Origins of Quantum Mechanics

Key Milestones in the Development of Quantum Theory

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Outline

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Introduction

- Until the end of the 19th century, most observations could be explained by principles of classical physics:
  - Matter $\rightarrow$ Newton's laws of motion
  - Radiation (waves) $\rightarrow$ Maxwell's laws of electromagnetism
- Einstein's theory of relativity (1905) only showed that physics is different at high velocities, without changing the boundary between matter and light.
- At the end of the 19th century and the beginning of the 20th, a series of observations were made which could not be explained by classical physics, especially at the very small scales.
- In this chapter, we will explore these key experiments and theories that led to the development of quantum mechanics.

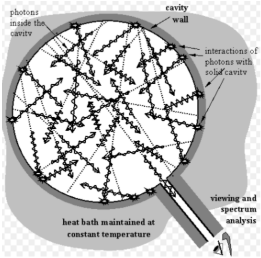
Outline

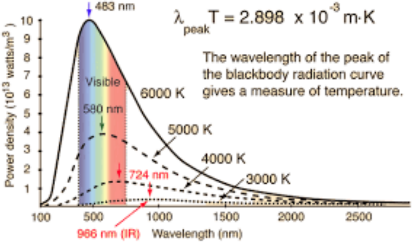
Blackbody Radiation

Observations

- A *blackbody* is an idealized physical body that absorbs incident electromagnetic radiation of all wavelengths.
- It emits radiation depending on its temperature.
- Classical theory failed to explain the emission behavior.

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1}$$





Blackbody Radiation

Failure of the classical theory – the ultraviolet catastrophe

- Lord Rayleigh and J. Jeans assumed a contribution of $k_B T$ for each electromagnetic wave.
- This resulted in a spectral distribution (monochromatic energy density) of

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} k_B T$$

- This distribution must be integrated over all wavelengths to find the total emission:

$$\rho_{tot} = \int_0^{\infty} \rho(\lambda, T) d\lambda \to \infty$$

- The integral is said to *diverge* at small wavelengths.
- This is the so-called *ultraviolet catastrophe*.

Blackbody Radiation

Planck's Hypothesis: Quantization of Energy

- In 1900, Max Planck proposed that energy is quantized to resolve the ultraviolet catastrophe – *quanta* of energy.
- The energy of each quantum is proportional to the frequency of radiation:

$$E = nh\nu \quad \text{where} \quad n = 1, 2, 3, \ldots$$

- E is the energy of the radiation, h is Planck's constant ($h = 6.626 \times 10^{-34}$ Js), and ν is the frequency.
- Planck's hypothesis led to a new formula for the radiation spectrum, known as Planck's law:

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1}$$

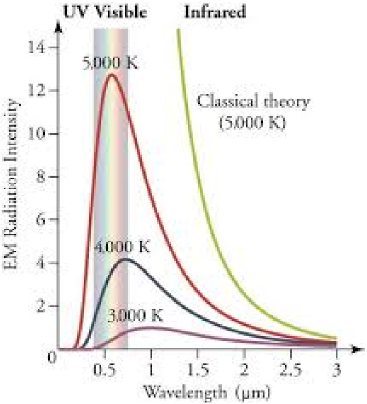
Blackbody Radiation

Planck's Law and the Ultraviolet Catastrophe

- At long wavelengths ($h\nu \ll kT$), the law reduces to the Rayleigh-Jeans law, which matches classical theory:

$$\rho(\lambda, T) \longrightarrow \frac{8\pi k_B T}{\lambda^4}$$

- At short wavelengths ($h\nu \gg kT$), Planck's law prevents the infinite radiation predicted by the classical theory.
- This resolved the divergence known as the ultraviolet catastrophe.



Outline

Heat Capacities

Classical Prediction of Heat Capacities

Equipartition Theorem

Each degree of freedom contributes $\frac{1}{2}k_B$ to the heat capacity.

- In a solid, there are $3N$ vibration modes of the nuclei (ignoring the electronic contribution), therefore the C_V should be:

$$C_V = \frac{3}{2}Nk_B$$

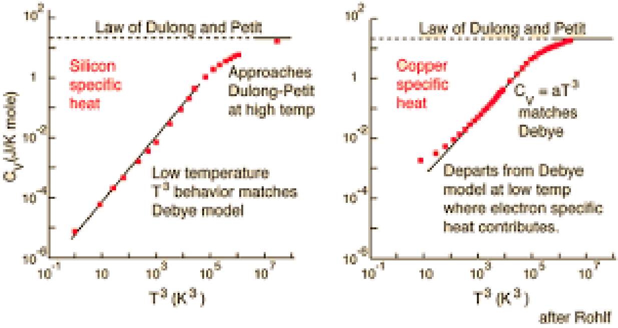
where N is the number of particles and k_B is Boltzmann's constant.

- In other words, classical thermodynamics predicts that heat capacity (C) should be constant at all temperatures.

Heat Capacities

Deviations at Low Temperatures

- Experimental data showed deviations from classical predictions at low temperatures.
- The approach to zero that C_V displays at low temperatures cannot be explained by classical physics.



Heat Capacities

Quantum Treatment – Einstein's Model of Heat Capacities (1907)

- In 1907, Einstein proposed a quantum model where each atom displayed vibration modes quantized with energy levels:

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

- The heat capacity at constant volume C_V is given by:

$$C_V = 3Nk_B \left(\frac{h\nu/k_B T}{\sinh(h\nu/2k_B T)}\right)^2$$

Heat Capacities

Quantum Treatment – Debye's Model of Heat Capacities (1912)

- In 1912, Debye extended Einstein's model to account for low-temperature behavior more accurately.
- Debye introduced a continuum of vibrational modes (phonons) instead of discrete oscillators.
- The Debye model predicts heat capacity at low temperatures:

$$C_V \approx 9Nk_B \left(\frac{T}{\Theta_D} \right)^3$$

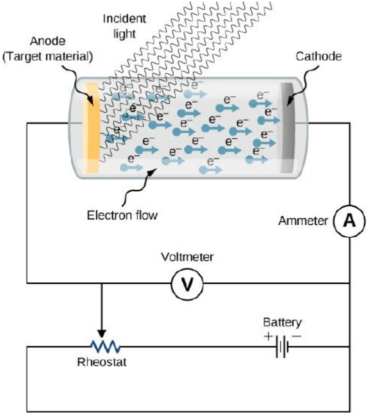
  where Θ_D is the Debye temperature.
- At high temperatures, the heat capacity approaches the classical value of $3Nk_B$.

Outline

Photoelectric Effect

Introduction to the Photoelectric Effect

- The photoelectric effect involves the emission of electrons from a metal surface when illuminated by light.



Photoelectric Effect

Classical Prediction vs. Experimental Results

- Whether electrons are ejected depends on
  - Classical: The intensity of light.
  - Quantum: The frequency of light.
- Kinetic energy of electrons depends on
  - Classical: The intensity of light.
  - Quantum: The frequency of light.
- At low intensities, electron ejection
  - Classical: Takes time.
  - Quantum: Occurs instantaneously above a certain threshold.

Photoelectric Effect

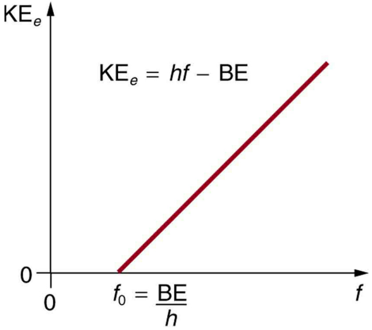
Quantum Treatment – Einstein's Explanation (1905)

- Einstein (1905) proposed that light is composed of quantized packets called photons.
- Energy of each photon is given by:

$$E = h\nu$$

  where h is Planck's constant and ν is the frequency of light.
- Electrons are ejected when the photon energy exceeds the work function ϕ of the metal:

$$KE_{\text{max}} = h\nu - \phi$$



Outline

Atomic Spectra

Early discoveries

- Melville (1752) showed that light from an incandescent gas is composed of discrete *emission lines*.
- Similarly, each element also has a discrete set of *absorption lines*.
- Kirchhoff (1859) noticed that absorption and emission lines coincide an are characteristic to each element.
- The energy of emitted photons is given by the difference in energy levels:

$$E_{\text{photon}} = E_n - E_m$$

  where E_n and E_m are the energies of the higher and lower energy states, respectively.

Atomic Spectra

Balmer Series

- Balmer studied the spectrum of hydrogen and discovered that the spacing between the lines of the spectrum (H_α, H_β, H_γ, $\cdots$) displayed regularies.
- Now known as the Balmer series, these lines describe the wavelengths of light emitted by hydrogen atoms when an electron falls from a higher energy level to the $n = 2$ level.
- The wavelengths of these spectral lines are given by the formula proposed by Rydberg (1889):

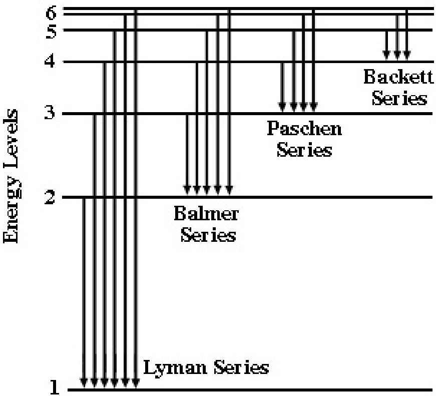
$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where λ is the wavelength, R is the Rydberg constant ($1.097 \times 10^7\,\mathrm{m}^{-1}$), and n is the principal quantum number ($n > 2$).

Atomic Spectra

Balmer Series

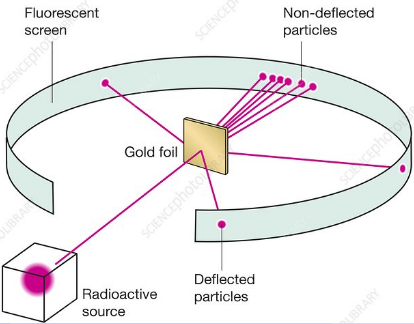
- The Balmer series was easy to discover since most of the transitions are in the visible range.
- There are other series distinguished from the Balmer series by the final state.



Atomic Spectra

The nuclear atom — Rutherford Experiment

- Rutherford's gold foil experiment provided evidence for the nuclear model of the atom.
- α particles were directed at a thin gold foil, and their scattering was observed.



Atomic Spectra

The nuclear atom — Rutherford Experiment

- Most particles passed through, but some were deflected at large angles, suggesting a dense, positively charged nucleus.
- The scattering angle θ is related to the nucleus radius R and the incident energy E by:

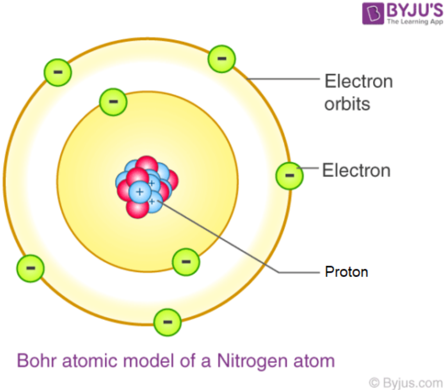
$$\frac{d\sigma}{d\Omega} = \frac{Z^2 e^4}{16\pi\epsilon_0^2 E^2} \cdot \frac{1}{\sin^4(\theta/2)}$$

where $\frac{d\sigma}{d\Omega}$ is the differential cross-section, Z is the atomic number, and e is the electron charge.

Atomic Spectra

Attempt at an Explanation — The Bohr Model

- The Bohr model, proposed by Niels Bohr in 1913, describes the hydrogen atom with quantized electron orbits combining ideas from Rutherford's nuclear atom, Planck's quanta, and Einstein's photons.



Atomic Spectra

Attempt at an Explanation — The Bohr Model

- Electrons orbit the nucleus in specific, quantized orbits without radiating energy.
- The energy levels of these orbits are given by:

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2}$$

where E_n is the energy of the nth orbit, Z is the atomic number, e is the electron charge, ϵ_0 is the permittivity of free space, $\hbar$ is Planck's constant divided by 2π, and $n = 1, 2, \ldots \infty$ is the principal quantum number.

Atomic Spectra

Successes and Limitations of the Bohr Model

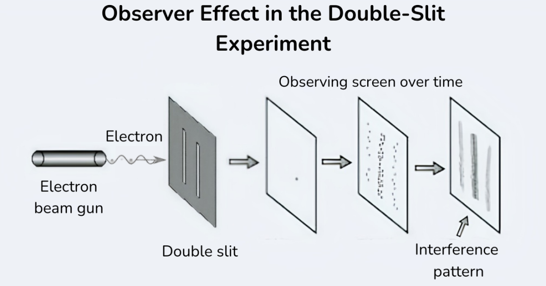
- **Successes:**
  - Explained the Hydrogen spectral lines.
  - Introduced the concept of quantized electron orbits.
  - Provided a theoretical basis for the stability of electrons in orbit without radiating energy, addressing the problem of electronic spiral.
- **Limitations:**
  - Does not accurately describe atoms with more than one electron.
  - Does not explain the fine structure of spectral lines observed in hydrogen, which arises from relativistic corrections and spin-orbit coupling.
  - Assumes well-defined electron orbits.

Outline

Wave-Particle Duality

Young's Double Slit Experiment

- Historically, light was considered a wave, as evidenced by diffraction and interference. However, the photoelectric effect and blackbody radiation suggested light also has particle-like properties.
- Similarly, very small particles like electrons can exhibit wave-like properties such as interference in Young's double slit experiment.



Wave-Particle Duality

De Broglie's Hypothesis and Matter Waves

- In 1924, Louis de Broglie extended the concept of wave-particle duality to matter, suggesting that all particles have an associated wavelength.
- De Broglie hypothesized that the wavelength λ of a particle is related to its momentum p by:

  $$\lambda = \frac{h}{p}$$

  where h is Planck's constant, and $p = mv$ is the momentum of the particle with mass m and velocity v.
- The de Broglie hypothesis has explained the double-slit experiment.