Electronic Structures of Atoms and Molecules

In this lecture, we will review the most significant discovery and scientific advances during late 1800s and early 1900s, **Quantum Mechanics**, which has contributed to the framework of the electronic structures of atoms and molecules, a microscopic world that used to be very difficult (if not impossible) to characterize and understand. Quantum mechanics continues serving as the basic framework for advancement of modern science and engineering.

Light, broadly defined as electromagnetic radiation, offers an important tool to characterize the electronic structures of atoms and molecules. It also played a crucial role in foundation and advancement of quantum mechanics.

The origin of quantum mechanics started from Planck's quantum assumption of light. Based on Planck's assumption, the energy of light is determined only by its frequency ($E = h\nu$, $c = \lambda\nu$, where h is Planck's constant, c is speed of light).

Johann Balmer's (1885) and Johannes Rydberg's formula that describes the mathematic relationship of the linear spectra of hydrogen atoms.

$$\frac{1}{\lambda} = (R_H)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Neils Bohr used this formula and Planck's assumption, and established for the first time the atomic model and energy configuration of electrons.

Another important discovery towards foundation of quantum mechanics is the mass-wavelength equation proposed by Louis de Broglie

$$\lambda = \frac{h}{mv}$$

where λ is the wavelength of a particle, m is the mass of the particle, v is the speed of the particle. (Note: actually combining Broglie's equation and $E = h\nu$, $c = \lambda\nu$, one can derive Einstein's energy-mass equation $E = mc^2$).

Broglie's mass-wavelength equation, in a quantitative way, describes the general wave nature of matter in the microscopic world such as electrons, atoms, and molecules.

The wave nature of microscopic matter was further developed by Heisenberg's uncertainty principle:

$$(\Delta x)\ (\Delta mv) \geq \frac{h}{4\pi}$$

The final mathematic framework of quantum mechanics is established by Schrödinger's wave equation

$$-\frac{\hbar^2}{2M}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) = E\Psi$$

(M: mass of a particle; E: energy of the particle; ψ: wave function; ψ^2: electron density or probability of where an electron is likely to be at any given time)

Schrödinger's wave equation provides a general mathematic framework to determine the electron configuration in atoms, which can be further extended to molecules.

Solving Schrödinger's wave equation, which will not be covered in this course and will be taught in advanced courses such as Physical Chemistry and Quantum Mechanics, gives a set of wave functions, or **orbitals**, and their corresponding energies. Each orbital is described by a set of three quantum numbers: principal (n), angular momentum (l), and magnetic (m_l) quantum number. (Note: the spin quantum number (m_s) describes the spin configuration of an electron, not an orbital)

Based on the quantum numbers of a certain atom, and Pauli Exclusion Principle and Hund's rule, one can determine the electronic configuration of an atom.

According to the electronic configuration of an atom, the outshell electrons are mostly related to the physical and chemical properties of the atom. We will further illustrate this point in next chapters of Periodic Properties and Chemical Bonding.

Periodic Properties of Elements

Development of the Periodic Table is another benchmark in chemistry. Periodic table provides a map or blueprint for understanding chemical/physical properties of elements and guiding the material design and synthesis.

The establishment of periodic table looks like play of puzzle to group a number of separated pieces into a pattern according to some clues. It involves discovery of new elements, characterization and understanding of their properties, and identify the common or distinct characteristics. In 1869, Mendeleev and Meyer independently published their same conclusion about how the elements should be grouped. The power of periodic table was demonstrated early by Mendeleev in predicting some nondiscovered elements such as Ga ("eka-alluminum") and Ge ("eka-silicon").

Exercise: To search the early version of Mendeleev's periodic table and find out how it is different from the completed version.

The early version of periodic table established by Mendeleev and Meyer was further developed by Henry Moseley according to the atomic number of the nucleus.

Periodic table tells that the elements show a trend of periodicity, similar to calendar to some extent. We will discuss how some physical/chemical properties show the periodical/repetitive trend in the periodic table.

A fundamental property that we will discuss first is Effective Nuclear Charge (ENC), which is used a lot in discussion of other properties of elements. According to Rutherford's atomic model, an atom is composed of a positively charged nucleus surrounded by multishell electron clouds. There is electrostatic attraction between the nucleus and the electron(s), and electrostatic repulsion between electrons. For an atom with multishell electrons, the electrostatic attraction from the nucleus for each shell of electrons is different, stronger for the inner shell and weaker for the outshell, due to the screening effect of the inner electrons. In order to quantify this difference of the attraction force, we introduce ENC.

$$Z_{eff} = Z - S$$

where Z is the atomic number (equal to the number of nuclear charge), and S is the screening constant (S = 0 for single shell electrons such as those from H and He or the most internal shell electrons (1s))

As out-shell electrons, also called valence electrons, are most related to the physical/chemical properties of elements, we mainly look at the trend of ENC for valance electrons.

1) For the elements in the same period, ENC for valence electrons increases from left to right.
2) For the elements in the same group (A group), ENC for valence electrons increases slightly from top to bottom.

Size of atoms: As there is no definite boundary for the electron cloud in an atom, one way to define the size of an atom is according to the distance between the nuclei of two atoms with chemical bonding or those in touch but no bonding. The atomic sizes decrease from left to right across a period, which could to attributed to effect of ENC, and increase from top to bottom in a group. Such principles could also be used to explain the repetitive behavior of ions, for example, isoelectronic series, ionization energy, electron affinity, …

Size of ions: A cation (positively charged) has small radius than its original atom, and an anion (negatively charged) has large radius than its parental atom.

Using the electron configuration and the periodic table, one can understand easily the trends of elements in different groups, such as alkali metals (1A), alkanine earth metals (2A), the oxygen group (6A), the halogens (7A), and the noble gases (8A). Through these examples, one can also appreciate the importance of electron configuration (determined by quantum mechanics) and the periodic table.

Basic Concepts of Chemical Bonding

Chemical bonding plays an important role in chemistry. It determines the physical and chemical properties of substances. Creating new materials through chemical reaction is a process of breaking chemical bonds and formation of new chemical bonds.

Chemical bonds can be ionic, metallic, covalent, hydrogen-bonding, dipole-dipole interaction, pi-pi interaction, etc.

The valence electrons (involved in chemical bonding, normally outmost shell electrons) can be presented by Lewis symbols. In the formation of chemical bonds, each atom tends to gain, lose, (ionic bonding), or share electrons (covalent bonding) until it is surrounded by eight valence electrons, also called octet rule.

The strength of ionic bonding can be defined by lattice energy, the energy required to completely separate a mole of a solid ionic compound into its gaseous ions. The equation for calculation of lattice energy is based on Coulomb's law (normally for quantification of ionic static interaction):

$$E_{el} = \kappa \frac{Q_1 Q_2}{d}$$

In contrast to ionic bonding where the electrons are completely transferred from the donor to the acceptor, atoms share electrons in covalent bonding.

Depending on the electronic structures of atoms, the covalent bonding could be single (sigma) bond, double (sigma + pi) bond, and triple (1 sigma + 2 pi) bond.

When two different atoms are linked by covalent bonds, electron density tend to concentrate on the atom with higher electron affinity or electronegativity. Such unequal electron distribution of the valence electrons involved in the covalent bonding is called polarity. Polar covalent bonds, at certain geometry, often introduce dipole-dipole interaction between molecules.

The periodic property of electronegativity is consistent with that of electron affinity, which can be explained according to effective nuclear charge (Z_{eff}).

Dipole moment can be calculated according to

$$\mu = Qr$$

A simple approach to judge whether a compound is ionic or covalent is:
Metal + nonmetal is ionic;
Nonmetal + nonmetal is covalent.
But there are many exceptions: $SnCl_4$ (covalent: colorless liquid at r.t.); MnO (ionic) and Mn_2O_7 (covalent).

Steps to write Lewis structures for covalent molecules:

1) Calculate the total valence electrons from all atoms, including the electrons that contribute to the overall charge of the molecule.

2) Connect atoms with single bonds.
3) Complete the octets around all atoms bonded to the central atom.
4) Place any leftover electrons on the central atom.

Resonance structures of molecules could be considered as superposition of different structures, analogy to "Schrodinger's cat" thought experiment.

The covalent bond strength can be quantified according to the change of bond enthalpy in the formation of the interest compound.

Molecular Geometry and Bonding Theories

This chapter mainly covers **geometry of chemical bonding** in covalently bond molecules, the principles of the **sigma bond (single bond) and pi bond (double or triple bond)**, and quantum mechanics of **molecular orbitals**.

To configure the geometry of a molecule:

1) Count the total valence electrons of the central atom.
2) Determine how many orbitals are required to fill the valence electrons, and whether orbital hybridization is needed.
3) Determine the number of electron domains. It is important to include nonbonding lone pair of electrons. Double bonds and triple bonds are considered as one electron domain, though their electron density is generally larger than that of single bonds.
4) Use VSEPR model to determine the geometry of the orbital.

Polarity of molecules are determined by both the polarity of the chemical bonds and the geometry of the molecules.

Orbital hybridization: For main-group elements, if involvement of only s or p orbitals and electrons cannot rationalize the geometry of a molecule, then hybridization of s and p orbitals (in some cases d orbitals are also involved, e.g. ClF_3) is considered in the chemical bonding. The type of the hybridization, including sp, sp^2, sp^3, sp^3d, etc., is determined by both the geometry of the molecule and the electronic structure of the central atom.

Sigma bonds are formed by head-to-head overlap of s-s or p-p orbitals, or between hybrid orbitals. Sigma bonds are often present as single covalent bonds.

Pi bonds are formed by side-by-side overlap of p-p orbitals. Pi-bonds are often involved in double or triple bonds.

The theory of **molecular orbitals** shares similar principles of quantum mechanics with those of atomic orbitals. The number of the molecular orbitals is the sum of the atomic orbitals from the composed atoms, and same for the number of the electrons.

Gases

The central part of this chapter is **ideal gas equation:**

$$PV = nRT$$

where P is pressure of the gas, V is the volume of the gas, n is the moles of the gas, T is the temperature of the gas, and R is a constant.

This equation is often used in calculation of gas-involved work-energy conversion in thermodynamics.

An essential learning outcome is to learn how this equation was established, and more importantly, how to apply this equation to address a specific engineering problem.

Ideal gas equation often applies to gases under a low pressure and/or at a high temperature, where the intermolecular interaction between gas molecules can be neglected.

For real gases in which the intermolecular interaction need to considered, their behavior are defined by a more accurate equation, so called the van der Waals Equation:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

where a,b are constants that are specific to different gases.

Liquids and Intermolecular Forces

There are mainly three states, i.e. gas, liquid, and solid, for a material, depending on the temperature and the pressure. The intermolecular (attraction) forces increase in the order of gas, liquid, and solid, while the average kinetic energy of the molecules decreases in the same order.

This chapter focuses on some general properties of liquids and intermolecular forces that relate to the properties. In contrast to the covalent bonding for nonmetals as discussed in the earlier chapters, the intermolecular forces here mainly refer to noncovalent interaction, including dispersion forces, dipole-dipole interaction, hydrogen bonding, and ion-dipole forces (for ionic solutions). An intermolecular force is usually weaker than covalent bonding individually, but the collective (associative) effect of many intermolecular forces could be strong and has a significant impact on the physicochemical properties.

Factors that influence the strength of dispersion force include number of electrons, size of atom of molecule (molecular weight), and shape of molecules with similar masses (more compact, less dispersion force). Overall, if a molecule is more **polarizable**, the larger the dispersion force. Based on this principal, one can rationalize the physical state of gas, liquid and solid in the order of Cl_2, Br_2, and I_2.

Physical properties of liquids that are affected by intermolecular forces (IFs) include: boiling point, viscosity, surface tension, and capillary action. The larger intermolecular forces, the higher boiling point, the larger viscosity and surface tension. Capillary action of liquid is determined by the nature of the interaction between the liquid molecules and the surface (substrate). If the cohesion force is larger than the adhesion force (molecule/substrate interaction), capillary action will occur.

Phase diagrams of liquids describe the evolution of the three physical states (gas, liquid, solid) with the function of temperature and pressure.

Liquid crystal is a physical state between liquid and crystal. The molecules in liquid crystals behave short-range ordering but no long-range ordering. Liquid crystals have played an important role in advancement of display devices.

Solids and Modern Materials

This chapter focuses on some general structural features of solids, particularly crystalline solids (metals and ionic solids), followed by properties of some specific and advanced solid materials such as covalent networks, semiconductors, polymers, and nanomaterials.

Crystals are solid materials with structural ordering at atomic scale. The atomic ordering in crystalline solids is defined by the size and shape of the unit cell and the locations of atoms within the unit cell. The latter is called lattice.

According to the electrical conductivity of a solid material, the materials can be sorted into three categories, conductors (mostly metals), semiconductors (silicon, etc.), and insulators. The differences in the electrical properties of solid materials are related to the electronic structures of the atomic components and the chemical bonding between atoms. The energy bands and the band gaps of solid materials could be explained according to molecular orbital theory. One well-known example is the three isomers of carbon materials: graphite is an electrical conductor, fullerene (C_{60}, etc.) is a semiconductor, and diamond is an insulator.

Doping of a semiconductor is a chemical process that introduce either negative charge carriers (mostly electrons, corresponding to n-doping) or positive ones (called holes by physicists, corresponding to p-doping). The common result of doping is the increase of charge carrier density, which contributes to the increase of the electrical conductivity of semiconductors.

Polymers, also called plastics in public and macromolecules in some literature, are large molecules composed of many repeating units. Many biological systems such as DNA and proteins are biomacromolecules. Synthetic polymers such as nylon, polyethylene, polypropylene, polyesters, polycarbonates, rubber and resins are widely used in our everyday life. Rubber and resins are crosslinked polymers which are resistant to physical and chemical impacts. While conventional polymers are mainly insulators, a new family of polymers containing pi-conjugated units have shown properties of semiconductors and metals, which was awarded with Nobel Prize of Chemistry in 2000.