. This particle perspective is crucial in explaining the photoelectric effect, where electrons are ejected from a metal surface upon light (photon) impact. The photoelectric effect can be described by the equation.

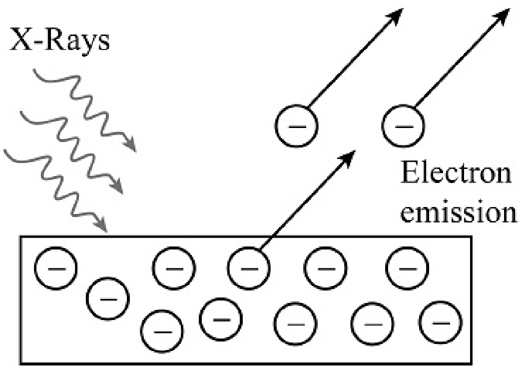


Diagram illustrating the photoelectric effect, showing photons ejecting electrons from a metal.

2.2 Wave Nature of Electrons

The wave nature of electrons, a fundamental aspect of quantum mechanics, is described by Louis de Broglie's hypothesis. This perspective shows that electrons can exhibit wave-like behaviors such as interference and diffraction. The key evidence for this is the double-slit experiment, where electrons create an interference pattern indicative of wave behavior.

De Broglie's wavelength formula $\lambda = \dfrac{h}{p}$

where λ is the wavelength,
h is Planck's constant,
p is the momentum of the electron, quantifies this wave nature.

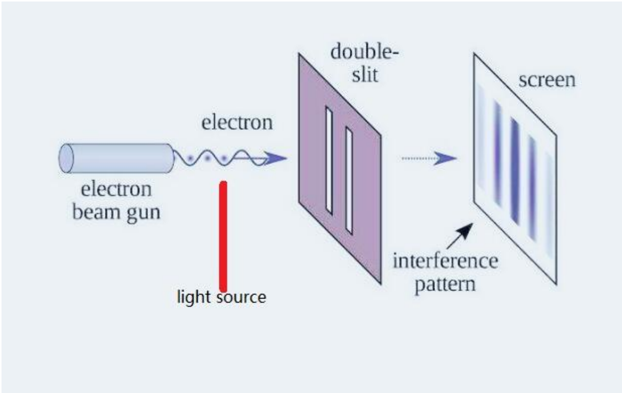


Figure depicting the double-slit experiment with electrons producing an interference pattern would effectively illustrate this concept.

3. Heisenberg uncertainty principle:

The Heisenberg Uncertainty Principle, established by Werner Heisenberg in 1927.

It states that *it is impossible to simultaneously determine with perfect accuracy both the position and momentum of a particle, like an electron*. The more precisely one of these properties is measured, the less precisely the other can be known.

The principle is mathematically represented as $\Delta x \times \Delta p \geq \dfrac{h}{2\pi}$

where:

Δx is the uncertainty in position,
Δp is the uncertainty in momentum,
h is the reduced Planck's constant.

This inequality means that the more accurately we know a particle's position (Δx), the less accurately we can know its momentum (Δp), and vice versa.

4. The Schrodinger equation:

Introduction

The Schrödinger Equation, formulated by Erwin Schrödinger in 1926, is a fundamental equation in quantum mechanics. It describes how the quantum state of a physical system changes over time and space.

The Equation

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0$$

where:

Ψ is the wave function.
m is the mass of the particle.
h is Planck's constant.
E is the total energy of the system.
V is the potential energy within the system.

The term $\frac{8\pi^2 m}{h^2}(E-V)\Psi$ represents the potential and kinetic energy contributions to the equation.

The equation essentially tells us that the total energy of the system is conserved and is a sum of its kinetic and potential energies. It's a key equation in quantum mechanics because it allows us to predict how a quantum system will behave over time.

4.1 Significance of wave functions:

In quantum mechanics, a wave function, written as Ψ, is a formula that tells us a lot about a particle, like where it might be and what it might be doing. Think of it as a set of instructions that gives the probabilities of where a particle, like an electron, could be at any time. When we calculate $|\Psi|^2$ (the square of the wave function), we get these probabilities, showing us where we're most likely to find the particle. Wave functions are important because they help us understand things in the quantum world, like where electrons are in an atom.

4.2 Normalization of wave function:

Normalization of a wave function in quantum mechanics ensures that the wave function accurately reflects the probabilities for a particle's location. It involves adjusting the wave function so that the total probability across all space equals 1. This is mathematically expressed as:

$$\int_{-\infty}^{\infty}|\Psi(x)|^2\, dx=1$$

Here, $\Psi(x)|^2$ is the probability density. The process of normalization ensures that the sum of all probabilities (the area under the probability density curve) equals 1, confirming that the particle exists somewhere in space. This step is crucial for the wave function to give meaningful and valid probabilities.

4.3 Radial and Angular Wave Functions

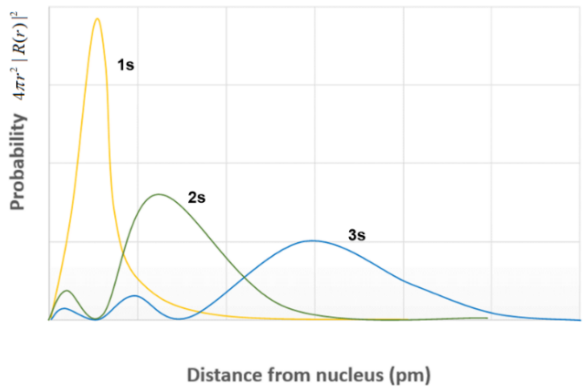
In quantum mechanics, the wave function Ψ for an electron in an atom can be separated into two parts: the radial part and the angular part. This separation is particularly useful in solving the Schrödinger equation for atoms with spherical symmetry, like the hydrogen atom. Radial and angular wave functions are integral for understanding the quantum state of electrons in atoms, dictating the distribution and shape of electron clouds.

4.4 Radial Wave Function

- The radial wave function, $R(r)$, depends only on the distance from the nucleus, denoted by r.
- It describes the probability of finding an electron at a certain distance from the nucleus.
  - The radial part of the wave function for the hydrogen atom is given by:

$$R(r) = R_{nl}(r) = A_{nl} \cdot e^{-\rho/2} \cdot \rho^l \cdot L_{n-l-1}^{2l+1}(\rho)$$

where A_{nl} is a normalization constant, $\rho = \dfrac{2r}{na_0}$, n is the principal quantum number, l is the angular momentum quantum number, a_0 is the Bohr radius, and L are the associated Laguerre polynomials.



4.5 Angular Wave Function

- The angular wave function, $Y(\theta,\phi)$, depends on the direction of the electron's position in spherical coordinates, given by the angles θ (theta) and ϕ (phi).
- It describes the shape of the electron's orbitals.
- The angular wave functions are called spherical harmonics and are given by:

$$Y(\theta,\phi) = Y_{lm}(\theta,\phi) = P_l^m(cos(\theta)) \cdot e^{im\phi}$$

where P_l^m are the associated Legendre polynomials, and m is the magnetic quantum number.

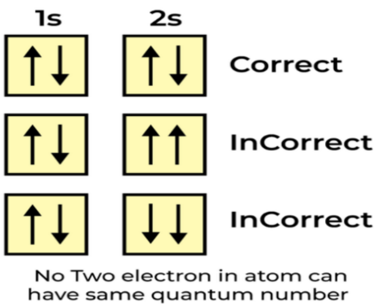
5. Pauli's Exclusion Principle

The Pauli Exclusion Principle, introduced by Wolfgang Pauli in 1925, is a quantum mechanical principle with profound implications in many fields, from atomic to solid-state physics.

Principle Statement

It states that *no two fermions (particles like electrons that have a half-integer spin) can occupy the same quantum state simultaneously*.

In simpler terms, *in an atom, no two electrons can have the same set of quantum numbers.*



The Pauli Exclusion Principle explains the structure of the periodic table and the behavior of electrons in different shells and subshells within an atom.

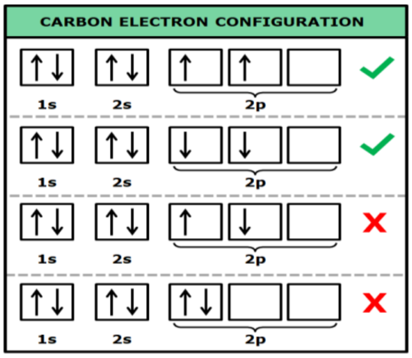
6. Hund's Rule

Hund's Rule, named after Friedrich Hund, is an empirical rule based on observations of atomic spectra. It is used to determine the ground state of an electron configuration for an atom or molecule with one or more open electronic shells.

Rule Statement

Hund's rule states that *for a given electron configuration, the lowest energy is attained when the number of electrons with the same spin is maximized in a set of degenerate orbitals (orbitals with the same energy level, such as the three p-orbitals, five d-orbitals, etc.).* In essence, *electrons will fill an empty orbital before they pair up with another electron in the same orbital.*

This rule helps to predict the electron configurations of atoms, particularly in the subshells.



7. Aufbau Principle

The Aufbau Principle, from the German word "aufbauen" meaning "to build up," is a guideline used to determine the electron configuration of an atom, ion, or molecule. It describes the sequence in which electrons fill subatomic orbitals and thus dictates the ground state of an electron configuration.

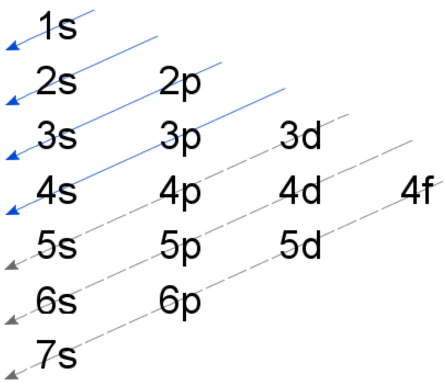
Principle Statement

According to the Aufbau Principle, *electrons are added one by one to the lowest energy orbitals available until all electrons have been placed.*

Energy Level Sequence

The typical order in which subshells are filled is as follows:

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p.



8. Periodicity: Periodic Law and Arrangement of Elements in the Periodic Table

Periodicity in chemistry refers to the recurring trends that are evident in the properties of the elements. It is these patterns that led to the development of the periodic table, a systematic organization of elements.

8.1 Periodic Law

The periodic law is a principle in chemistry that states *the properties of the elements are a periodic function of their atomic numbers.*

This means that when the elements are arranged in order of increasing atomic number, elements with similar properties recur at regular intervals or periods. This periodic recurrence of properties allows the elements to be systematically categorized into the periodic table, where elements with similar characteristics are grouped together, reflecting the periodic nature of their chemical and physical properties.

8.2 Arrangement of Elements

- The periodic table is organized into rows called periods and columns called groups or families. Elements in the same group have similar chemical properties and the same number of valence electrons.
- The table starts with the simplest element, hydrogen, and builds up, adding protons, neutrons, and electrons to create all the other elements.
- The current periodic table has 7 periods and 18 groups, with elements categorized into s, p, d, and f blocks based on their electron configurations according to the Aufbau principle.

8.3 IUPAC Nomenclature and Group Number

The International Union of Pure and Applied Chemistry (IUPAC) is responsible for standardizing chemical nomenclature. This includes the naming of elements, compounds, and the designation of their group numbers on the periodic table.

IUPAC Nomenclature for Groups

- Groups in the periodic table are numbered from 1 to 18 according to IUPAC guidelines. This numbering system reflects the number of valence electrons in the outer shell of the elements within the group, which dictates their chemical behavior.
- For example, Group 1 (also known as the alkali metals) contains elements with one valence electron in their outer shell, while Group 17 (the halogens) contains elements with seven valence electrons.

Group Numbers

- The groups are the columns of the periodic table. Elements within the same group have similar properties due to their similar valence electron configurations.
- The older system of Roman numerals and letters (e.g., Group IIIB) has been largely replaced by the IUPAC 1-18 system for simplicity and clarity.

9. Horizontal, Vertical, and Diagonal Relationships

9.1 Horizontal Relationships

- The horizontal rows in the periodic table are known as periods. As one moves across a period from left to right, the atomic number increases, and the elements show a progression in properties.
- Across a period, elements gradually change from metallic on the left to non-metallic on the right.

9.2 Vertical Relationships

- The vertical columns, as mentioned earlier, are the groups. Elements in the same group exhibit similar chemical and physical properties due to having the same number of electrons in their outermost shell.
- Down a group, elements generally become more metallic, have higher atomic radii, lower ionization energies, and lower electronegativities.

9.3 Diagonal Relationships

- Diagonal relationships refer to similarities between pairs of elements in adjacent groups and periods. For example, lithium (Li) in Group 1 has similar properties to magnesium (Mg) in Group 2, one period below Li.
- These relationships are less pronounced than horizontal and vertical relationships but are important for understanding the gradual change in element properties.

10. General Properties of Atoms and their trends in Periodic Table:

The size of an atom or ion is a fundamental property that influences its chemistry, including bonding, polarity, and reactivity. The atomic size is often described in terms of atomic, ionic, and covalent radii.

10.1 Atomic Radii

- Atomic radius is the distance from the center of the nucleus to the outermost shell of an electron.
- It is not a fixed value because the electron cloud doesn't have a hard boundary, and the size can change depending on the atom's bonding and environment.
- In general, atomic radii increase down a group as additional electron shells are added and decrease across a period due to the increase in the effective nuclear charge pulling electrons closer to the nucleus.

10.2 Ionic Radii

- Ionic radius is the measure of an atom's ion in a crystal lattice. Ions can be either larger or smaller than the parent atoms depending on whether they lose or gain electrons during ion formation.
- Cations (positively charged ions) are typically smaller than their parent atoms due to the loss of an electron shell and increased nuclear charge acting on fewer electrons.
- Anions (negatively charged ions) are typically larger than their parent atoms because the addition of electrons increases electron-electron repulsion in the outer shell.

10.3 Covalent Radii

- Covalent radius refers to the size of an atom that forms part of a single covalent bond - the distance between the nucleus of one atom to the nucleus of the other atom divided by two.
- Covalent radii tend to decrease across a period and increase down a group, like atomic radii trends.

10.4 Trend in Ionization Potential (Ionization Energy)

- Ionization potential, also known as ionization energy, is the energy required to remove an electron from a gaseous atom or ion.
- Across a period: Ionization potential generally increases. This increase is due to the growing effective nuclear charge, which holds the electrons more tightly and requires more energy to remove them.
- Down a group: Ionization potential decreases. The outer electrons are farther from the nucleus and are more easily removed due to increased shielding by inner electrons.

10.5 Trend in Electron Affinity

- Electron affinity is the energy change that occurs when an electron is added to a neutral atom in the gas phase to form a negative ion.
- Across a period: Electron affinity becomes more negative (more energy is released when an electron is added), reflecting the increasing nuclear charge which attracts additional electrons more strongly.
- Down a group: Electron affinity becomes less negative or even positive in some cases. This is due to the increased distance of the outer electrons from the nucleus and the increased electron shielding.

11. Electronegativity

Electronegativity is a chemical property that describes the tendency of an atom to attract electrons towards itself in a chemical bond. It is a key concept in understanding chemical bonding and molecular structure.

Pauling Electronegativity

- Developed by Linus Pauling, this is the most widely used scale for electronegativity.
- Pauling's method is based on bond energies. He noticed that the actual bond energy between two different atoms (A and B) is usually greater than the average of the bond energies of A-A and B-B.
- Pauling electronegativity is calculated using the formula:

$$\chi_A - \chi_B = \sqrt{\Delta_{AB}}$$

- where χ_A and χ_B are the electronegativities of atoms A and B, and Δ_{AB} is the difference in the bond dissociation energy of A-B from the average of A-A and B-B.

- The scale typically ranges from 0.7 (for cesium) to 4.0 (for fluorine).

Mulliken-Jaffe Electronegativity

- Proposed by Robert S. Mulliken, this scale is based on the electron affinity and ionization potential of an atom.
- Mulliken defined electronegativity as the average of an atom's electron affinity (EA) and ionization energy (IE), given by:

$$\chi = \frac{IE + EA}{2}$$

- This approach provides a more physical basis for electronegativity, linking it to measurable atomic properties.

Allred-Rochow Electronegativity

- Developed by A.L. Allred and E.G. Rochow, this scale considers the electrostatic force exerted by the effective nuclear charge on valence electrons.
- The Allred-Rochow electronegativity is given by the equation:

$$\chi = 0.359 \times \frac{Z_{eff}}{r^2} + 0.744$$

where

Z_{eff} is the effective nuclear charge, and r is the covalent radius of the atom in angstroms.

This method emphasizes the role of atomic size and nuclear charge in determining electronegativity.

Trends in Periodic tables:

- Across a period (from left to right), electronegativity generally increases. For example, in the second period, lithium (Li) has a lower electronegativity than fluorine (F).
- Down a group (from top to bottom), electronegativity generally decreases. For instance, in Group 17 (the Halogens), fluorine has the highest electronegativity, while it decreases moving down to iodine and astatine.

12. Trends of Oxidation States and Variable Valency

12.1 Oxidation States

- The oxidation state of an element is a measure of its degree of oxidation or reduction; essentially, it's the hypothetical charge an atom would have if all bonds were ionic.

- Across periods, the range of oxidation states typically increases. For example, transition metals exhibit a wide range of oxidation states due to the involvement of their d-orbitals.
- Down groups, the maximum oxidation state usually remains the same, but the stability of the lower oxidation states increases (e.g., in group 15, the stability of the +3 oxidation state increases from nitrogen to bismuth).

12.2 Variable Valency

- Many elements exhibit variable valency, meaning they can form ions or covalent compounds with different charges.
- Transition metals are notable for their variable valency, which is due to the similar energy levels of their s and d orbitals.
- The variability in valency is less pronounced in main group elements and is more common in heavier elements of a group.

12.3 Isoelectronic Relationship

- Isoelectronic species are atoms, molecules, or ions that have the same number of electrons.
- Examples include N^{2-}, O^{2-}, F^-, Ne, and Na^+, which all have 10 electrons.
- Understanding isoelectronic relationships is important for predicting the stability and reactivity of ions. For instance, ions that are isoelectronic with noble gases tend to be particularly stable.

12.4 Inert-Pair Effect

- The inert-pair effect refers to the reluctance of the s-electrons of the outermost shell (especially in heavy p-block elements) to participate in bonding.
- This effect becomes more pronounced down a group and is particularly notable in groups 13 to 16.
- For example, lead (Pb) commonly exhibits a +2 oxidation state, despite having a +4 state as well, due to the inert-pair effect.