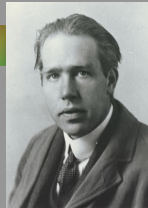


CHAPTER 4 Structure of the Atom

- 4.1 The Atomic Models of Thomson and Rutherford
- 4.2 Rutherford Scattering
- 4.3 The Classic Atomic Model
- 4.4 The Bohr Model of the Hydrogen Atom
- 4.5 Successes & Failures of the Bohr Model
- 4.6 Characteristic X-Ray Spectra and Atomic Number
- 4.7 Atomic Excitation by Electrons



Niels Bohr (1885-1962)

The opposite of a correct statement is a false statement. But the opposite of a profound truth may well be another profound truth.

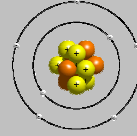
An expert is a person who has made all the mistakes that can be made in a very narrow field.

Never express yourself more clearly than you are able to think.

Prediction is very difficult, especially about the future.

- Niels Bohr

Structure of the Atom



Evidence in 1900 indicated that the atom was **not** a fundamental unit:

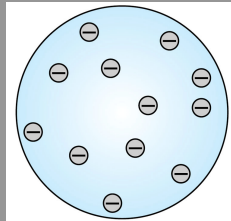
- 1) There seemed to be too many kinds of atoms, each belonging to a distinct chemical element (way more than earth, air, water, and fire!).
- 2) Atoms and electromagnetic phenomena were intimately related (magnetic materials; insulators vs. conductors; different emission spectra).
- 3) Elements combine with some elements but not with others, a characteristic that hinted at an internal atomic structure (valence).
- 4) The discoveries of radioactivity, x rays, and the electron (all seemed to involve atoms breaking apart in some way).

Knowledge of atoms in 1900

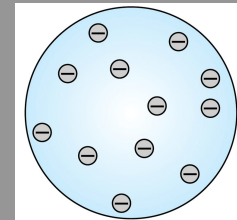
Electrons (discovered in 1897) carried the negative charge.

Electrons were very light, even compared to the atom.

Protons had not yet been discovered, but clearly positive charge had to be present to achieve charge neutrality.



Thomson's Atomic Model



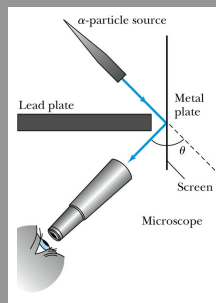
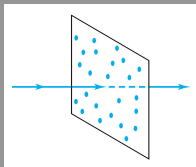
Thomson's "plum-pudding" model of the atom had the positive charges spread uniformly throughout a sphere the size of the atom, with electrons embedded in the uniform background.

In Thomson's view, when the atom was heated, the electrons could vibrate about their equilibrium positions, thus producing electromagnetic radiation.

Unfortunately, Thomson couldn't explain spectra with this model.

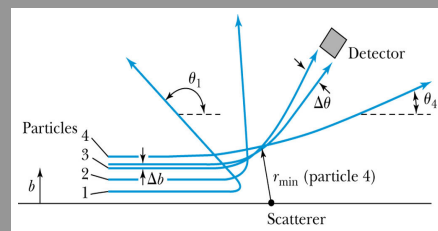
Experiments of Geiger and Marsden

Rutherford, Geiger, and Marsden conceived a new technique for investigating the structure of matter by scattering α particles from atoms.

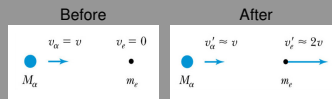


Experiments of Geiger and Marsden 2

Geiger showed that many α particles were scattered from thin gold-leaf targets at backward angles greater than 90° .



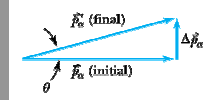
Electrons can't back-scatter α particles.



Calculate the maximum scattering angle—corresponding to the maximum momentum change.

It can be shown that the maximum momentum transfer to the α particle is: $\Delta p_{\max} = 2m_e v_\alpha$

Determine $\theta_{\max}$ by letting $\Delta p_{\max}$ be perpendicular to the direction of motion:



$$\theta_{\max} = \frac{\Delta p_\alpha}{p_\alpha} = \frac{2m_e v_\alpha}{M_\alpha v_\alpha} = 2.7 \times 10^{-4} \text{ rad} = 0.016^\circ \quad \text{too small!}$$

Try multiple scattering from electrons

If an α particle is scattered by N electrons: $\langle \theta \rangle_{\text{total}} \approx \sqrt{N} \theta$

N = the number of atoms across the thin gold layer, $t = 6 \times 10^{-7} \text{ m}$:

$$n = \frac{\text{Number of molecules}}{\text{cm}^3} = \left[\frac{\text{Avogadro's no. (molecules/mol)}}{\text{gram} \cdot \text{molecular weight} \left(\frac{\text{mol}}{\text{g}} \right)} \right] \left[\text{density} \left(\frac{\text{g}}{\text{cm}^3} \right) \right]$$

$$= \left(\frac{6.02 \times 10^{23} \text{ molecules}}{\text{mol}} \right) \left(\frac{1 \text{ mol}}{197 \text{ g}} \right) \left(19.3 \frac{\text{g}}{\text{cm}^3} \right)$$

$$= 5.9 \times 10^{22} \frac{\text{molecules}}{\text{cm}^3} = 5.9 \times 10^{23} \frac{\text{atoms}}{\text{m}^3}$$

The distance between atoms, $d = n^{-1/3}$, is: $d = (5.9 \times 10^{23})^{-1/3} \text{ m} = 2.6 \times 10^{-10} \text{ m}$

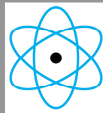
$$N = t/d = \frac{6 \times 10^{-7} \text{ m}}{2.6 \times 10^{-10} \text{ m}} = 2300 \text{ atoms}$$

$$\langle \theta \rangle_{\text{total}} = \sqrt{2300} (0.016^\circ) = 0.8^\circ \quad \text{still too small!}$$

Rutherford's Atomic Model

$\langle \theta \rangle_{\text{total}} = 6.8^\circ$ even if the α particle is scattered from all 79 electrons in each atom of gold.

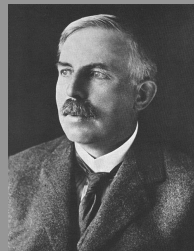
Ernest Rutherford
(1871-1937)



Experimental results were not consistent with Thomson's atomic model.

Rutherford proposed that an atom has a positively charged core (**nucleus**) surrounded by the negative electrons.

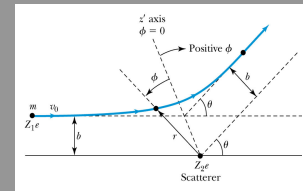
Geiger and Marsden confirmed the idea in 1913.



4.2: Rutherford Scattering

Scattering experiments help us study matter too small to be observed directly.

There's a relationship between the **impact parameter** b and the **scattering angle** θ .



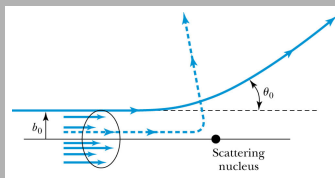
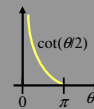
When b is small,

r is small.

the Coulomb force is large.

θ can be large and the particle can be repelled backward.

$$b = \frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \cot \frac{\theta}{2} \quad \text{where } K = \frac{1}{2} m v_0^2$$



Rutherford Scattering

Any particle inside the circle of area πb_0^2 will be similarly (or more) scattered.

The cross section $\sigma = \pi b^2$ is related to the **probability** for a particle being scattered by a nucleus (t = foil thickness):

$$= \pi n t \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \right)^2 \cot^2 \frac{\theta}{2}$$

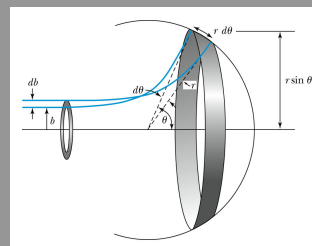
The fraction of incident particles scattered is:

$$f = \frac{\text{target area exposed by scatterers}}{\text{total target area}}$$

The number of scattering nuclei per unit area:

$$n t = \frac{\rho N_A N_{\text{atoms}}}{M_R} \frac{t}{\text{cm}^2}$$

Rutherford Scattering Equation



In actual experiments, a detector is positioned from θ to $\theta + d\theta$ that corresponds to incident particles between b and $b + db$.

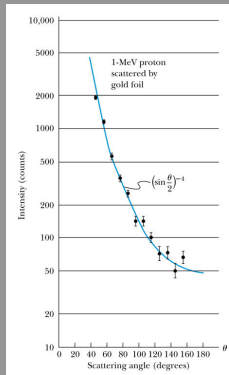
The number of particles scattered per unit area is:

$$N(\theta) = \frac{N_A \rho t}{16} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{Z_1^2 Z_2^2}{r^2 K^2 \sin^4(\theta/2)}$$

Rutherford scattering experiment

1 MeV protons scattering off gold foil.

Note the correct dependence on scattering angle.



4.3: The Classical Atomic Model

Consider an atom as a planetary system. The Newton's 2nd Law force of attraction on the electron by the nucleus is:

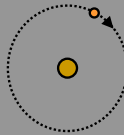
$$F_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{mv^2}{r}$$

where v is the tangential velocity of the electron:

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}} \Rightarrow K = \frac{1}{2}mv^2 = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r}$$

The total energy is then:

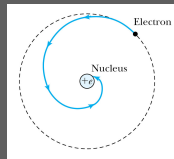
$$E = K + V = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r}$$



This is negative, so the system is bound, which is good.

The Planetary Model is Doomed

From classical E&M theory, an accelerated electric charge radiates energy (electromagnetic radiation), which means the total energy must decrease. So the **radius r must decrease!!**



Electron crashes into the nucleus!?

Physics had reached a turning point in 1900 with Planck's hypothesis of the quantum behavior of radiation, so a radical solution would be considered possible.

4.4: The Bohr Model of the Hydrogen Atom

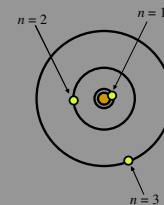
Bohr's general assumptions:

1. **Stationary states**, in which orbiting electrons do **not** radiate energy, exist in atoms and have well-defined energies, E_n . Transitions can occur between them, yielding light of energy:

$$E = E_n - E_{n'} = h\nu$$

2. Classical laws of physics do not apply to transitions between stationary states, but they do apply elsewhere.

3. The angular momentum of the n^{th} state is: $n\hbar$ where n is called the Principal Quantum Number.



Angular momentum is quantized!

Consequences of the Bohr Model

The angular momentum is:

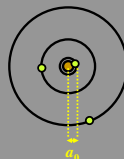
$$L = mvr = n\hbar$$

So the velocity is: $v = n\hbar / mr$

$$\text{But: } v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}} \quad \text{So: } \frac{n^2 \hbar^2}{m^2 r^2} = \frac{e^2}{4\pi\epsilon_0 mr}$$

$$\text{Solving for } r_n: \quad r_n = n^2 a_0 \quad \text{where: } a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

a_0 is called the Bohr radius. It's the diameter of the Hydrogen atom (in its lowest-energy, or "ground," state).



Bohr Radius

The **Bohr radius**,

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

is the radius of the unexcited hydrogen atom and is equal to:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = \frac{(1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2}{(9.11 \times 10^{-31} \text{ kg})(1.6 \times 10^{-19} \text{ C})^2} = 0.53 \times 10^{-10} \text{ m}$$

The "ground" state Hydrogen atom diameter is:

$$2r_1 = 2a_0 \approx 10^{-10} \text{ m}$$



The Hydrogen Atom Energies

Use the classical result for the energy:

$$E = -\frac{e^2}{8\pi\epsilon_0 r}$$

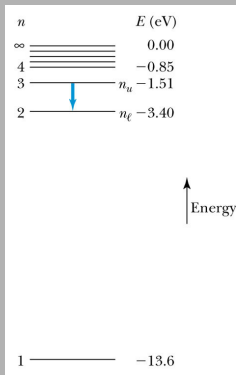
and: $r_n = \frac{4\pi\epsilon_0 n^2 \hbar^2}{me^2}$

So the energies of the stationary states are:

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}$$

or: $E_n = -E_0/n^2$

where $E_0 = 13.6 \text{ eV}$.



The Hydrogen Atom

Emission of light occurs when the atom is in an excited state and decays to a lower energy state ($n_u \rightarrow n_l$).

$$h\nu = E_u - E_l$$

where ν is the frequency of a photon.

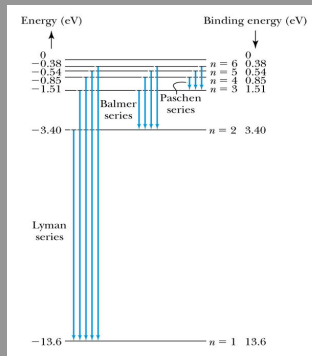
$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{h\nu}{hc} = \frac{E_u - E_l}{hc} = R_\infty \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

R_∞ is the **Rydberg constant**.

$$R_\infty \equiv \frac{me^4}{(4\pi\hbar)^3 c \epsilon_0^2}$$

Transitions in the Hydrogen Atom

The atom will remain in the excited state for a short time before emitting a photon and returning to a lower stationary state. In equilibrium, all hydrogen atoms exist in $n = 1$.



4.6: Characteristic X-Ray Spectra and Atomic Number

Shells have letter names:

K shell for $n = 1$

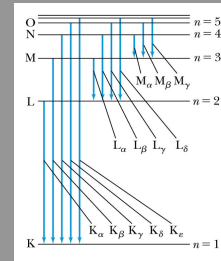
L shell for $n = 2$

...

The atom is most stable in its ground state.

An electron from higher shells will fill the inner-shell vacancy at lower energy.

When it occurs in a heavy atom, the radiation emitted is an **x-ray**. It has the energy $E(x\text{-ray}) = E_u - E_l$.



Atomic Number and Moseley

The x-rays have names:

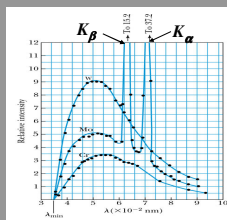
L shell to K shell: K_α x-ray
M shell to K shell: K_β x-ray
etc.

G.J. Moseley studied x-ray emission in 1913.

Atomic number Z = number of protons in the nucleus. Moseley found a relationship between the frequencies of the characteristic x-ray and Z .

Moseley found this relation holds for the K_α x-ray:

$$\nu_{K_\alpha} = \frac{3cR}{4} (Z-1)^2$$



Moseley's Empirical Results

The K_α x-ray is produced from the $n = 2$ to $n = 1$ transition.

In general, the K series of x-ray wavelengths are:

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

We use $Z-1$ instead of Z because one electron is already present in the K-shell and so shields the other(s) from the nucleus' charge.

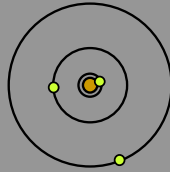
Moseley's research clarified the importance of Z and the electron shells for all the elements, not just for hydrogen.



The Correspondence Principle

Bohr's correspondence principle is rather obvious:

In the limits where classical and quantum theories should agree, the quantum theory must reduce to the classical result.



The Correspondence Principle

The frequency of the radiation emitted $\nu_{\text{classical}}$ is equal to the orbital frequency ν_{orb} of the electron around the nucleus.

$$\nu_{\text{classical}} = \nu_{\text{orb}} = \frac{\omega}{2\pi} = \frac{v/r}{2\pi} = \frac{1}{2\pi} \left(\frac{e^2}{4\pi\epsilon_0 m r^3} \right)^{1/2} = \frac{m e^4}{4\epsilon_0^2 \hbar^3 n^3}$$

This should agree with the frequency of the transition from $n+1$ to n (when n is very large):

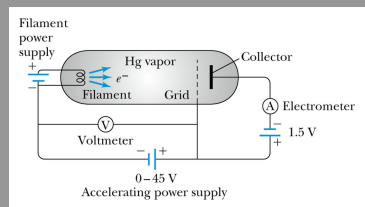
$$\begin{aligned} \nu_{\text{Bohr}} &= \frac{E_n}{h} \left[\frac{1}{n^2} - \frac{1}{(n+1)^2} \right] \\ &= \frac{E_0}{h} \left[\frac{n^2 + 2n + 1 - n^2}{n^2(n+1)^2} \right] = \frac{E_0}{h} \left[\frac{2n+1}{n^2(n+1)^2} \right] \end{aligned}$$

For large n : $\nu_{\text{Bohr}} \approx \frac{2nE_0}{h n^3} = \frac{2E_0}{h n^2}$

Substituting for E_0 : $\nu_{\text{Bohr}} = \frac{m e^4}{4\epsilon_0^2 \hbar^3 n^3} = \nu_{\text{classical}}$

4.7: Atomic Excitation by Electrons

Franck and Hertz studied the phenomenon of ionization.



Accelerating voltage is below 5 V: electrons did not lose energy.
Accelerating voltage is above 5 V: sudden drop in the current.

Atomic Excitation by Electrons

Ground state has E_0 to be zero.

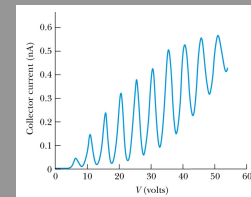
First excited state has E_1 .

The energy difference $E_1 - 0 = E_1$ is the **excitation energy**.

Hg has an excitation energy of 4.88 eV in the first excited state

No energy can be transferred to Hg below 4.88 eV because not enough energy is available to excite an electron to the next energy level

Above 4.88 eV, the current drops because scattered electrons no longer reach the collector until the accelerating voltage reaches 9.8 eV and so on.



Fine Structure Constant

The electron's velocity in the Bohr model:

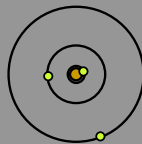
$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0\hbar}$$

In the ground state,

$$v_1 = 2.2 \times 10^6 \text{ m/s} \sim 1\% \text{ of the speed of light.}$$

The ratio of v_1 to c is the **fine structure constant**.

$$\alpha = \frac{v_1}{c} = \frac{\hbar}{ma_0c} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$$



4.5: Successes and Failures of the Bohr Model

Success:

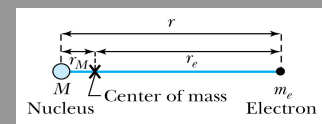
The electron and hydrogen nucleus actually revolve about their mutual center of mass.

The electron mass is replaced by its **reduced mass**:

$$\mu = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \frac{m_e}{M}}$$

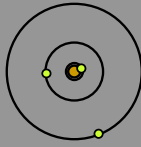
The Rydberg constant for infinite nuclear mass, R_∞ , is replaced by R .

$$R = \frac{\mu}{m_e} R_\infty = \frac{1}{1 + \frac{m_e}{M}} R_\infty = \frac{\mu e^4}{4\pi\epsilon_0 \hbar^3 (4\pi\epsilon_0)^2}$$



Limitations of the Bohr Model

The Bohr model was a great step in the new quantum theory, but it had its limitations.



Failures:

Works only for single-electron ("hydrogenic") atoms.

Could not account for the intensities or the fine structure of the spectral lines (for example, in magnetic fields).

Could not explain the binding of atoms into molecules.