Chapter 5: Quantization of Atomic Energy Levels

Modern Physics Lecture Notes

Chapter Overview

This chapter explores how the energy of electrons in atoms is quantized. While classical mechanics and electromagnetism treat energy as continuous, experiments showed that energy changes occur in discrete packets. The failure of classical physics to explain this led Niels Bohr (1913) to propose a new atomic model that successfully described spectral lines and atomic stability.

1 5.1 Introduction

In Chapter 4, we saw that electromagnetic radiation is quantized into discrete photons with energy

$$E = hf,$$

where h is Planck's constant and f is the frequency. This chapter extends that idea to matter — showing that electrons within atoms also occupy only discrete energy states.

Classical physics could not explain:

- Why atoms emit light at specific frequencies instead of a continuous spectrum.
- Why atoms are stable, despite the prediction that orbiting electrons should radiate energy and collapse into the nucleus.

Bohr's model introduced quantized electron orbits to solve both puzzles. Though later superseded by quantum mechanics, Bohr's ideas were the first to correctly link observed atomic spectra to atomic structure.

2 5.2 Atomic Spectra

Historical Background

- **Isaac Newton (1666):** Demonstrated that white light, when passed through a prism, splits into a continuous spectrum of colors.

- **Fraunhofer (1814):** Discovered dark absorption lines in sunlight — now known as *Fraunhofer lines* — showing missing wavelengths absorbed by gases in the Sun's outer layers.
- **Kirchhoff & Bunsen (1859):** Linked these spectral features to specific elements, creating the field of **spectroscopy**.

Each element produces a distinct spectral pattern, which serves as a unique fingerprint.

Types of Spectra

Emission Spectrum: Bright colored lines on a dark background. Produced when excited atoms release photons as electrons fall to lower energy levels.

Absorption Spectrum: Dark lines on a continuous bright background. Formed when a cool gas absorbs photons of certain wavelengths from passing white light.

Interpretation

These spectra prove that atoms exchange energy only at discrete amounts — energy is **quantized**. If an atom changes from an energy E_2 to a lower energy E_1, it emits a photon with energy:

$$E_\gamma = E_2 - E_1 = hf = \frac{hc}{\lambda},$$

where

- E_γ is the photon energy,
- f is its frequency,
- λ is its wavelength,
- c is the speed of light.

This relation directly connects atomic transitions to observable light spectra.

3 5.3 The Balmer–Rydberg Formula

Hydrogen's spectral lines follow a simple mathematical pattern discovered empirically by Johann Balmer (1885):

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \quad n = 3, 4, 5, \ldots$$

Later, Johannes Rydberg generalized it for all transitions:

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)}, \qquad n > n',$$

where

- $R = 1.097 \times 10^7\,\mathrm{m}^{-1}$ is the **Rydberg constant**,
- n' and n are integers labeling the lower and upper energy levels.

In terms of photon energy:

$$E_\gamma = hcR\left(\frac{1}{n'^2} - \frac{1}{n^2}\right).$$

The formula predicted all known hydrogen wavelengths with extraordinary accuracy — though at the time, no one understood *why* it worked. Bohr's theory would soon provide the explanation.

4 5.4 The Problem of Atomic Stability

Rutherford's (1911) nuclear model described electrons orbiting a positive nucleus, similar to planets orbiting the Sun. However, classical electrodynamics predicts that an accelerating charge (like an orbiting electron) should radiate electromagnetic waves and lose energy. This loss would cause the electron to spiral into the nucleus within 10^{-11} seconds, making atoms unstable — a clear contradiction to reality.

The question became: *How can atoms be stable, and why do they emit light at specific frequencies?*

Bohr's model answered both by proposing that electrons can only occupy specific, non-radiating orbits.

5 5.5 Bohr's Explanation of Atomic Spectra

Bohr proposed three postulates to explain atomic stability and discrete spectra:

1. **Stationary States:** Electrons orbit only in certain stable orbits where they do not emit radiation.
2. **Quantized Energies:** Each allowed orbit has a specific total energy E_n.
3. **Photon Transitions:** Radiation occurs only when an electron transitions between two allowed states:

   $$E_\gamma = E_n - E_{n'},$$

   where E_γ is the emitted or absorbed photon energy.

Key insight: Atomic emission and absorption lines correspond to energy differences between quantized levels.

Example

For helium with $E_{3p} = 23.1\,\text{eV}$ and $E_{2s} = 20.6\,\text{eV}$:

$$E_\gamma = 2.5\,\text{eV}, \qquad \lambda = \frac{1240}{2.5} = 496\,\text{nm}.$$

The emitted light is blue-green.

6 5.6 The Bohr Model of the Hydrogen Atom

Classical Force Balance

An electron of mass m and charge $-e$ orbits a stationary proton ($+e$) at radius r. The Coulomb attraction provides the centripetal force:

$$\frac{mv^2}{r} = \frac{ke^2}{r^2}, \qquad \text{where } k = \frac{1}{4\pi\varepsilon_0} = 8.99 \times 10^9\,\text{N}\,\text{m}^2/\text{C}^2.$$

Total Energy

$$E = K + U = \frac{1}{2}mv^2 - \frac{ke^2}{r} = -\frac{ke^2}{2r}.$$

The negative sign means the electron is bound to the proton.

Quantization of Angular Momentum

Bohr's central assumption:

$$L = mvr = n\hbar, \quad \text{where } \hbar = \frac{h}{2\pi},\ n = 1, 2, 3, \ldots$$

Only these discrete orbits are allowed.

Allowed Radii and Energies

Combining the above relations gives:

$$r_n = \frac{n^2\hbar^2}{mke^2} = n^2 a_B,$$

where the **Bohr radius** is

$$a_B = \frac{\hbar^2}{mke^2} = 0.0529\,\text{nm}.$$

Thus, higher energy levels have larger radii.

The total energy for level n becomes:

$$E_n = -\frac{me^4k^2}{2\hbar^2n^2} = -\frac{13.6\,\text{eV}}{n^2}.$$

Transition Energies

The energy difference between two levels ($n > n'$) is

$$E_\gamma = 13.6\,\text{eV}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right),$$

which matches the Rydberg formula derived empirically.

7 5.7 Properties of the Bohr Atom

Energy Levels and Radii

n	E_n (eV)	r_n (nm)
1	-13.6	0.0529
2	-3.4	0.212
3	-1.51	0.476
4	-0.85	0.846

Spectral Series

Each series of lines corresponds to transitions ending at a specific lower level n':

Series	n'	Region
Lyman	1	Ultraviolet
Balmer	2	Visible
Paschen	3	Infrared

Example: Transition $n = 3 \to 2$ gives

$$E_\gamma = 13.6\left(\frac{1}{4} - \frac{1}{9}\right) = 1.89\,\text{eV}, \quad \lambda = \frac{1240}{1.89} = 656\,\text{nm},$$

the red Balmer-α line of hydrogen.

Bohr Radius Scaling

The orbit size increases with n^2. Atoms with very large n values (e.g., $n = 100$) can have radii $\sim 0.5\,\text{mm}$, called **Rydberg atoms**.

8 5.8 Hydrogen-Like Ions

For one-electron ions such as He^+ or Li^{2+}:

$$r_n = \frac{n^2 a_B}{Z}, \qquad E_n = -\frac{Z^2 \times 13.6}{n^2}\,\text{eV}.$$

Increasing the nuclear charge Z decreases the orbit radius and increases the binding energy.

Reduced Mass Correction

Because both the nucleus and electron move around a common center of mass, we replace m with the reduced mass:

$$\mu = \frac{m_e m_{\text{nuc}}}{m_e + m_{\text{nuc}}}.$$

For hydrogen, this correction reduces the energy levels by about 1/1800, but is measurable experimentally.

9 5.9 X-Ray Spectra and Moseley's Law

In multi-electron atoms, the innermost electrons behave like hydrogen-like systems. When an inner ($n = 1$) electron is ejected, an outer electron (e.g., $n = 2$) can fall inward, emitting an X-ray photon.

Photon Energy for Inner Transitions

$$E_{K\alpha} = \frac{3}{4} Z^2 E_R,$$

where $E_R = 13.6\,\text{eV}$.

Moseley's Law

Experimentally, Henry Moseley (1913) found:

$$f \propto (Z-1)^2,$$

where f is the X-ray frequency and $(Z-1)$ accounts for partial shielding of the nuclear charge by other electrons.

Significance:

- Established Z as the true atomic number (number of protons).
- Allowed prediction of undiscovered elements and precise identification of atomic species using X-rays.

Summary of Key Equations

$$E_\gamma = hf = \frac{hc}{\lambda} \qquad \text{Photon energy}$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \qquad \text{Rydberg formula}$$

$$L = n\hbar \qquad \text{Quantized angular momentum}$$

$$a_B = \frac{\hbar^2}{mke^2} = 0.0529\,\text{nm} \qquad \text{Bohr radius}$$

$$r_n = n^2 a_B \qquad \text{Orbit radius}$$

$$E_n = -\frac{13.6}{n^2}\,\text{eV} \qquad \text{Energy levels for hydrogen}$$

$$E_\gamma = 13.6\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)\,\text{eV} \qquad \text{Transition energy}$$

$$E_n(\text{ion}) = -\frac{Z^2 \times 13.6}{n^2}\,\text{eV} \qquad \text{Hydrogen-like ions}$$

$$f_{X\text{-ray}} \propto (Z-1)^2 \qquad \text{Moseley's law}$$