The First Modern Model of the Atom

CHEM 361B: Introduction to Physical Chemistry

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Lecture 4

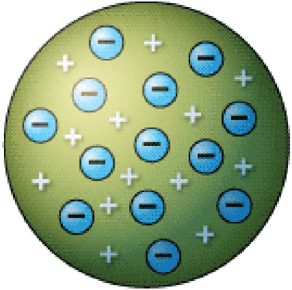
Table of contents

Learning Objective: Understand the basis of the first modern model of the atom.

References:

- McQuarrie §1.5 - 1.14

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.

An Introduction to Spectroscopy

Spectroscopy is the interpretation of light emitted or absorbed from your sample.

Johann Balmer in originally discovered that $\nu \propto 1/n^2$ for the visible spectrum of hydrogen. Later Johannes Rydberg generalized the complete hydrogen emission spectrum with

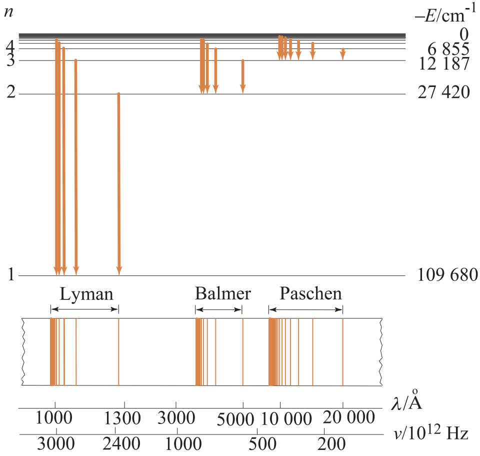
$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where $R_H = 109,677.57\text{cm}^{-1}$, $c = \lambda\nu$, and $n_2 > n_1$.

Note: The emission spectrum typically is reported using wave numbers $(1/\lambda)$ which has units of cm^{-1}.

Emission Spectra

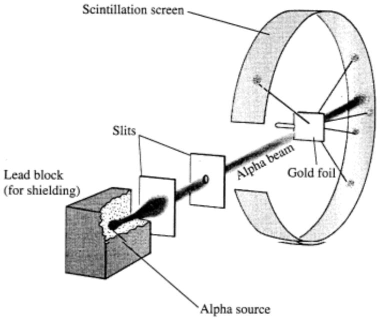
The Balmer Series is a series of hydrogen emission lines where $n_1 = 2$. They occur in the visible range of the spectrum. As n_2 increases, $1/n_2$ decreases until it is essentially inconsequential.



Emission Spectra Examples

1. Determine the wave number and then the frequency for a transition between $n_1 = 2$ and $n_2 = 4$.
2. Determine the Balmer Series limit.

The Gold Foil Experiment



In 1911, Ernest Rutherford suggested an atom is made mostly of empty space.

This conclusion was based on the gold foil experiment where he sent α-particles at a very thin gold foil and observed that they principally went through.

Therefore, instead of the atom being composed of a large blob of positive charge (plum pudding) it must instead be a small, positively charged nucleus, surrounded by electrons.

Problems with Rutherford's Atom

Rutherford's view of the atom was inconsistent with spectroscopy

- There is no stationary configuration of charges possible $\rightarrow$ electrons must be orbiting
- Circular motion requires the electrons accelerate toward the nucleus $\rightarrow$ would emit light and lose energy
- The electron orbit would decay and eventually spin into the nucleus
- During this decay the light emitted would produce a continuous spectrum $\rightarrow$ not experimentally observed

Enter Neils Bohr

In 1913, Neils Bohr combined the Rutherford atom with Planck's quantum hypothesis. This theory accounted for the observed hydrogen spectrum.

It had two basic postulates:

1. The electron can only revolve around the nucleus in certain allowed orbits. Each orbit represents a stationary energy state that does not radiate energy.
2. Emission or absorbtion of radiation occurs when an electron jumps to a different orbit. The change in energy is represented by the energy of the photon emitted/absorbed:

$$E_f - E_i = h\nu$$

Enter Neils Bohr (cont.)

The force holding the electron in orbit is governed by Coulomb's Law:

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}$$

The first postulate quantized the angular momentum of an orbiting electron:

$$L = mvr = \frac{nh}{2\pi} \qquad n = 1, 2, \ldots$$

Putting these two equations together yields

$$r = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2} \qquad n = 1, 2, \ldots$$

Enter Niels Bohr (cont.)

The total energy of an electron is

$$\begin{aligned} E =& E_k + E_p = \frac{1}{2} m_e v^2 - qV \\ =& \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} \\ =& -\frac{e^2}{8\pi\epsilon_0 r} \end{aligned}$$

Substituting in the allowed orbital radii gives

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}$$

Enter Niels Bohr (cont.)

Using the second postulate ($\Delta E = h\nu$) gives

$$\frac{1}{\lambda} = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

This result agrees with the Rydberg equation if

$$R_H = 109677.57 \text{ cm}^{-1}$$
$$\frac{m_e e^4}{8\epsilon_0^2 h^3 c} = 109737 \text{ cm}^{-1}$$

which it does to within 0.5%.

Bohr Atom Examples

1. Calculate the frequency of a photon that is produced when an electron drops from $n = 3$ to $n = 2$ in the hydrogen atom.
2. Calculate the ionization energy of the hydrogen atom in the ground state.

Wavelike Properties of Matter

Enter de Broglie

The dual nature of light prompted de Broglie in 1924 to question if matter had wavelike properties.

This provides a nice symmetry in nature.

de Broglie argued that both light and matter obey the equation:

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

Matter Wave Examples

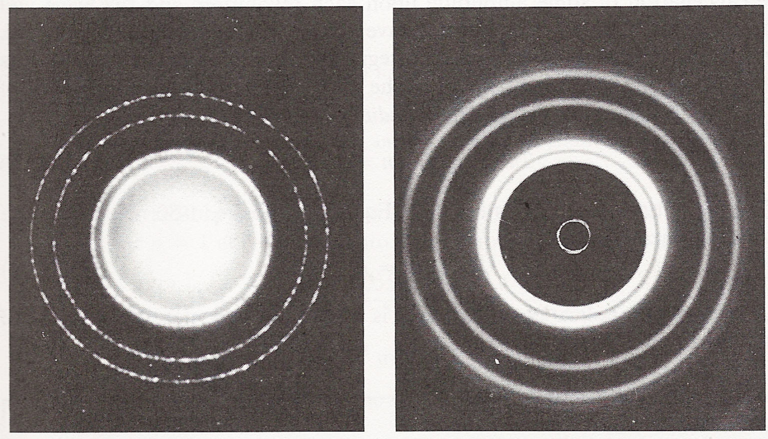
1. Calculate the de Broglie wavelength of a 0.17kg puck travelling at $40\text{m}\cdot\text{s}^{-1}$.

   Hint: $p = mv$

2. Calculate the de Broglie wavelength of an electron travelling at 1% of the speed of light ($c = 2.998 \times 10^8\ \text{m}\cdot\text{s}^{-1}$).

Matter Waves Measured

X-ray (left) and electron (right) diffraction patterns from aluminum foil.



Alterative Interpretation to Bohr's First Postulate

Recall Bohr's first postulate:

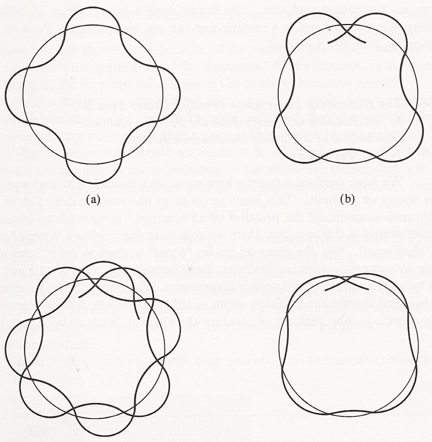
The electron can only revolve around the nucleus in certain allowed orbits.

If the particle is a wave, then it must match up with itself. Hence:

$$2\pi r = n\lambda$$

Substituting in the de Broglie relation yields:

$$L = mvr = \frac{nh}{2\pi}$$



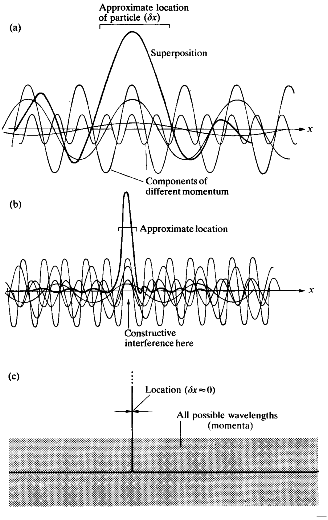
Heisenberg Uncertainty Principle

It is impossible to know both the position and momemtum of a particle to a greater precision than:

$$\Delta x \Delta p \geq h$$

This uncertainty is due to the act of measurement itself and nothing to do with the skill of the observer.

When h can be neglected, Classical mechanics can be used.



Heisenberg Uncertainty Examples

1. Calculate the uncertainty of the position of a puck (0.17kg) travelling at $40\text{m}\cdot\text{s}^{-1}$ if we can measure its velocity to 4.0×10^{-7} m s^{-1} .
2. Calculate the uncertainty in velocity of an electron (9.11×10^{-31}kg) when its position can be measured to a precision of 50pm.

Summary

- Spectroscopy is a measurement technique where light emitted by an atom or molecule is analysed to determine its composition and properties.
- The modernization of the model of the atom provided an explanation to the spectra from the Hydrogen atom quantified empirically by the Rhydberg equation.
  - Rutherford: Atoms are akin to solar systems with small massive positive cores with electrons orbiting them.
  - Bohr: Quantized the angular momentum of the electrons travelling in the orbits requiring that energy is only emitted/absorbed as light when the electrons change orbit
  - de Broglie: Matter exhibits wavelike properties, which explains how Bohr's postulates were true.
- Furthermore, the wave/particle duality also affects the act of measuring things which is quantified by the Heisenberg Uncertainty Principle.