

Materials Engineering Science
MESc. 5025

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Chapter 2.
Bonding

Atomic Structure

- Matter consists of Atoms ($d=10^{-8}$ cm)
 - Electrons ($m_e=9.11 \cdot 10^{-28}$ g, $q=-1.6 \cdot 10^{-19}$ C)
 - Protons ($m_p=1.67 \cdot 10^{-24}$ g, $q=+1.6 \cdot 10^{-19}$ C)
 - Neutrons ($m_n=1.67 \cdot 10^{-24}$ g, $q=0$ C)
 - Nuclear Forces hold the nucleus together, while electrostatic forces hold the electrons around the nucleus.
 - The nucleus accounts for most of the mass of the atom, while it is much smaller in size (density : ca. 10^{15} g/cm³)
 - All atoms are composed of the same particles. However different atoms have different properties while isotopes have similar physico-chemical properties. Why ?
- ⇒ Physico-Chemical Properties of elements are determined by their electronic configuration

Example of Variation in Properties: Cohesive Energy of Molecular Crystals

- The attractive electrostatic interactions between the negative charge of electrons and the positive charges of nuclei and the repulsive electrostatic interaction between unlike charges entirely control the cohesive properties of solids. Other interactions are negligible.
- **Cohesive Energy** of a crystal: energy required to separate its components into neutral free atoms at rest at infinite separation with the same electronic configuration.

- The crystal cohesive energy (melting temperature, bulk moduli) vary systematically with respect to the position of an element in the periodic table.
 - The periodic table is organized by consideration of the number of electrons in and the electronic configuration of an atom.
- ⇒ To understand the organization and properties of matter, one must consider the electron distribution in atoms, ions, molecules, molecular ions that constitute the state of matter.

Properties of Inert Gas Crystals

	d_{nn} (Å)	E_i (eV)	ϵ
He		24.6	14:2.6
Ne	3.13	21.6	50:2.7
Ar	3.76	15.8	170:3.4
Kr	4.01	14.0	225:3.7
Xe	4.35	12.1	320:4.0

- The above table describes the properties (distance between nearest neighbors, ionization potential, Lennard-Jones potential parameters) of inert gas crystals. Note that in the series He, Ne, Ar, Kr, Xe the number of electrons is steadily increasing.
- There are specific correlations between the atomic structure, the number of electrons, the electronic configuration, the bonding between atoms and the resulting properties.

Atomic Structure

- **Fundamental Concepts:**

Each element is characterized by the number of protons in the nucleus (Atomic Number= Z). For an electrically neutral element, Z is also the number of electrons. Atomic numbers range from 1 for Hydrogen to 94 for Plutonium.

- **Introduction to Quantum Mechanics :**

Many phenomena involving electrons (e.g. emission spectra, photoelectric effect, etc..) cannot be explained by classical physics (late 19th century).

A number of laws were then derived that govern the behavior of atomic and subatomic entities (**Quantum Mechanics**)

Bohr Atomic Model: First Step in QM.

- Electrons are assumed to revolve around the nucleus in discrete orbitals and the atomic position is well defined in terms of the location of the electron on the orbital.
- The energy of the electron is quantized (only specific values of the energy are allowed).
- Electrons may change energy only through a quantum jump (orbital change). Emission vs Absorption.
- Allowed electron energy : Energy Level or State
- Energies are taken to be negative with the zero energy referring to the unbound free electron.
- Bohr's model was eventually dismissed, but the quantization of energy levels was retained and turned out to be a fundamental result of modern quantum mechanics.

Wave Mechanical Model

- In Wave Mechanical models the electron is considered to exhibit both wave-like and particle-like behaviors and the electron motion is described by mathematics governing wave motion (string vibration).
- Using Wave Mechanics Schrodinger and De Broglie treated the electron bound to the nucleus as a **Standing Wave (String vibration) defined by a wave function.** Electrons are no longer treated as particles moving in well defined orbitals. **Position is replaced by the probability distribution function or an electron cloud (square of the wave function).**

Schrodinger Equation and Solution for the One-Electron Atom

- Ψ = Schrodinger Equation

= Electron Wave Function

E = Energy of Electron

$$\hat{H} = -\frac{\hbar^2}{2m_r} \nabla^2 + V(\mathbf{r})$$

- H: Hamiltonian Operator

- $\hbar = h/2\pi$ where h : Planck's constant

m_r : Reduced mass

V(r): potential energy (electrostatics: $Ze^2/4\pi\epsilon_0 r$)

- An exact solution to the Schrodinger equation can only be obtained for the 1 electron system.
- The solutions are sets of wave functions $\Psi_{n,l,m_l}(\mathbf{r}, \theta, \phi)$ and energy levels, E_n , associated with these wave functions.

- When an electron is described by one of these wave functions, it is said to occupy that orbital.
- n, l, m_l are the quantum numbers characterizing that orbital

$\psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) \cdot Y_{l,m_l}(\theta, \phi)$
 where $R_{n,l}(r)$ is the radial part and $Y_{l,m_l}(\theta, \phi)$ is the angular part of the wave function.

- Electron Energy

$$E_n = -\frac{Z^2 m_r e^4}{32\pi\epsilon_0 \hbar^2} \cdot \frac{1}{n^2}$$

- The discrete values that the energy can take (i.e. the quantization of the energy) arises from the fact that the quantum wave number n , must be an integer.
- The discrete values of n, l, m_l arise either because of boundary conditions (n for R , m_l for Y) or because of constraints placed on the wave function (single and finite value).

Radial Part of the Wave Function

Orbital	n	l	$R_{n,l}(r)$
1s	1	0	$2 \frac{Z}{a_0}^{3/2} e^{-1/2\rho}$
2s	2	0	$\frac{1}{2\sqrt{2}} \frac{Z}{a_0}^{3/2} (2 - \rho)e^{-1/2\rho}$
2p	2	1	$\frac{1}{2\sqrt{6}} \frac{Z}{a_0}^{3/2} \rho e^{-1/2\rho}$
3s	3	0	$\frac{1}{9\sqrt{3}} \frac{Z}{a_0}^{3/2} (6 - 6\rho + \rho^2)e^{-1/2\rho}$
3p	3	1	$\frac{1}{9\sqrt{6}} \frac{Z}{a_0}^{3/2} (4 - \rho)\rho e^{-1/2\rho}$
3d	3	2	$\frac{1}{9\sqrt{30}} \frac{Z}{a_0}^{3/2} \rho^2 e^{-1/2\rho}$

Angular Part of the Wave Function: Spherical Harmonics Y_{l,m_l}

l	m_l	Y_{l,m_l}
0	0	$\frac{1}{4\pi}^{1/2}$
1	0	$\frac{3}{4\pi}^{1/2} \cos\theta$
1	± 1	$\mp \frac{3}{8\pi}^{1/2} \sin(\theta) e^{\pm i\phi}$
2	0	$\frac{5}{16\pi}^{1/2} (3\cos^2\theta - 1)$
2	± 1	$\mp \frac{15}{8\pi}^{1/2} \cos(\theta)\sin(\theta) e^{\pm i\phi}$
2	± 2	$\frac{15}{32\pi}^{1/2} \sin^2(\theta) e^{\pm 2i\phi}$
3	0	$\frac{7}{16\pi}^{1/2} (5\cos^3(\theta) - 3\cos(\theta))$
3	± 1	$\mp \frac{21}{64\pi}^{1/2} (5\cos^2(\theta) - 1)\sin(\theta) e^{\pm i\phi}$
3	± 2	$\frac{105}{32\pi}^{1/2} \sin^2(\theta)\cos(\theta) e^{\pm 2i\phi}$
3	± 3	$\frac{35}{64\pi}^{1/2} \sin^3(\theta) e^{\pm 3i\phi}$

Meaning of Quantum Numbers

- n is the **principal quantum number**, specifies the energy of the electron and determines the radial part of the wave function (in Bohr's model it was viewed as defining the orbital number and energy). n defines the **orbital shell** number and takes on strictly positive values.
- l is the **angular momentum quantum number** and specifies the magnitude of the electron's orbital angular momentum $(l(l+1))^{1/2}\hbar$ l is an integer and varies between 0 and $n-1$
- m_l specifies the direction of the electron's orbital angular momentum. It takes integral values between $-l$ and $+l$
- m_s is the fourth quantum number and specifies the orientation of the electron's spin angular momentum $s = 1/2 \Rightarrow m_s = -1/2$ or $+1/2$

Probability of Finding an Electron

- The probability to find an electron at the position defined by r , θ , and ϕ is given by the product of the wave function by its complex conjugate: $\psi_{n,l,m_l}(r, \theta, \phi) \cdot \psi_{n,l,m_l}^*(r, \theta, \phi)$
- For a spherically symmetrical orbital (such as an “ns” orbital), $P(r) dr = 4\pi r^2 |\psi(r)|^2 dr$. $P(r)$ is the probability to find an electron between the spheres of radius r and $r+dr$
- $P(r)$ is called the Radial Distribution Function of the electron
- For a 1-s electron: $P(r) = r^2 \exp(-2r/a_0)$
the most probable radius is obtained for $dP/dr = 0 \dots r_{1-s} = a_0$
- For a 2-s electron: the most probable radius is $r_{2-s} = 5.2 a_0$

Polyelectronic Atoms

- So far we dealt with the Hydrogen atom (1 electron and 1 proton). We can readily extend this treatment to the case of **one-electron ions** such as He^+ , Li^{2+} , Be^{3+} , etc..
- The problem is to deal with atoms or ions which have more than one electron. How do we account for repulsions between electrons in the context of **Heisenberg Uncertainty Principle**
- Need for Approximation: Account for electron repulsions by assuming that each electron moves in a field that is the net result of the nuclear attraction and the averaged repulsions between the electron of interest and all other electrons. This is done by replacing the actual nuclear charge by an **effective nuclear charge** Z_{eff}
- Wave function = $\psi(r_1, r_2, r_3 \dots r_n) = \psi(r_1) \cdot \psi(r_2) \dots \psi(r_n)$

Effective Nuclear Charge and Shielding Constant

- The effective nuclear charge varies from electron to electron, reflecting the varying shielding effects of various electrons (i.e. the various depths of penetration of different orbitals).
- Z_{eff} for a given electron can be estimated from the experimental knowledge of the energy required for removal of that electron from the atom (ionization potential, E_i)
- With this model one can calculate the various hydrogen-like orbitals for all electrons in a given atom or ion. Although these orbitals have the same shape as those described for H, He⁺, Li²⁺, Be³⁺, they will have different energies and sizes as Z_{eff} differs from Z

- The actual value of Z_{eff} is controlled by the penetration of the orbitals close to the nucleus. **Penetration** affects **Shielding** which in turns affects **Electron Energy**.
- In single-electron systems, orbitals within the same shell (given n) have identical energies. In polyelectron systems, the electrons in a given shell have different values for Z_{eff} , therefore different energy levels.
- Sub-shell orbitals are ranked as follows on the basis of their respective value for Z_{eff} .

$$E_{\text{ns}} < E_{\text{np}} < E_{\text{nd}} < E_{\text{nf}} \quad E = -k Z_{\text{eff}}/n^2$$
- The larger the penetration, the lower the shielding, the larger Z_{eff} , the lower E_n , the more stable the orbital.

- All orbitals having the same “ n ” belong to one shell. There are “ n ” sub-shells per shell of quantum number “ n ”. The sub-shells are defined by their “ l ” value between 0 & $n-1$
 - $n = 1$ shell K
 - $n = 2$ shell L
 - $n = 3$ shell M
 - $n = 4$ shell N
 - $n = 5$ shell O
 - $n = 6$ shell P
 - $n = 7$ shell Q
- All orbitals having the same “ l ” and the same “ n ” belong to the same sub-shells. There are $2l+1$ orbitals per sub-shell. m_l vary between $-l$ and $+l$
 - $l = 0$ sub-shell s
 - $l = 1$ sub-shell p
 - $l = 2$ sub-shell d
 - $l = 3$ sub-shell f

The Aufbau:

The Building of the Electronic Configuration of Atoms

- Electrons are placed in orbitals of increasing energies, starting with the lowest (most negative) energy level.
- In a given atom, no two electrons can have the same four quantum numbers : **Pauli Exclusion Principle**
- The lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli's principle in a particular set of degenerate (i.e. of the same energy) orbitals. In addition, all unpaired electrons have parallel spins: **Hund's Rule**
- $s^2 p^6 d^{10} f^{14}$
- Valence electrons are the electrons in the outermost shell (highest principal quantum number shell). Core electrons are the inner shell electrons.

Electronic Configurations

- H: $Z = 1$: $1s^1$
- He: $Z = 2$: $1s^2$
- Li: $Z = 3$: $1s^2 2s^1$
- Be: $Z = 4$: $1s^2 2s^2$
- B: $Z = 5$: $1s^2 2s^2 2p^1$
- C: $Z = 6$: $1s^2 2s^2 2p^2$
- N: $Z = 7$: $1s^2 2s^2 2p^3$
- O: $Z = 8$: $1s^2 2s^2 2p^4$
- F: $Z = 9$: $1s^2 2s^2 2p^5$
- Ne: $Z = 10$: $1s^2 2s^2 2p^6$
- Na: $Z = 11$: $1s^2 2s^2 2p^6 3s^1$
- Mg : $Z = 12$: $1s^2 2s^2 2p^6 3s^2$
- Al: $Z = 13$: $1s^2 2s^2 2p^6 3s^2 3p^1$