Lecture # 3

Physical Organic Chemistry

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Chemistry is an empirical science but is increasingly influenced by understanding and prediction. Before starting an experiment in the laboratory, a chemist would like to know the following:

(1) Is the reaction possible thermodynamically?

(2) How long is it going to take?

(3) What will be the properties of the reaction products?

This course introduces and documents models that enable chemists to answer these questions and to understand the reasons behind the answers.

Reactions involving organic, organometallic, and biochemically important reactants and catalysts will be presented.

We teach the tools that can be used to understand Nature and to control and create new chemistry to achieve a betterworld.

Givenspecificcombinationsofsolvent, concentration, temperature, pressure, the presence or absence of catalysts and inhibitors, light, or other types of radiation, a given system of reactants will be converted into a mixture of products.

Rates of product formation or attainment of equilibria define chemical reactivity.

Living systems are made of ensembles of molecules that are connected through ensembles of chemical reactions.

We try to understand Nature and to imitate its efficiency and diversity.

Molecular scientists, especially chemists, are not passive observers. Chemists can even surpass Nature, by inventing new molecular entities – chemicals! And new reactions that have not been observed yet in our Universe, at least on our planet!

Molecular orbital theories

Molecular orbital (MO) theories and various approximations have been extremely useful to understand the electronic structures of complicated molecules, bonding in molecules and molecular assemblies, substituent effects on the relative stabilities of neutral or charged species, deviations from thermochemical additivity rules (such as π-conjugation, aromaticity, and antiaromaticity), bonding in π- and σ-complexes, hyperconjugation, hypervalency, and the relative stability of transition structures of concerted reactions. Simple molecular orbital theory has demonstrated the similarities in bonding between organic, organometallic, and inorganic compounds.

Background of quantum chemistry

- Molecular orbital theories are based on quantum chemistry.

- The experimental observations that eventually led to quantum mechanics began in 1828 with the discovery of cathode rays by Faraday (light arc beginning at the negative electrode and ending at the anode [positive electrode] when current passes through rarefied air).
- In 1859, Kirchhoff stated the blackbody radiationproblem.
- In1877,Boltzmannsuggested that energy states of physical system (atoms and molecules) could be discrete.
- In 1900, Planck proposedthequantumhypothesisthatenergy-irradiating atomic systems can be divided into numbers of discreteenergyelements εsuchthateachoftheseenergy elements is proportional to the frequency ν with whichtheyradiateenergy,asdefinedby $\varepsilon = h\nu$,where h is a numerical value (Planck's constant).
- In 1905, Einsteinexplainedthephotoelectriceffectdiscovered in1839byBecquerelwhilestudyingtheeffectoflight on electrolytic cells and by Hertz in 1887 when heobservedthatelectronsareemittedfrommatterwhen hit by light.
- Based on Planck's quantum hypothesis, Einstein stated that light itself consists of individual quantum particles, the latter being called photons since 1926.
- In parallel with developments leading to quantum mechanics, the structural theory of organic chemistrywasdeveloped.
- In1852,Frankland proposed that atoms of a given element have finite capacity to combine with atoms of other elements, i.e. a definite valence.
- In 1858, Kekulé and Couper, independently, introduced the concept of valence bonds between atoms, including bonds between two carbon atoms, and proposed the tetravalency of carbonatom.

- In 1861, Butlerow stated that the properties of a compound are determined by its molecular structure.
- In 1874, Van’t Hoff recognized that the optical activity of carbon compounds, discovered by Pasteur in 1848, can be explained by the postulate that the four-valence bonds of carbon atom are directed in space to the corners of a tetrahedron.
- In 1916, Lewis stated that the chemical bond between two carbon atoms in alkanes or between one carbon atom and a hydrogen atom consists of a pair of electrons held jointly by the two atoms connected by a single bond. Lewis also suggested that atoms tend to reach the electronic configuration of a noble gas through the sharing of electrons with other atoms or through electron transfer.
- Although this theory predated quantum mechanics, chemists nevertheless find it a useful model for the understanding of bonding in organic molecules.
- Dirac recognized at the time when all of chemistry could be understood quantitatively by the equations of quantum mechanics but could not predict the advent of powerful computers of today.
- In 1911, Rutherford established that atoms consisted of a diffuse cloud of electrons surrounding a small positively charged nucleus and proposed the planetary model atom.
- In 1913, Bohr proposed that electrons travel in certain orbits at discrete distances from the nucleus, with specific energies. The electrons can lose or gain a fixed energy amount by jumping from one allowed orbit to another allowed orbit, absorbing or emitting electromagnetic radiation with a determined frequency ν.

- .This is the basis of atomic spectroscopy: atoms heated in a flame emit (Na emits yellow light, Sr emits red light, etc.) or absorb (flame atomic absorption spectroscopy established by Bunsen and Kirchhoff during the 1870s).
- The foundation of quantum chemistry is the wave model in which the positively charged nucleus of an atom is surrounded by a cloud of electrons moving in orbitals, and their positions are represented by probability distributions rather that discrete points.
- This model predicts the pattern of similar elements as found in the Mendeleev periodic table of elements. It models properties of electrons and of any other fundamental particles.
- The mathematical basis of quantum chemistry was made by Dirac and Schrödinger in 1926. Heisenberg in 1932 and Dirac and Schrödinger in 1933 received Nobel Prizes for quantum mechanics.
- There is perhaps no more famous quote about quantum mechanics than Dirac's in 1929 (three years after his PhD): "The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

Schrödinger equation

The starting point of any theoretical description of the energy and electronic properties of a chemical system (stable or unstable species) with a given geometry is the Schrödinger equation:

$$H\Psi(r)=E\Psi(r)$$

where Ψ(r) is a stationary, electronic wave function, E is the electronic energy, and H is the Hamiltonian operator (symbolˆH also used) for a system assumed to be in a fixed nuclear configuration.ˆH is given by the following equation:

$$\mathrm{H} = \sum_{i}\left(\frac{\hbar^{2}}{2m_{e}}\nabla_{i}^{2}\right) - \sum_{i}\sum_{m}\frac{Z_{m}e^{2}}{r_{im}} + \sum\sum_{i<j}\frac{e^{2}}{r_{ij}}$$

wherethesuccessivetermsrepresentoperators(∇_i^2 = $(\partial^2/\partial x^2{}_i)+(\partial^2/\partial y^2{}_i)+(\partial^2/\partial z^2{}_i)$)forthekinetic energy of the electrons (i)ofmassm_e,thenuclear–electronic attraction (Z_m istheatomicnumberofnucleus$m$and r_{im} isthedistancebetweenelectron$i$andnucleus$m$), andtherepulsion between electrons (r_{ij}isthedistance).

The wave function Ψ(r), which is understood to depend on the position vectors (r) of all particles, describes the state of the system.

Ψ(r) is the probability amplitude, whereas $\Psi(r)\cdot\Psi(r)d\tau_1\cdots d\tau_i\cdots d\tau_N$ ($d\tau i$isthe volume element of electron i) represents the probability distribution function for the N particles.

For bound states, it is commontonormalize the probability to unity.

$$\int \Psi(\mathbf{r})\cdot\Psi(\mathbf{r})\ldots d\tau\ldots =<\Psi(\mathbf{r})^{2}>= 1 \quad \text{all space}$$

In 1927, Burrau presented a solution to the Schrodinger equation for hydrogen molecule ion, H_2^+, which describes the nature of the one-electron bond in this two atomic, one electron species.

The same year, Heitler and London proposed an approximate solution to the Schrodinger equation for H_2 and were able to explain for the first time the covalent bond.

Their approximate solution requires the two electrons of H_2 to be separated, each being close to one of the two nuclei (protons).

Simultaneously, Condon presentedanothersolutiontothewavefunctionfor H_2 that permits the electrons to be distributed betweenthetwonucleiindependentlyofoneanother, each occupying a wave function similar to Burrau's function for H_2^+.

Pauling introduced in 1932 the concept of electronegativity and the theory ofhybridizationofatomicorbitals(AOs).

For chemical systems with more than two electrons, the solution to the Schrodinger equation is mathematically impossible unless one makes assumptions.

One of the earliest methods has been proposed in 1930 by Hückel for π-systems and appliedbyseveralauthorstosolveallkindofchemical problems.

As computers have become more and more powerful, solutions of the Schrödinger equation for complex chemical systems are now possible; although exact analytical solutions are not possible, "chemical accuracy," which is solutions within the experimental error of measurements, often taken as $1kcalmol^{-1}$, is usually possible.

One very much applied calculation method to relatively large molecules including organometallic systems is based on Kohn's density functional theory (DFT) of electronic structure.

In common calculations, the total energy is estimated by approximate solutions of the time-dependent Schrödingerequation, usually with no relativistic terms and by making use of the Born–Oppenheimer approximation, whichseparates electronic and atomic motions.

Since the 1960s, semiempirical MO calculations (e.g. Hückel, extended Hückel theory, Pariser–Parr–Pople[PPP] treatments, complete neglect of differential overlap [CNDO], Dewar's modified intermediate neglect of differential overlap, version 3 [MINDO/3], modified neglect of differential overlap [MNDO], Austin model1[AM1],andnowStewart's parametric model numbers 3 and 6 [PM3 and PM6]) have become routine.

These semiempirical methods set various integrals to quantities that are not computed but are obtained from empirical experimental data.

The first *ab initio* Hartree–Fock (HF) calculations on diatomic molecules were carried out in 1956 using Slater orbitals as the basis set.

Ab initio (from the beginning), solve approximations to the Schrödinger equation without recourse to experimental data. However, various approximations are made in order to make the computations feasible.

Ab initio does not imply that the solution is an exact one because approximations are invariably made.

The simplest type of *ab initio* calculation is the HF scheme, commonly known as molecular orbital theory. HF theory makes the assumption that the repulsion between an electron and all other electrons can be treated as the interaction of one electron with the average position of the others. This assumption leads to an error, which is known as electron correlation.

Electron correlation is the difference between the HF energy using a very large basis set (mathematical representation of atomic orbitals) and the actual energy.

It arises for the factthat electrons do correlate their motions to avoid eachother, an energy-reducing effect that is missed when electron–electron repulsion is calculated based onthe average position of electrons.

Most approximatequantum mechanical theories of electronic structureare independent electron theories. Independent electron theories start off by assuming a solution Ψ ofthe Schrödinger equation with precisely the form itwould have if **H** were a sum of one-electron termswithout any instantaneous correlation of the electronpositions or electron motions.

The full wave function,Ψ, is the product of these one-electron functions.Each of these one-electron functions is a molecular orbital.

Mulliken defined an AO as an eigenfunction of one-electron Schrödinger equation for an atom. AMO is defined as an eigenfunction of one-electronSchrödinger equation, which is based on the attractionsof two or more nuclei plus the average repulsionsof the other electrons.

An orbital (AO, MO) is a mathematical function in an ordinary three-dimensional space. When an electron is occupying an orbital, theshape of the orbital gives the fraction of time theelectron spends in different regions of space around the nucleus, or nuclei.

One of the most powerful methods of quantum mechanics is called the variation theorem and states the following: "Given any approximate wave function satisfying the boundary conditions of the problem, the expectation value ofthe energy calculated from this function will always behigher than the true energy of the ground state."

Thisprinciple allows us to guess several functions called trial functions and calculate the expectation valueof the energy for each function that can be obtainedfrom the original guesses. One way to be more systematicis to start with a trial function containingseveral arbitrary parameters. The expectation value of the energy, E_i, is then calculated and is minimized with respect to the arbitrary parameters.

In this way,a large number of “guesses” can be made with a singlefunction.The resulting wave function is then the bestavailable for the particular parametric form chosen.

The usual way to carry out such a calculation is tomake use of a linear variation function, and this is thebasis for the “linear combination of basis functions”φ_k(Following equation). The basis functions can be taken asatomic orbitals, or now commonly, several functionsfor each orbital plus other functions that do notnecessarily resemble atomic orbitals; this approach isthe linear combination of atomic orbitals or LCAOmethod introduced by Lennard-Jones in 1929.

$$\Psi_i = \sum_k c_{ik}\varphi_k$$

As molecules are made up of atoms, it is fairlyreasonable to assume that the electron distributionin a molecule can be approximately represented asa sum of atomic electron distributions. This is thephysical basis for the molecular orbital or LCAO–MOmethod of solving quantum mechanical problems.

In this method, one chooses as a trial function for a molecular orbital Ψ_i, a linear variation function where the coefficients c_{ik} are the parameters that willbe obtained so as to minimize the energy.

For eachset of c_{ik}, one obtains for a given molecule a value E_i.The expectation value of the energy, E_i, is given by the variation principle (E_0 is the true ground-stateenergy).

In order to obtain the best possible solution Ψ_i, one chooses the parameters c_{ik} in such a way that they give the smallest possible value for Ei. The minimal value of E_i will be obtained if the conditions are satisfied (The following figure).

$$E_i = \frac{\langle \Psi_i | \mathrm{H} | \Psi_i \rangle}{\langle \Psi_i / \Psi_i \rangle} \geq E_0$$

$$\frac{\partial E_i}{\partial c_{il}} = \cdots = \frac{\partial E_i}{\partial c_{ik}} = \cdots = \frac{\partial E_i}{\partial c_{in}} = 0$$