Lecture No: 8

QUANTUM CHEMISTRY

Atoms, molecules, electrons, protons and all the subatomic particles are very small. They move too fast, in femtoseconds. We cannot see them. We cannot take their pictures or photos. We cannot localize them. If we can localize, we lose information where they are going. Atoms and molecules use a different language. They don't obey classical mechanics laws or principals. Their behavior can only be explained by quantum mechanical principals.

The principals of quantum mechanics are quite far from everyday experience. They are difficult to understand. You have to believe in them. You cannot justify them. They are justified only by their ability to predict experimental data.

1. The Atom

Matter consists of atoms. Atoms are very small particles. They are discrete and indivisible. The atom is composed of even smaller particles ~ 20. But the three of them are the most important;

- The electron : has a unit negative charge. The mass of it is negligible
- The proton : has a unit positive charge and has a unit mass.
- The neutron: has a unit positive charge and a unit mass.

The nucleus of the atom consists of protons and neutrons. The electrons move around the nucleus. The electrons are not distinct particles. They form a cloud around the nucleus.

An atom is identified by two numbers;

- ***The Atomic Number Z***: is the number of protons in the nucleus. It is also the number of electrons.

- ***The Mass Number A***: is the total number of protons and neutrons.

the # of neutrons = A - Z

An atom of an element is designated by its chemical symbol with the atomic number placed at the lower left and the mass number placed at the upper left. Atoms that have the same atomic number but different mass numbers are called 'isotopes'.

2. Electromagnetic Radiation

Electromagnetic radiation travels through space in a wave motion. An electromagnetic wave has an electric and a magnetic field mutually perpendicular to each other and to the direction of propagation of the wave. The following terms are used to describe these waves;

$$u = \frac{8pk_B T}{l^4}$$

- ***Wavelength*** l
- ***Speed*** ***c***
- ***Frequency*** n ***= c /*** l
- ***Wavenumber*** n ***= 1 /*** l

3. Blackbody Radiation

- Material bodies give off ***radiation*** when heated. The burner of an electric stove turns red when heated.

  Red $\rightarrow$ Blue
  Low ν $\rightarrow$ High ν
- A body which absorbs and emits all frequencies is called ***a blackbody***.
- ***Stefan-Boltzmann Law***

  Rate of emission of energy from the cavity = $\sigma . T^4$
- ***Wien's Displacement Law***

  The maximum wavelength is inversely proportional to the temperature:

  ?max *T* = 0.2898 x 10-2 m • K

  ?max is the wavelength

  T is the absolute temperature of the object emitting the radiation
- ***Ultraviolet Catastrophe***

  At long wavelengths, the theoretical results are good. At short wavelengths, classical principals predicted infinite energy but experiments showed no energy. This contradiction is called the *ultraviolet catastrophe*

- ***Rayleigh-Jeans Formula***

$$u_l = \frac{8pk_B T}{l^4}$$

They applied the law of equipartition of energy and assumed a continuous distribution of wavelengths.

$$\lambda \to 0 \quad u \to \infty \quad \text{Energy} \to \infty$$

- ***Planck's Hypothesis***

Radiation emitted was caused by the oscillations of the electrons. The energies of the electrons are discrete.

$E = h.\nu$ Energy of e- is quantized.

The energy is in small packages called quanta.The distribution of the wavelengths is discontinuous.

4. Photoelectric Effect

If a beam of light falls on a metal plate, the plate emits electrons. This is called the *photoelectric effect.* The emitted electrons are called *photoelectrons.* The effect was first discovered by Hertz and explained by Einstein.

In the experiment, a metal plate is placed in an evacuated flask as a cathode and a metal wire as an anode. At the beginning, there is no current. But as soon as the metal is irradiated, current begins to flow. The metal ejects electrons. There are 3 important observations:

- Whether or not e- s are emitted depends only on the frequency of the light. The # of e- s is proportional to the intensity.
- There is no time lag between the light beam striking the metal and the emission of e-s.
- Below a certain frequency characteristic of the metal, no electrons are ejected.

Einstein stated that there is a certain potential energy that the electron is bound to the metal atom. The energy of radiation is in small packages called photons. Each electron takes only one photon. Einstein's photoelectric equation;

$$h\nu = W + K.E.$$

In this equation, W is the potential energy called the"threshold energy", K.E. is the kinetic energy of the ejected electron and $h\nu$ is the energy of the incident radiation. The critical or the threshold frequency is defined as;

$$h\nu_o = W$$

As the intensity of light is increased, the # of photons and the # of ejected electrons increase. The K.E. of the electron depends only on the frequency of the incident light.

So, we may conclude that the energy of radiation is in small packages, photons (=particle). Electromagnetic wave with a frequency ν is a particle with energy $h\nu$. This is called *Particle - Wave duality.*

5. Atomic Spectra

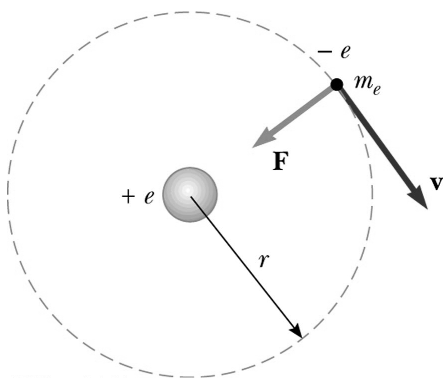
When a ray of light is passed through a prism, the ray is refracted. A wave with a short λ refracts more than a wave with a long λ. Spectrum is the shape of light separated into λ s.

When a chemical substance is heated in an electric arc or Bunsen flame light is emitted. If a ray of this light is passed through a prism a line spectrum is produced. The line spectrum of each element is unique.

When left alone, every atom is in the ground state. When the atoms are heated, electrons absorb energy and jump to higher energy levels. The excited state is thermodynamically unstable, so the electron returns back to the lower energy state by emitting the extra amount of energy. This energy is equal to the difference between the energies of the two levels. The emitted radiation has a certain frequency and wavelength. So, line spectra are produced.

6. Bohr's Model of the Atom

According to the Bohr Model, the hydrogen atom consists of a central nucleus with a charge +e, and an electron with a charge –e rotating about the nucleus with velocity v in a circular orbit of radius r.



For mechanical stability, the electrical force of attraction must balance the centrifugal force. As a result, in Bohr's model;

- The electron can move around the nucleus only in certain orbits
- These allowed orbits correspond to definite stationary states of the atom. The energy of the electron depends upon the orbit in which it is moving.
- In a stationary state, the atom is stable and does not radiate
- Only in the transition of the electron from one stable orbit to another, radiation is emitted or absorbed. The frequency of the radiation is given by;

  $$\Delta E = h\nu$$

  where ΔE is the difference in the energies of the two orbits.
- The certain orbits are defined by the "angular momentum condition"

$$mvr = \frac{nh}{2p} \cdots\cdots\cdots\cdots n = 1,2,3,4,\cdots\cdots$$

n is the quantum number.

- The radius of the orbit is expressed by;

$$r = \frac{n^2h^2}{4p^2me^2} \cdots\cdots\cdots n = 1,2,3,4,\cdots\cdots\cdots$$

If n = 1 , then r = a_o which is the radius of the first Bohr orbit; $r = n^2 a_o$

- The total energy of the electron is;

$$E_n = -\frac{e^2}{2r} = -\frac{e^2}{2a_o}\left(\frac{1}{n^2}\right)$$

E depends upon the integer, the quantum number n.

- If the electron moves from E_1 to E_2, it emits the energy equal to $\Delta E = E_2 - E_1$ to go back to the lowest energy orbit.

$$\Delta E = E_2 - E_1 = hn = \frac{hc}{l} = \frac{e^2}{2a_o}\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

$$\frac{1}{l} = \frac{e^2}{2a_ohc}\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right) = R\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

The above equation is called "Rydberg Formula" and R is the Rydberg constant. This equation is for all the lines in the 5 groups of the hydrogen atom spectrum.