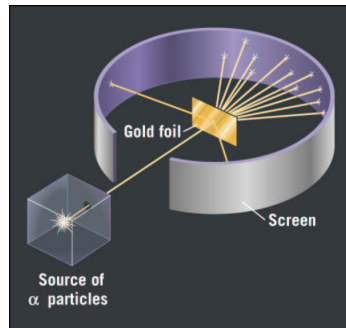


The Nature of the Atom

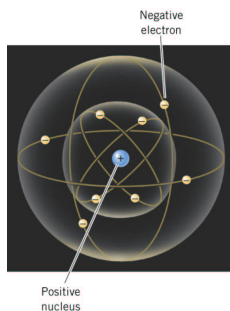
1 – Early Models of the Atom

- **Thompson's model:** The atom is a volume of positive charge, with electrons embedded throughout the volume.
- In 1911, Geiger and Marsden (under supervision of Rutherford) directed a beam of **alpha particles** (nuclei of helium atoms) against a thin metal foil. Most of the alpha particles passed through the foil as if it were empty space. Some were deflected at very large angles, some even backward.



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- Rutherford explained these observations as follows:



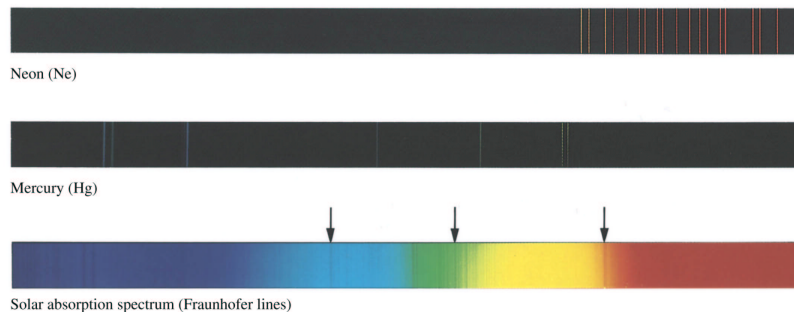
the positive charge in an atom is concentrated in a very small nucleus sitting at the center. The electrons were assumed to be outside the nucleus, orbiting the nucleus like planets orbiting the sun.

- However, Rutherford's model had two problems:
 - 1) It could not explain the discrete characteristic frequencies of electromagnetic radiation sent out by atoms.
 - 2) Electrons orbiting a positively charged nucleus are continuously accelerated by the centripetal force provided by the electrostatic force between the electron and the nucleus. Accelerated electrons radiate electromagnetic waves. As they radiate, the electrons lose energy and should plunge into the nucleus.

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2 – Atomic Spectra

- Suppose an evacuated glass tube is filled with hydrogen (=atom made of 1 proton and 1 electron) at low pressure. If a sufficiently high voltage is applied between metal electrodes in the tube, an electric current flows. The gas then emits light.
- Analyzing the emitted light with a spectrograph, a series of discrete lines is observed (so-called **emission spectrum**), each corresponding to a different color (wavelength). The wavelengths are characteristic of the element:



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- The emission spectrum of hydrogen in the visible region can be described by the following equation (**Balmer series**):

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

where $n = 3, 4, 5, \dots$ is an integer. R is the so-called **Rydberg constant**: $R = 1.097 \times 10^7 \text{ m}^{-1}$

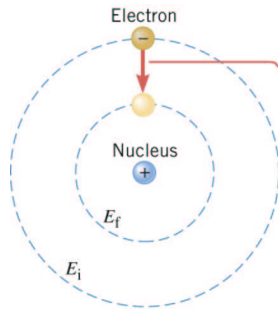
- The **Lyman** and **Paschen** series can be obtained by replacing $1/2^2$ in the Balmer series by $1/1^2$ and $1/3^2$, respectively.
- An element can also absorb light at specific wavelengths. The corresponding spectral lines are called the **absorption spectrum**. An absorption spectrum can be obtained by passing a continuous radiation spectrum through a vapor of the element to be analyzed.
- The absorption spectrum consists of a series of dark lines superimposed on the otherwise continuous spectrum. Each line in the absorption spectrum coincides with a line of the emission spectrum.

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3 – Bohr's Theory of the Hydrogen Atom

- In 1913 Bohr provided an explanation for atomic spectra. Bohr's theory is based on the following assumptions:

- 1) The electron moves in circular orbits about the nucleus under the influence of the attractive Coulomb force.
- 2) Only certain electron orbits are stable. These are orbits in which the atom does not emit energy in form of radiation.



- 3) Radiation is emitted by the atom when the electron jumps from a more energetic to a less energetic state (or orbit).

The frequency of the emitted radiation is given by $E_i - E_f = hf$, where E_i (E_f) is the energy of the initial (final) state ($E_i > E_f$).

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- 4) Bohr conjectured that the electron's angular momentum $L = I\omega = (mr^2) \cdot (v/r) = mvr$ can only assume discrete values.
- 5) The radii for the allowed electron orbits are then determined by imposing the following condition:

$$mvr = n\hbar, \quad n = 1, 2, 3, \dots$$

where $\hbar = h/(2\pi)$.

- Allowed energies in an atom with Z protons:
 - 1) The electrical potential energy of the electron is

$$PE = kZ \frac{q_1 q_2}{r} = -kZ \frac{e^2}{r}$$

- 2) The kinetic energy of the electron results from setting Coulomb force = centripetal force:

$$kZ \frac{e^2}{r^2} = m \frac{v^2}{r} \quad \text{or} \quad KE = \frac{1}{2} mv^2 = \frac{kZe^2}{2r}$$

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3) Total energy, $E = PE + KE$, is then given by

$$E = -\frac{kZe^2}{2r} \quad (1)$$

- For the quantization condition $mvr = n\hbar$ and the expression for KE one obtains the following expression for r :

$$r_n = n^2 \frac{\hbar^2}{mkZe^2} = a_0 \frac{n^2}{Z}, \quad n = 1, 2, 3, \dots$$

The electron can only exist in certain allowed orbits.

- The orbit with the smallest radius, called the **Bohr radius**, has the value

$$a_0 = \frac{\hbar^2}{mke^2} = 5.29 \cdot 10^{-11} \text{ m}$$

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- Using the expression for E and r_n , one arrives at the following formula for the energies of the quantum states:

$$E_n = -\frac{mk^2e^4}{2\hbar^2} \left(\frac{Z^2}{n^2} \right), \quad n = 1, 2, 3, \dots$$

Plugging in numbers:

$$E_n = -(2.18 \cdot 10^{-18} \text{ J}) \frac{Z^2}{n^2} = -13.6 \text{ eV} \frac{Z^2}{n^2} \quad (2)$$

where we used that $1\text{eV} = 1.602 \cdot 10^{-19} \text{ J}$.

- When an electron jumps from an orbit with quantum number n_i to one with quantum number n_f , a photon with frequency

$$f = \frac{E_i - E_f}{h} = Z^2 \frac{mk^2e^4}{4\pi\hbar^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

is emitted.

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- Using $\lambda f = c$ and identifying the Rydberg constant with

$$R = \frac{mk^2e^4}{4\pi c\hbar^3}$$

one finds

$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (3)$$

For $n_f = 2$ this is the Balmer series. For $n_f = 1$ it is called the **Lyman series**, and for $n_f = 3$ the **Paschen series**.

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4 – Modifications of Bohr's Theory

- **Sommerfeld** extended the results of the Bohr's theory to include elliptical orbits. Besides the **principal quantum number** n he introduced the **orbital quantum number** ℓ which ranges from 0 to $n - 1$ in **integer steps**. The angular momenta of the electrons are $L = \sqrt{\ell(\ell + 1)}\hbar$.
- The following notation has become customary:
 - 1) All states with the same principal quantum number are said to form a shell. These are identified by the letters K, L, M, \dots corresponding to $n = 1, 2, 3, \dots$
 - 2) States having the same n and ℓ are said to form a sub-shell. The letters s, p, d, f, g, \dots correspond to $\ell = 0, 1, 2, 3, 4, \dots$
- The maximum number of electrons in a given sub-shell is $2(2\ell + 1)$.

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- Experiments show that the energy of an electron is slightly modified when the atom is subjected to strong magnetic field. To explain this phenomenon, a new quantum number m_ℓ (so-called **orbital magnetic quantum number**) was introduced. m_ℓ is restricted to the range $-\ell$ to $+\ell$ in integer steps.
- Finally, high resolution data showed that each spectroscopic line is in fact a closely spaced pair of lines. This necessitates the introduction of the **spin magnetic quantum number** m_s which can assume the values $+1/2$ and $-1/2$. In order to describe m_s , it is convenient to think of the electron as spinning while it orbits the nucleus. $m_s = +1/2$ ($m_s = -1/2$) corresponds to spin “up” (“down”).

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5 – De Broglie Waves and the Hydrogen Atom

- Where is Bohr’s quantization condition

$$mvr = n\hbar$$

coming from? De Broglie provided an explanation using the concept of matter waves.

- The quantization condition corresponds to **standing matter waves**. The condition for standing waves in an electron orbit is

$$2\pi r = n\lambda, \quad n = 1, 2, 3, \dots$$

The wavelength of an electron is $\lambda = h/p = h/mv$. Substituting this into the condition for standing waves one finds

$$2\pi r = \frac{nh}{mv} \quad \text{or} \quad mvr = n\hbar$$

The wave nature of matter is at the heart of the behavior of atomic systems.

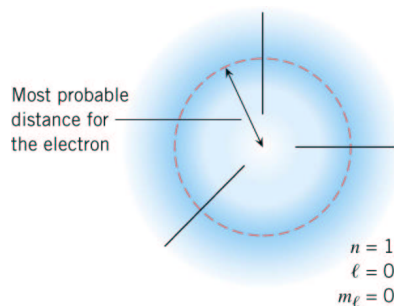
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- Why do we need standing matter waves? The answer to this question naturally comes when the Schrödinger equation is solved for the hydrogen atom. In 1926, Schrödinger proposed a wave equation that described how matter waves change in space and time. The Schrödinger equation is a key element in the theory of quantum mechanics.
- The basic quantity of the Schrödinger equation is the **wave function**, Ψ . Each particle is represented by a wave function which depends on the position of the particle and time.
- The solution to Schrödinger's equation describes how Ψ changes with space and time.
- $|\Psi|^2$ represents the probability to find a particle at a certain position at a given time.
- The Schrödinger equation leads to energy levels which exactly agree with those from the theories of Bohr and Sommerfeld (without making their somewhat ad hoc assumptions).

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6 – Electron Clouds

- The solution of the Schrödinger equation for the wave function Ψ yields a quantity which depends on the quantum numbers n, ℓ, m_ℓ .
- Lets focus on the simplest case: $n = 1, \ell = 0, m_\ell = 0$, the so-called **ground state**. $|\Psi|^2$ represents the probability to find the electron at a given position. The curve peaks at the Bohr radius, $r = a_0$.
- In contrast to Bohr's theory, quantum mechanics predicts that the electron is not confined to an orbit with radius a_0 . There is a non-zero probability that the electron is found at other distances.



Quantum mechanics also predicts that the wave function for the ground state is spherically symmetric. In fact all wave functions for $\ell = 0$ are spherically symmetric.

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7 – Pauli's Exclusion Principle and the Periodic Table

- The four quantum numbers n , ℓ , m_ℓ and m_s can be used to describe all the electronic states of an atom.
- How many electrons in an atom can have the same set of quantum numbers? Pauli's **exclusion principle** provides an answer:

No two electrons can ever be in the same quantum state,

that is no two electrons can have the same set of values for the four quantum numbers n , ℓ , m_ℓ and m_s .

- Electrons fill sub-shells one by one, starting with the lowest energy shell. A sub-shell is filled when it contains $2(2\ell + 1)$ electrons. Once it is filled, the next electron goes into the next higher-energy sub-shell.
- The chemical similarities of the elements in the periodic table can all be explained by how many electrons they contain in their highest energy sub-shell.

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