QUANTUM CHEMISTRY: HYDROGEN ATOM   [REF: Ch 9]

QUANTUM   Latin for "amount"
THEORY

In this part of the Course (Part III), we shall look at matter "*nano*scopically", which deals with the basic elements of chemistry: atoms and molecules. Here, we shall first examine atoms - their physical properties and electronic structure - and the periodic table (Ch 9-10). Later, we shall examine making up "bonds" between atoms to form molecules (Ch 11-12). Before we can discuss atoms, we need to give a clash course on quantum theory.

Classical mechanics (Newton's laws) is very good at explaining "everyday-life" physics but it is wrong when it comes to small things, like the atoms. It is based on two presumptions:

1. A particle travels in a trajectory with a "precise" position and a "precise" velocity (momentum) at each instant.
2. Any type of motion can be excited to a state of arbitrary energy.

As we shall see, the first violates the Uncertainty Principle while the second violates the idea of quantization of energy. There are 3 key experimental results that point to the fundamental flaws in classical mechanics.

❶ BLACK-BODY RADIATION and QUANTIZATION OF ENERGY

Black body − an ideal body that absorbs and emits all frequencies.

Radiation   − electromagnetic radiation or EM radiation or light

Light as "EM waves" (Newton's optics): Linearly polarized (or circularly polarized) light can be thought of waves of electric and magnetic field (or EM field).

wavelength x frequency = speed of light
$$\lambda \nu = c = 2.9979 \times 10^8 \text{ m/s}$$

EM spectrum (REF: Fig. 9.3)

Absorption or emission spectroscopy (more in Chem 129)

A black-body radiator can be thought of as a pinhole in a heated cavity (e.g. a burner in a train engine). Any radiation inside is reflected many times and in thermal equilibrium with a temperature T. The pinhole allows some radiation (called black-body radiation) to escape and be detected.

Two experimental observations:

Wilhelm Wien (1893): $\lambda_{max} \propto 1/T$

Josef Stefan (1879): power per unit area $\propto T^4$

Classical explanation by Lord Rayleigh and James Jeans (1899):

energy density from λ to $\lambda + \delta\lambda$ = $\dfrac{8\pi kT}{\lambda^4}\delta\lambda$

To explain the so-called ultraviolet catastrophe, Max Planck (1900) proposed the quantization of energy:

$$E = n\,h\nu$$

where   E is the energy of an oscillator (dipole) of frequency ν
       n is an integer (= 0, 1, 2, ... etc.)
       h is later known as the Planck's constant (= 6.626×10^{-34} J/Hz)

Then, energy density from λ to $\lambda + \delta\lambda$ = $\dfrac{8\pi hc}{\lambda^5}\left(\dfrac{1}{e^{hc/(\lambda kT)} - 1}\right)\delta\lambda$

The effect of energy quantization is to eliminate the contribution from the high frequency oscillators (because they cannot be excited with the energy available) and so short-λ radiation is not emitted.

We can then think of radiation as excitation of an oscillator to its evenly spaced energy levels or as particles coined by G.N. Lewis as photons.

EG   Calculate the number of photons emitted by a 100W yellow lamp in 1.0 s. Take the wavelength of yellow light as 560 nm and assume 100% efficiency.

Since   energy = power x time = (100 W)(1 s) = (100 J/s)(1s) = 100 J

For λ = 560 nm, ν = c/(560 nm) = 5.4×10^{14} Hz, the energy of 1 yellow photon is   E = hν = (6.626×10^{-34} J/Hz)(5.4×10^{14} Hz) = 3.7×10^{-19} J

Number of yellow photons in 100 J = 100 J / 3.7×10^{-19} J = 2.7×10^{20}

❷ PHOTOELECTRIC EFFECT, ELECTRON DIFFRACTION, and WAVE-PARTICLE DUALITY

Electrons as particles

J.J. Thomson (1897):   measured charge-to-mass ratio of a "cathode" ray. [Nobel Prize in 1906 and knighted in 1908]

Photoelectric effect: electron ejection from a metal by UV radiation.
Facts: (1) ν must be above a certain threshold characteristic of the metal before electrons can be ejected; (2) the intensity of the light does not affect whether the electron will be ejected or not; (3) the kinetic energy of the photoelectron is directly proportional to ν.

Kinetic energy of the photoelectron is

$$\tfrac{1}{2}\, m_e\, v^2 = h\,\nu - \Phi \qquad \text{Einstein's equation (1905)}$$
$$[\text{Nobel Prize 1926}]$$

where Φ is the work function (unique to the metal).

Electrons as waves

Clinton Davisson and Lester Germer (1927): A beam of electrons was directed at a Ni surface and the scattered electrons showed angular variation consistent with diffraction.

George Thomson (1927): measured diffraction pattern of a transmitted electron beam through a metal foil.

Louis de Broglie relation (1924) [Nobel Prize 1929]:

$$\lambda = h / p = h / (mv)$$

where p is the momentum of the particle, and λ is known as the de Broglie wavelength of the matter wave.

EG Calculate the de Broglie wavelength of a baseball (5 oz) travelling at 100 mph.

m = (5 oz)(1 lb/16 oz)(1 kg/ 2.2 lb) = 0.14 kg
v = (100 mi/h)(1610 m/mi)(1 h/3600 s) = 44.7 m/s
p = mv = (0.14 kg)(44.7 m/s) = 6.3 kg m/s

λ = h/p = 6.626x10^{-34} J s / (6.3 kg m/s) = 1.1x10^{-34} m
= 1.1x10^{-22} pm

This is thus a very tiny wavelength and is completely undetectable.

❸ **"LINE" SPECTRUM OF H, and THE BOHR ATOM**

Recall emission spectroscopy (REF Fig. 9.9)
Excite the gas by high temperature or electrical discharge from the ground state to an excited state; measure EM radiation (emitted as the gas deexcites from the excited state to the ground state) as function of ν to get an emission spectrum.

1885 Johann Balmer   saw a series of lines with discrete ν's –
                                 Balmer series in the visible region
                                 REF: Fig. 9.10

The "discreteness" of the transitions suggests that the target (atoms or molecules) possesses only discrete energies, and not any arbitrary energy. Here, in a spectrum, we observe the change in E between an initial state and a final state, and $\nu = \Delta E/h$.

Bohr's model: assumed quantization of angular momentum ($L = p\mathbf{x}r$), which gave rise to "planetary" motion of electron around the nucleus – there are "well-defined" definite circular orbits. This turns out to be brilliant (i.e. it gives the right answer) but wrong!

The "Bohr" radius: $\quad$ $r = a_0 n^2$ $\quad$ where $a_0 = 0.529$ Å = 52.9 pm

The energies of the allowed "Bohr" orbits are:

$$E = -h\nu = - h (R/n^2) \quad \text{where} \quad n = 1, 2, 3, ...$$
$$R = \text{Rydberg constant} = 3.29 \times 10^{15} \text{ Hz}$$
$$hR = \text{Rydberg constant} = 2.179 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$$

The transition energies:

$$\Delta E = E_{final} - E_{initial} = - h R \left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2} \right)$$

When $n_{lower} = 2$ and $n_{upper} = 3, 4, 5...$, we have the Balmer series.

EG $\quad$ Calculate the ionization energy of the H atom.

The ionization energy (IE) is the energy required to take the electron from its ground state ($n_{lower} = 1$) to the first unbound state ($n_{upper} = \infty$)

$$IE = - hR (1/\infty^2 - 1/1^2) = - hR (0 - 1) = hR = 2.18 \times 10^{-18} \text{J} = 13.6 \text{ eV}$$

Conclusion: Forget classical theory, think quantum mechanically!