Quantization: A Scientific Revolution

CHEM 361B: Introduction to Physical Chemistry

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Lecture 3

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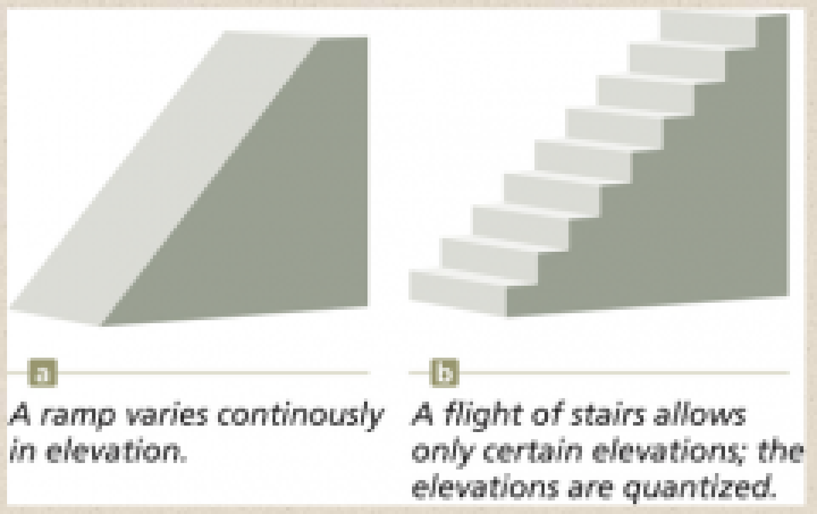
Learning Objective: Learn about large failures in classical mechanics and where the idea of quantization of energy solved these problems

References:

- McQuarrie §1.1 - 1.4

Continuous Vs Quantized



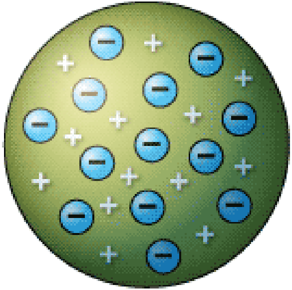
Physics in the 19^{th} century

The scientific community believed that physics was a dead science

- Newtonian mechanics was well defined
- Gibbs developed a theory of thermodynamics still in use today
- Maxwell, Boltzmann and Gibbs had developed statistical mechanics
- Maxwell also unifed the fields of optics, electricity and magnitism

However, several problems existed that were explained by introducing quantized energy which revolutionized science

Inability to produce a clear picture of an atom



Three discoveries:

- The electron by J.J. Thomson
- The x-ray by Röentgen
- Radioactivity by Becquerel

showed that the atom was far more complex than originally thought.

This complexity was never resolved classically and was the basis for all future failures of the theory.

Black-body Radiation

When objects are heated they radiate according to the Stefan-Boltzmann law:

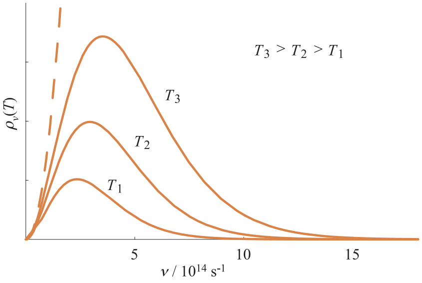
$$E = \frac{4\sigma}{c} T^4$$

The colour goes from a dull red to white and then blue.

An ideal body would absorb and emit all frequencies.

These are called black bodies.

The Classical Explanation



The Rayleigh-Jeans law

$$\rho_\nu(T)\delta\nu = \frac{8\pi\nu^2}{c^3} k_B T \delta\nu$$

where

- $\rho_\nu(T)d\nu$ - Radiant energy density between the frequencies ν and $\nu + d\nu$
- ν - Frequency (Hz)
- c - Speed of light $(3.0 \times 10^8 m \cdot s^{-1})$
- k_B - Boltzmann's constant $(1.38 \times 10^{-23} J \cdot K^{-1})$
- T - Temperature (K)

The Ultraviolet Catastrophe

The Rayleigh-Jeans law only predicted emission densities for small frequencies. Furthermore:

$$
\begin{aligned}
E &= \int_0^\infty \rho_\nu(T)\delta\nu \\
&= \frac{8\pi}{c^3} k_B T \int_0^\infty \nu^2 \delta\nu \\
&= \frac{8\pi}{c^3} k_B T \frac{\nu^3}{3}\Big|_0^\infty \\
&= \infty!
\end{aligned}
$$

This implies that the total energy radiated per unit time for all $T > 0$ is infinite.

This is obviously false and is referred to as the ultraviolet catastrophe.

Explaining the Spectrum

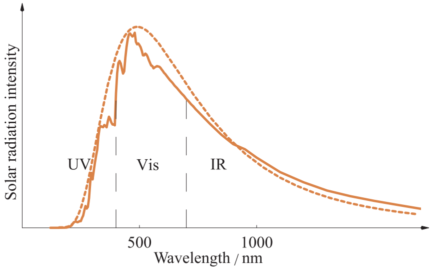
Max Planck in 1901 published a revolutionary idea to explain the blackbody problem: Atoms can not assume any energy but can only vibrate at discrete energy levels given by

$$\epsilon_n = nh\nu \qquad n = 0, 1, 2, \ldots$$

where h was a contant of proportionality but is now called Planck's Constant and has a value of $6.626 \times 10^{-34} J \cdot s$.

In essense, the **energy in the system is quantized**.

The Planck Distribution Law for Black-body Radiation



Planck assumed that the Rayleigh-Jeans law was fundamentally correct but that the average energy of the oscillators with frequency ν was incorrect. His relation

$$\rho_\nu(T)\delta\nu = \frac{8\pi h\nu^3}{c^3}\frac{\delta\nu}{e^{h\nu/k_B T} - 1}$$

properly assigned the correct spectrum.

The Photoelectric Effect

When a metal surface is illuminated with ultraviolet light, electrons are emitted

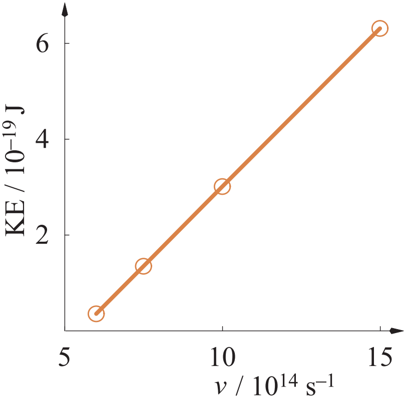
Two experimental observations contradict CM

1. The kinetic energy of an ejected electron is independent of light intensity

   Kinetic energy is measured by determining the stopping potential: $\frac{1}{2}mv^2 = -eV_s$

2. There is a threshold frequency to observe electron emission

Explaining the Photoelectric Effect



Einstein proposed in 1905 that light also is quantized ($\epsilon = h\nu$). Using conservation of energy he showed that

$$\frac{1}{2}mv^2 = h\nu - \phi$$

where ϕ is the work function. This relationship can be re-written as

$$\frac{1}{2}mv^2 = h(\nu - \nu_0)$$

where the slope of the line is equal to h.

Photoelectric Effect Example

1. When lithium is illuminated with light one finds that it has a kinetic energy of 2.935×10^{-19} J for $\lambda = 300.0$ nm and 1.280×10^{-19} J for $\lambda = 400.0$ nm. Calculate:
    - Planck's constant (Answer: $h = 6.625 \times 10^{-34}$J·s)
    - The threshold frequency (Answer: $\nu_0 = 5.564 \times 10^{14}$Hz)
    - The work function of lithium (Answer: $\phi = 3.69 \times 10^{-19}$J)

Heat Capacity in Solids

Classically, the mean energy of a solid for one mole is

$$U = 3RT$$

where $R = 8.314\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$ (molar gas constant), and T is the absolute temperature.

The heat capacity can then be calculated as

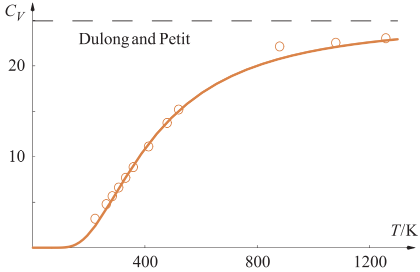
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3R$$

This explanation concludes that the heat capacity is independent of temperature.

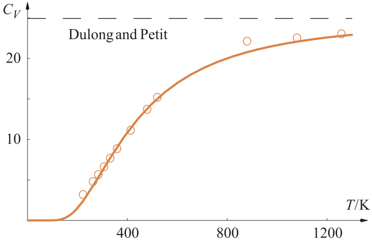
Heat Capacity in Solids (cont.)

Classical view was incompatible with experiment at low temperatures.

Einstein, in 1907, followed Planck, and assumed that the solid could be represented as a collection of harmonic oscillators with discrete energy values $nh\nu$.



Heat Capacity According to Einstein



Assuming that all oscillators had the same frequency ν_0 the internal energy of a solid is

$$U = N\frac{3h\nu_0}{(e^{h\nu_0/k_BT} - 1)}$$

where N is the number of atoms. The heat capacity is now calculated as:

$$C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{[e^{\theta_E/T} - 1]^2}$$

where $\theta_E = h\nu_0/k_B$

Summary

- The basic principles of science were thought to be solved by the end of the 19th century except for a few key exceptions.
  - Blackbody radiation
  - Photoelectric effect
  - Heat Capacities in solids
- Using the idea that energy was quantized, with a new constant of proportionality, Planck's Constant (h), naturally emerging from the solutions of these problems, these key exceptions were resolved. This was the beginning of the quantum era.