

Chapter 6

Electronic Structure of Atoms

Waves

- To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation.
- The distance between corresponding points on adjacent waves is the wavelength (λ).

- The number of waves passing a given point per unit of time is the frequency (ν).
- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency.

Electromagnetic Radiation

- All electromagnetic radiation travels at the same velocity: the speed of light (c), 3.00×10^8 m/s.

- Therefore,

$$c = \lambda\nu$$

The Nature of Energy

- The wave nature of light does not explain how an object can glow when its temperature increases.
- Max Planck explained it by assuming that energy comes in packets called quanta.

Einstein used this assumption to explain the photoelectric effect.

- He concluded that energy is proportional to frequency:

$$E = h\nu$$

where h is Planck's constant, 6.63×10^{-34} J-s.

The Nature of Energy

- Therefore, if one knows the wavelength of light, one can calculate the energy in one photon, or packet, of that light:

$$c = \lambda\nu$$

$$E = h\nu$$

The Nature of Energy

Another mystery involved the emission spectra observed from energy emitted by atoms and molecules.

- One does not observe a continuous spectrum, as one gets from a white light source.
- Only a line spectrum of discrete wavelengths is observed.

Niels Bohr adopted Planck's assumption and explained these phenomena in this way:

ØElectrons in an atom can only occupy certain orbits (corresponding to certain energies).

- Niels Bohr adopted Planck's assumption and explained these phenomena in this way:
 - ØElectrons in permitted orbits have specific, "allowed" energies; these energies will not be radiated from the atom.

Niels Bohr adopted Planck's assumption and explained these phenomena in this way:

ØEnergy is only absorbed or emitted in such a way as to move an electron from one "allowed" energy state to another; the energy is defined by

$$E = h\nu$$

The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation:

The Wave Nature of Matter

- Louis de Broglie posited that if light can have material properties, matter should exhibit wave properties.

- He demonstrated that the relationship between mass and wavelength was

The Uncertainty Principle

- Heisenberg showed that the more precisely the momentum of a particle is known, the less precisely is its position known:

- In many cases, our uncertainty of the whereabouts of an electron is greater than the size of the atom itself!

Quantum Mechanics

- Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.

- It is known as quantum mechanics.

Quantum Mechanics

- The wave equation is designated with a lower case Greek *psi* (ψ).
- The square of the wave equation, ψ^2 , gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time.

Quantum Numbers

- Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies.
- Each orbital describes a spatial distribution of electron density.
- An orbital is described by a set of three quantum numbers.

Principal Quantum Number, n

- The principal quantum number, n , describes the energy level on which the orbital resides.
- The values of n are integers ≥ 0 .

Azimuthal Quantum Number, l

- This quantum number defines the shape of the orbital.
- Allowed values of l are integers ranging from 0 to $n - 1$.
- We use letter designations to communicate the different values of l and, therefore, the shapes and types of orbitals.

Magnetic Quantum Number, m_l

- Describes the three-dimensional orientation of the orbital.
- Values are integers ranging from $-l$ to l :
 $-l \leq m_l \leq l$
- Therefore, on any given energy level, there can be up to 1 s orbital, 3 p orbitals, 5 d orbitals, 7 f orbitals, etc.

- Orbitals with the same value of n form a shell.
- Different orbital types within a shell are subshells.

s Orbitals

- Value of $l = 0$.
- Spherical in shape.
- Radius of sphere increases with increasing value of n .

s Orbitals

Observing a graph of probabilities of finding an electron versus distance from the nucleus, we see that s orbitals possess $n-1$ nodes, or regions where there is 0 probability of finding an electron.

p Orbitals

- Value of $l = 1$.
- Have two lobes with a node between them.

d Orbitals

- Value of l is 2.
- Four of the five orbitals have 4 lobes; the other resembles a p orbital with a doughnut around the center.

Energies of Orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- That is, they are degenerate.

Energies of Orbitals

- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in many-electron atoms, orbitals on the same energy level are no longer degenerate.

Spin Quantum Number, m_s

- In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy.
- The “spin” of an electron describes its magnetic field, which affects its energy.

Spin Quantum Number, m_s

- This led to a fourth quantum number, the spin quantum number, m_s .
- The spin quantum number has only 2 allowed values: $+1/2$ and $-1/2$.

Pauli Exclusion Principle

- No two electrons in the same atom can have exactly the same energy.
- For example, no two electrons in the same atom can have identical sets of quantum numbers.

Electron Configurations

- Distribution of all electrons in an atom
- Consist of
 - Number denoting the energy level

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 - Number denoting the energy level.
 - Letter denoting the type of orbital.
 - Superscript denoting the number of electrons in those orbitals.

Orbital Diagrams

- Each box represents one orbital.
- Half-arrows represent the electrons.
- The direction of the arrow represents the spin of the electron.

Hund's Rule

“For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.”

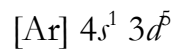
Periodic Table

- We fill orbitals in increasing order of energy.
- Different blocks on the periodic table, then correspond to different types of orbitals.

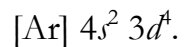
Some Anomalies

Some irregularities occur when there are enough electrons to half-fill s and d orbitals on a given row.

For instance, the electron configuration for copper is



rather than the expected



This occurs because the $4s$ and $3d$ orbitals are very close in energy.

• These anomalies occur in f -block atoms, as well.