

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 1

Sep 4th, 2013

Objective

- To provide a brief historical motivation of the need of quantum mechanics.
- To remind the student basic concepts and equations related with quantization of energy and the quantum theory of light.
- To show examples the use of the equations presented.

What is quantum chemistry?

- Molecules and solids consist of two types of particles: positively charged nuclei and negatively charged electrons.
- Chemical reactions are processes that involve transfer of nuclei and electrons from one group of such particles to another.
- Motivated by this and for the purposes of this course we can “define” **chemistry** as the mechanics of nuclei and electrons.
- In order to understand the behaviour of molecules we need to learn the laws that describe systems of electrons and nuclei.
- **Quantum chemistry** formulates equations to describe the mechanics of nuclei and electrons. It also provides solution methods to those equations.
- For *any given electronic structure* (collection of electrons and nuclei) there exists an equation that determines the structure’s properties.

How trivial is quantum mechanics?



“I don't like it, and I'm sorry I ever had anything to do with it.”

Erwin Schrödinger

Nobel Prize in Physics 1933



“I think I can safely say that nobody understands quantum mechanics.”

Richard P. Feynman

Nobel Prize in Physics 1965

Classical vs. quantum mechanics



- **Classical mechanics.** (Newton's equations of motion) correctly describe macroscopic bodies. It fails for the description of microscopic objects (electrons and nuclei).
- In 1910s it was learned that the hydrogen atom was composed of a nucleus and an electron “orbiting” around it. Classical physics predicted that the electron should spiral down toward the nucleus, resulting in the collapse of the hydrogen atom.
- **Quantum mechanics** was able to explain the stability of the hydrogen atom. This is one of the reasons why quantum mechanics is crucial in chemistry.
- In classical mechanics particles have definite trajectories. This is not the case in quantum mechanics. One way to understand this is due to the particle-wave duality.

Classical theories of physics and chemistry

Some of the key assumptions of **classical physics and chemistry** are:

- All physical properties vary continuously
- There is a clear distinction between particles and waves
- Determinism (classical determinism): the behaviour of physical objects can, in principle, be determined at any time.

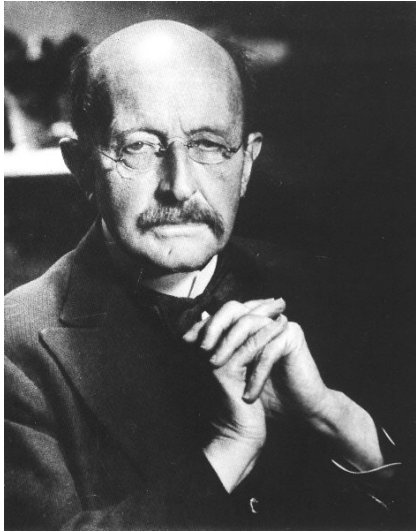
The “discovery” of quantum mechanics came as a shock for scientists, specially because many of them believed that all the physical laws of the universe were already known and there was nothing else left to be discovered (end of the 19th century)

Experiments that classical physics cannot explain

- Rapid decrease of heat capacity of atomic crystals near 0 K.
- Realization that the kinetic energy of electrons ejected from a metal surface is independent on the intensity of the incident light (photoelectric effect).
- Characteristic peaked distribution of the intensity of *blackbody* radiation as a function of light frequency (ultraviolet catastrophe)
- Observation that atomic emission/absorption spectra are not continuous. They consist of a series of sharp lines.

These “contradictions” were not resolved within classical physics until a radically new theory arose. That theory was **quantum mechanics**

Energy is quantized

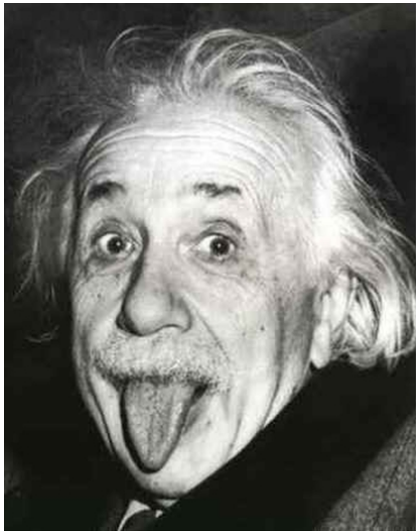


- Max Planck proposed in 1900 that the energy absorbed or emitted by a heated body, ΔE , comes in multiples of $h\nu$, where ν is the frequency of the radiation:

$$\Delta E = nh\nu ; n = 1, 2, 3, 4...$$

Planck's constant (universal constant)

$$h = 6.626069 \times 10^{-34} \text{ J s}$$



- Albert Einstein suggested in 1905 that light and all other form of electromagnetic radiation of frequency ν consist of **quanta** of energy

$$E = h\nu$$

- These **quanta** is what we know today as **photons**

Basic equations related with quantum theory of light

- Energy of a photon: $E = h\nu$

Planck's constant

$$h = 6.626069 \times 10^{-34} \text{ J s}$$

- Wavelength: $\lambda = cT = c/\nu$

T – Period of the wave

c – Speed of light in vacuum

Speed of light in vacuum

$$c = 2.99792458 \times 10^8 \text{ m/s}$$

- Frequency: $\nu = 1/T = c/\lambda$

- Wavenumber: $\tilde{\nu} = 1/\lambda = \nu/c$

- Radiation power: $P = E/t = \frac{(\text{energy})}{(\text{time})}$

Example 1.1

Compute the number of benzene molecules that can be excited by a 6.00 mJ light pulse at 180 nm assuming that each molecule absorbs just one photon and that each absorption results in an excitation (quantum yield of 100%)

Solution. The energy of a single photon of wavelength λ is

$$\begin{aligned} E_{\text{photon}} &= h\nu = \frac{hc}{\lambda} = \frac{(6.626069 \times 10^{-34} \text{ J} \cdot \text{s})(2.99792458 \times 10^8 \text{ m/s})}{180 \times 10^{-9} \text{ m}} \\ &= 1.1 \times 10^{-18} \text{ J} \end{aligned}$$

The total number of photons (and therefore the number of excited benzene molecules) in the pulse is then

$$N = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{6.00 \times 10^{-3} \text{ J}}{1.1036 \times 10^{-18} \text{ J}} = 5.437 \times 10^{15}$$

What is the new number if the quantum yield is 60% ?

Example 1.2

Compute the theoretical amount of energy, in kJ , that would be stored in 1 mol of benzene if each molecule absorbed one photon at 180 nm and remained indefinitely in the excited state. How does this compare to the energy density of TNT which is of the order of 1000 kJ/mol ?

Solution. One mole of benzene contains Avogadro's number of molecules. Since each molecule stores E_{photon} (example 1.1) then 1 mol of benzene would store the energy

$$\begin{aligned} E_{\text{photon}} &= N_{\text{A}} E_{\text{photon}} = \left(6.022142 \times 10^{23} \text{ mol}^{-1} \right) \left(1.1036 \times 10^{-18} \text{ J} \right) \\ &= 664.6 \text{ kJ / mol} \end{aligned}$$

which is of the order of the energy density of TNT.