Undergraduate Semester – VI

MJC – 12 (T): Physical Chemistry: Quantum Chemistry & Spectroscopy (T)

**Quantum Chemistry & Spectroscopy**
Theory: 4 credits

Unit 1: Elementary Quantum Mechanics

Quantizing Electrons in the Radiator:

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is quantized rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1 (previous class), so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus, energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

Quantization:

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also similar to going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but not −1.33 electron charges.
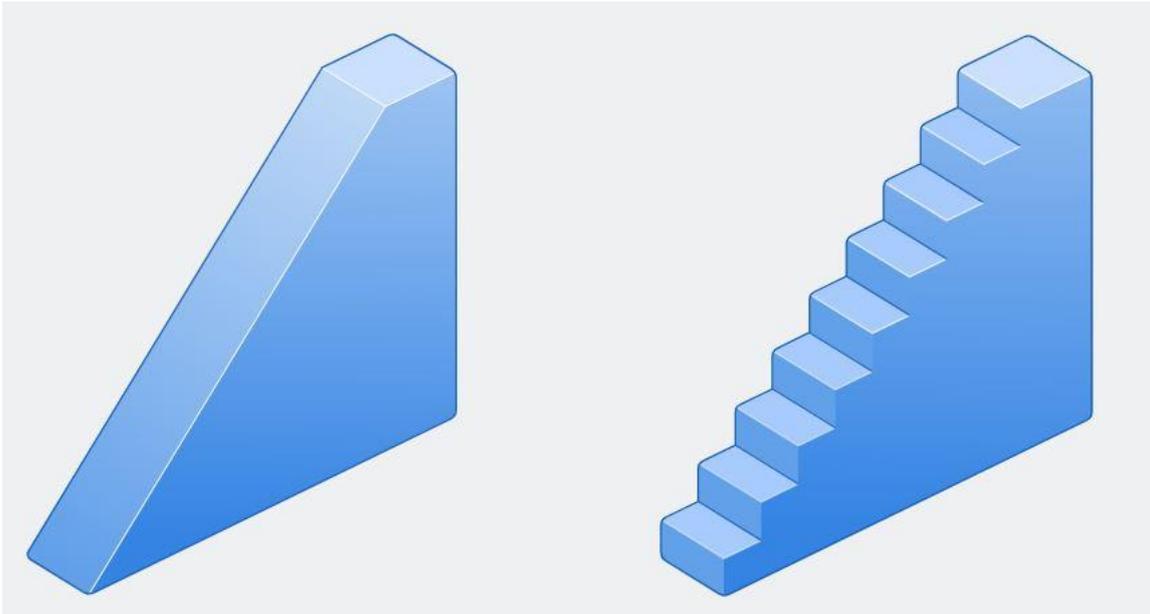
A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed).

Planck's quantization of energy is described by his famous equation:

$E = h\upsilon$

where the proportionality constant h is called Planck's constant, one of the most accurately known fundamental constants in science.

$h = 6.626070040(81) \times 10^{-34}$ J.s

However, for our purposes, its value to four significant figures is sufficient:

$h = 6.626 \times 10^{-34}$ J.s

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\upsilon$, Planck devised an equation that fit the experimental data shown in Figure 1. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-

energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature. At the time he proposed his radical hypothesis, Planck could not explain why energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.