CHAPTER 4
Structure of the Atom

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In the present first part of the paper the mechanism of the binding of electrons by a positive nucleus is discussed in relation to Planck's theory. It will be shown that it is possible from the point of view taken to account in a simple way for the law of the line spectrum of hydrogen.

- Niels Bohr, 1913

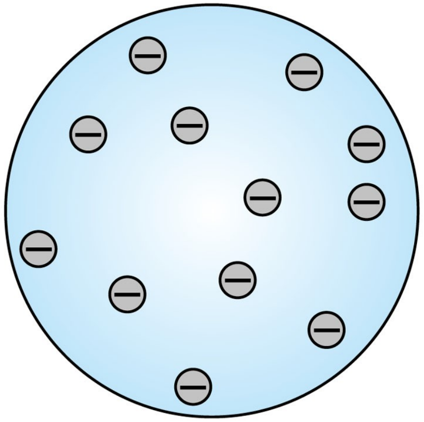
Structure of the Atom

Pieces of evidence that scientists had in 1900 to indicate 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.
2) Atoms and electromagnetic phenomena were intimately related.
3) The problem of **valence**. Certain elements combine with some elements but not with others, a characteristic that hinted at an internal atomic structure.
4) The discoveries of radioactivity, of x rays, and of the electron.

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.

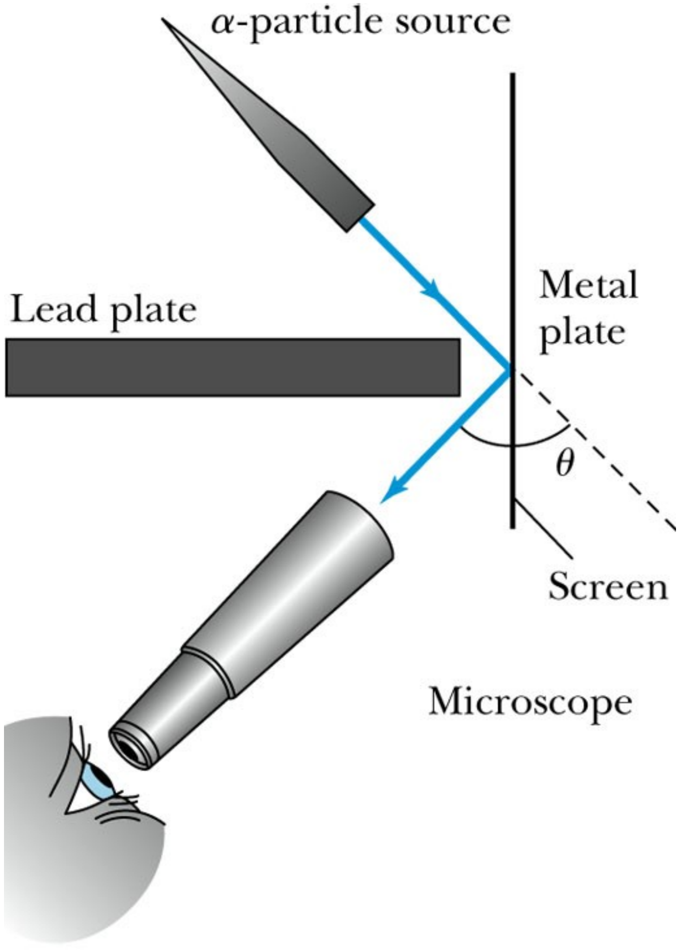


- In Thomson’s view, when the atom was heated, the electrons could vibrate about their equilibrium positions, thus producing electromagnetic radiation.

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.

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

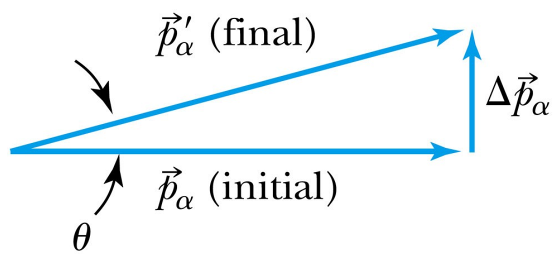


Example 4.1

- The maximum scattering angle corresponding to the maximum momentum change.
- Maximum momentum change of the α particle is

$$\Delta\vec{p}_\alpha = M_\alpha \vec{v}_\alpha - M_\alpha \vec{v}\,'_\alpha = M_e \vec{v}\,'_e \text{ or } \Delta p_{\max} = 2 m_e v_\alpha$$

- Determine θ by letting $\Delta p_{\max}$ be perpendicular to the direction of motion.



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

Multiple Scattering from Electrons

- If an α particle were scattered by many electrons and N electrons results in $\langle\theta\rangle_{\text{total}} \approx \sqrt{N}\theta$.
- The number of atoms across the thin gold layer of 6 × 10^{-7} m:

$$\frac{\text{Number of molecules}}{\text{cm}^3} = [\text{Avogadro's no. (molecules/mol)}] \times \left[\frac{1}{\text{gram} - \text{molecular weight}}\left(\frac{\text{mol}}{\text{g}}\right)\right]\left[\text{density}\left(\frac{\text{g}}{\text{cm}^3}\right)\right]$$

$$= \left(6.02\times10^{23}\,\frac{\text{molecules}}{\text{mol}}\right)\left(\frac{1\text{ mol}}{197\text{ g}}\right)\left(19.3\,\frac{\text{g}}{\text{cm}^3}\right)$$

$$= 5.9\times10^{22}\,\frac{\text{molecules}}{\text{cm}^3} = 5.9\times10^{28}\,\frac{\text{atoms}}{\text{m}^3}$$

- Assume the distance between atoms is $d = (5.9\times10^{28})^{-1/3}\text{m} = 2.6\times10^{-10}\text{m}$

  and there are $N = \dfrac{6\times10^{-7}\text{m}}{2.6\times10^{-10}\text{m}} = 2300\text{ atoms}$.

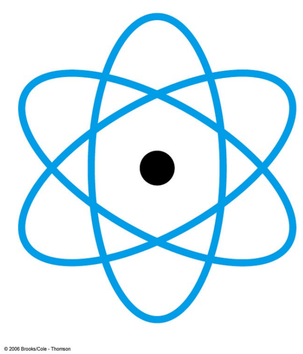
  That gives $\langle\theta\rangle_{\text{total}} = \sqrt{2300}(0.016^\circ) = 0.8^\circ$.

Rutherford's Atomic Model

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

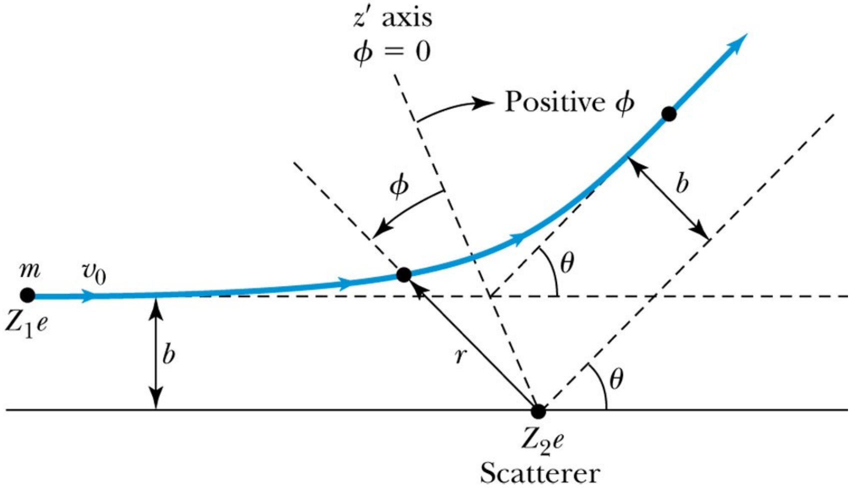
  The experimental results were not consistent with Thomson's atomic model.

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



4.2: Rutherford Scattering

- Scattering experiments help us study matter too small to be observed directly.
- There is a relationship between the impact parameter *b* and the scattering angle *θ*.



When *b* is small,

➞ *r* gets small.

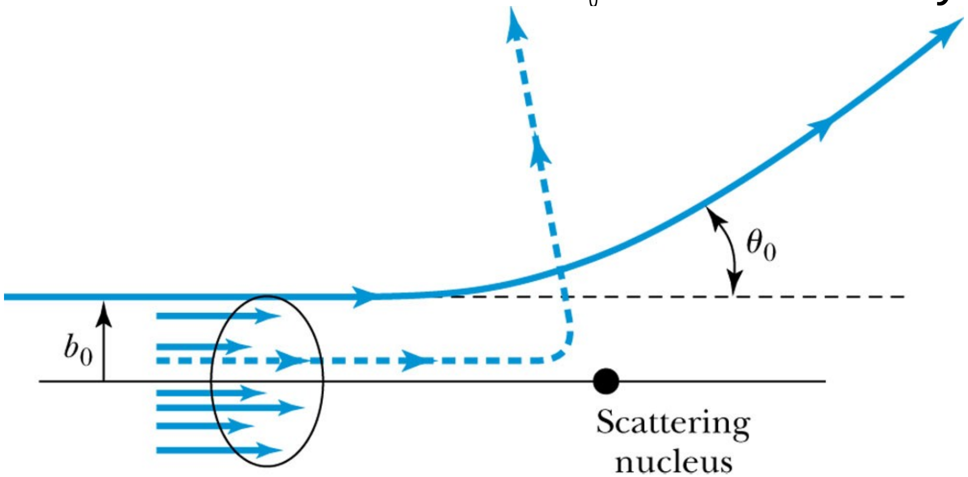
➞ Coulomb force gets large.

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

$$b = \frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\cot\frac{\theta}{2} \qquad \text{where } K = mv_0^{\ 2}/2$$

Rutherford Scattering

- Any particle inside the circle of area πb_0^2 will be similarly scattered.



- The cross section $\sigma = \pi b^2$ is related to the **probability** for a particle being scattered by a nucleus.

$$= \pi n t \left(\frac{Z_1 Z_2 e^2}{8 \pi \varepsilon_0 K} \right)^2 \cot^2 \frac{\theta}{2}$$

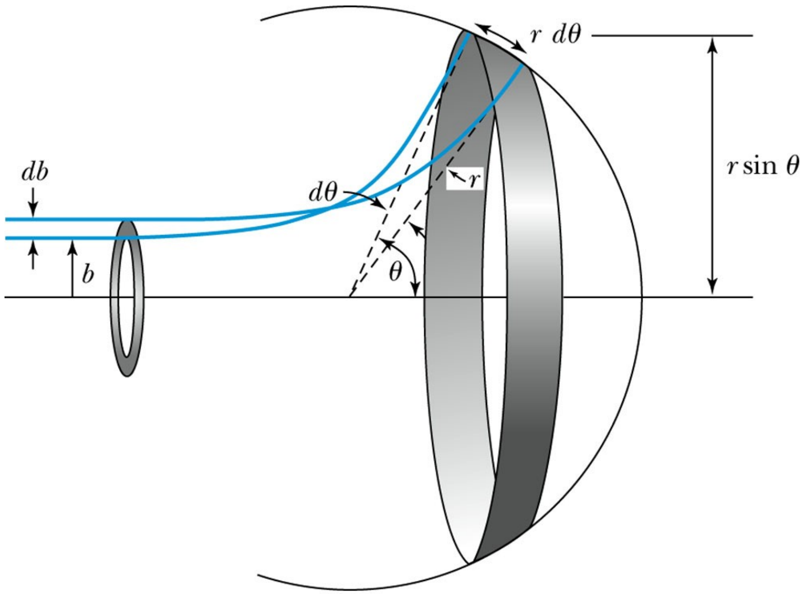
- The fraction of incident particles scattered is

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

- The number of scattering nuclei per unit area $nt = \dfrac{\rho N_A N_M t}{M_g} \dfrac{\text{atoms}}{\text{cm}^2}$

Rutherford Scattering Equation

- In actual experiment 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

$$N(\theta) = \frac{N_i n t}{16}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z_1^{\,2} Z_2^{\,2}}{r^2 K^2 \sin^4(\theta/2)}$$

4.3: The Classical Atomic Model

Let's consider atoms as a planetary model.

- The force of attraction on the electron by the nucleus and Newton's 2nd law give

$$\vec{F}_e = \frac{-1}{4\pi\varepsilon_0}\frac{e^2}{r^2}\hat{e}_r = \frac{mv^2}{r}$$

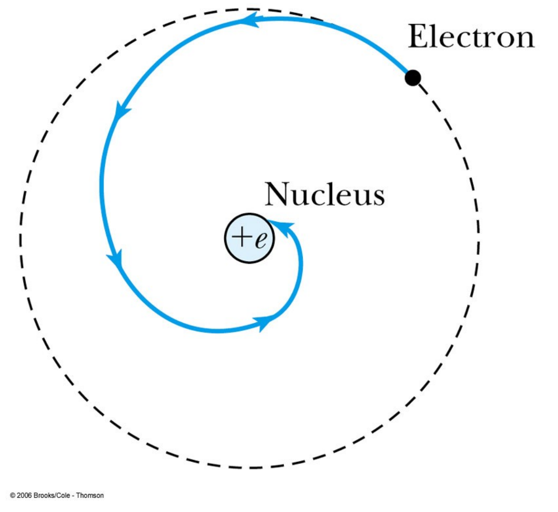
  where *v* is the tangential velocity of the electron.

- The total energy is

$$E = K + V = \frac{e^2}{8\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r} = \frac{-e^2}{8\pi\varepsilon_0 r}$$

The Planetary Model is Doomed

- From classical E&M theory, an accelerated electric charge radiates energy (electromagnetic radiation) which means total energy must decrease. ⟶ *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.

4.4: The Bohr Model of the Hydrogen Atom

Bohr's general assumptions:

1) "Stationary states" (orbiting electrons do not radiate energy) exist in atoms.
2) $E = E_1 - E_2 = hf$
3) Classical laws of physics do not apply to transitions between stationary states.
4) The mean kinetic energy of the electron-nucleus system is $K = nhf_{orb}/2$, where f_{orb} is the frequency of rotation.

Bohr Radius

- The diameter of the hydrogen atom for stationary states is

$$r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{me^2} \equiv n^2 a_0$$

Where the **Bohr radius** is given by

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = \frac{(1.055\times10^{-34}\ \mathrm{J\cdot s})^2}{\left(8.99\times10^9\,\frac{\mathrm{N\cdot m^2}}{\mathrm{C^2}}\right)(9.11\times10^{-31}\ \mathrm{kg})(1.6\times10^{-16}\ \mathrm{C})^2} = 0.53\times10^{-10}\ \mathrm{m}$$

- The smallest diameter of the hydrogen atom is

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

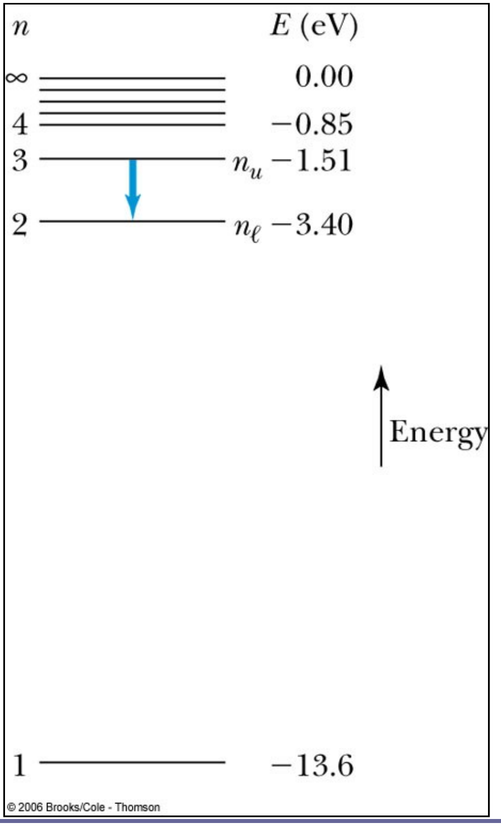
- *n* = 1 gives its lowest energy state (called the “ground” state)

The Hydrogen Atom

- The energies of the stationary states

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2}$$

where E_0 = 13.6 eV.



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

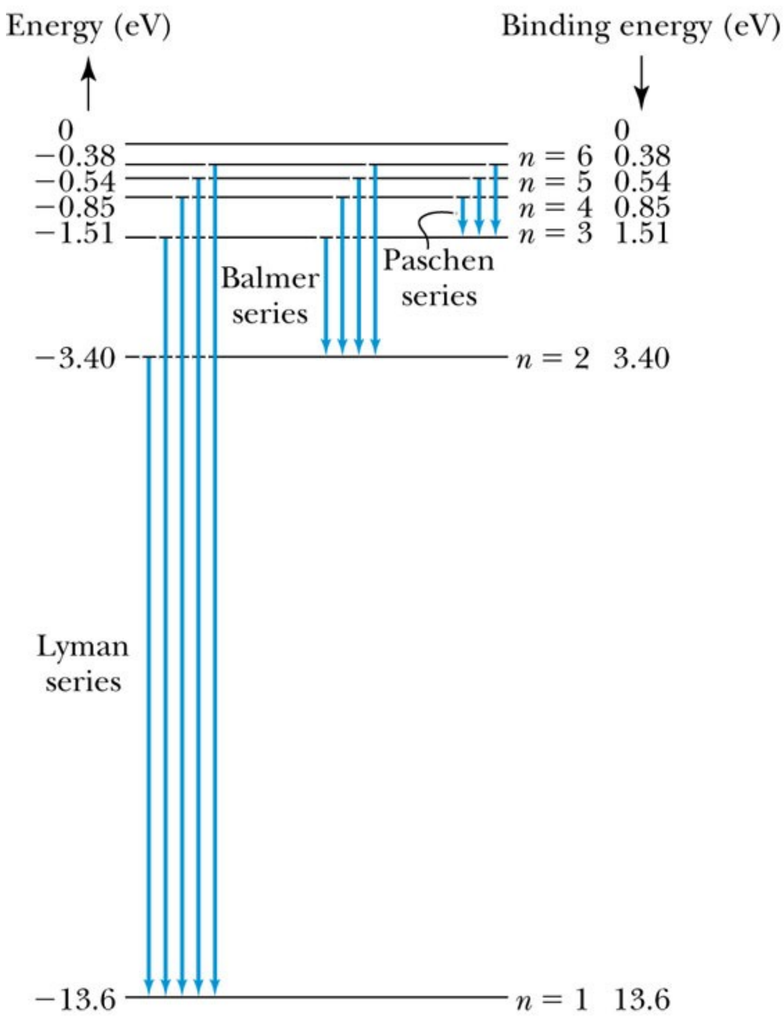
$$hf = E_u - E_\ell$$

where f is the frequency of a photon.

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{E_u - E_\ell}{hc} = R_\infty\left(\frac{1}{n_\ell^2} - \frac{1}{n_u^2}\right)$$

R_∞ is the **Rydberg constant**.

Transitions in the Hydrogen Atom



Lyman series

The atom will remain in the excited state for a short time before emitting a photon and returning to a lower stationary state. All hydrogen atoms exist in *n* = 1 (invisible).

Balmer series

When sunlight passes through the atmosphere, hydrogen atoms in water vapor absorb the wavelengths (visible).

Fine Structure Constant

- The electron's velocity in the Bohr model:

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n}\frac{e^2}{4\pi\varepsilon_0\hbar}$$

- On the ground state,

  v_1 = 2.2 × 10^6 m/s ~ less than 1% of the speed of light.

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

$$\alpha \equiv \frac{v_1}{c} = \frac{\hbar}{ma_0c} = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$$

The Correspondence Principle

Classical electrodynamics + Bohr's atomic model

Determine the properties of radiation

Need a principle to relate the new modern results with classical ones.

Bohr's correspondence principle

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

The Correspondence Principle

- The frequency of the radiation emitted $f_{classical}$ is equal to the orbital frequency f_{orb} of the electron around the nucleus.

$$f_{\text{classical}} = f_{\text{orb}} = \frac{\omega}{2\pi} \qquad f_{\text{classical}} = \frac{1}{2\pi}\left(\frac{e^2}{4\pi\varepsilon_0 m r^3}\right)^{1/2} = \frac{me^4}{4\varepsilon_0{}^2 h^3}\frac{1}{\mathrm{n}^3}$$

- The frequency of the transition from $n + 1$ to n is

$$f_{\text{Bohr}} = \frac{E_0}{h}\left[\frac{1}{n^2} - \frac{1}{(n+1)^2}\right]$$

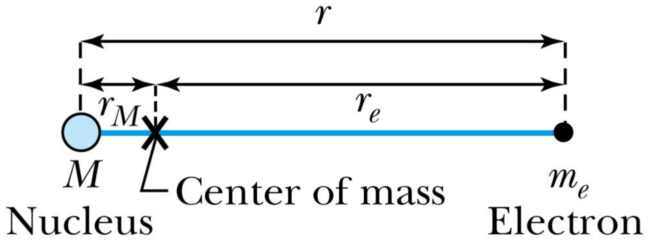
$$= \frac{E_0}{h}\left[\frac{n^2 + 2n + 1 - n^2}{n^2(n+1)^2}\right] = \frac{E_0}{h}\left[\frac{2n+1}{n^2(n+1)^2}\right]$$

- For large n, $f_{\text{Bohr}} \approx \frac{2nE_0}{hn^4} = \frac{2E_0}{hn^3}$

Substitute E_0: $f_{\text{Bohr}} = \frac{me^4}{4\varepsilon_0{}^2 h^3}\frac{1}{n^3} = f_{\text{classical}}$

4.5: Successes and Failures of the Bohr Model

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



- The electron mass is replaced by its **reduced mass**.

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

- The Rydberg constant for infinite nuclear mass is replaced by *R*.

$$R = \frac{\mu_e}{m_e} R_\infty = \frac{1}{1 + \frac{m_e}{M}} R_\infty = \frac{\mu_e e^4}{4\pi c \hbar^3 (4\pi\varepsilon_0)^2}$$

Limitations of the Bohr Model

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

1) Works only to single-electron atoms.
2) Could not account for the intensities or the fine structure of the spectral lines.
3) Could not explain the binding of atoms into molecules.

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.

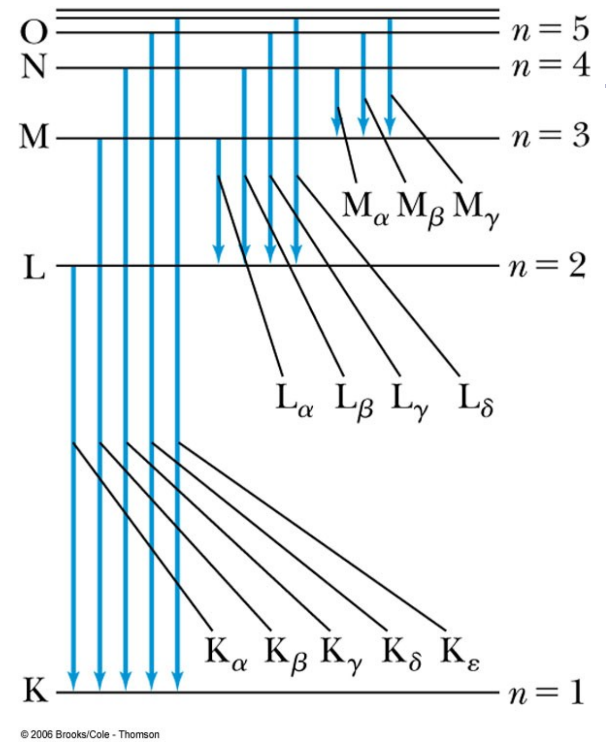
→ An electron from higher shells will fill the inner-shell vacancy at lower energy.

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

Atomic Number

L shell to K shell ⟶ K_α x ray

M shell to K shell ⟶ K_β x ray



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

  This holds for the K_α x ray.

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

Moseley's Empirical Results

- The x ray is produced from $n = 2$ to $n = 1$ transition.
- In general, the K series of x ray wavelengths are

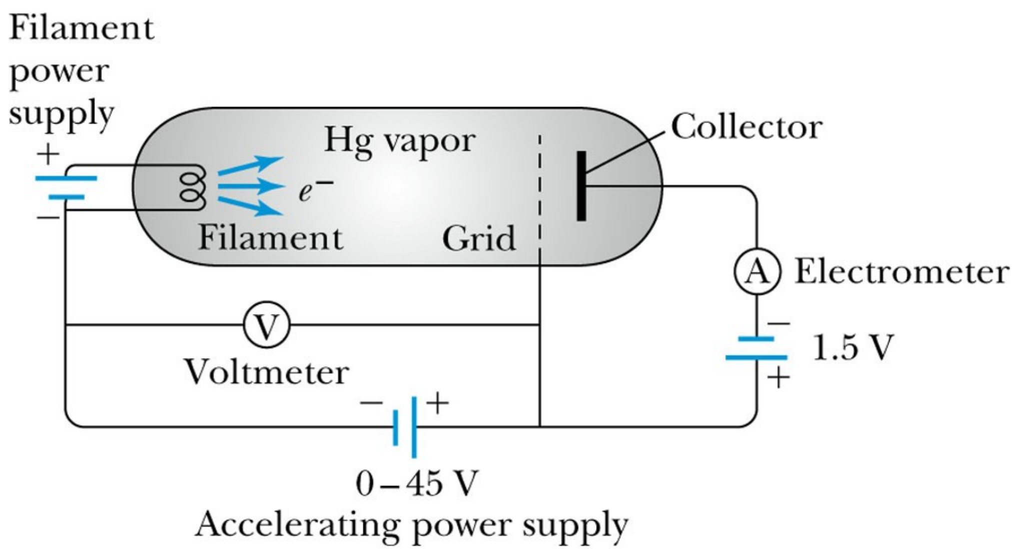
$$\frac{1}{\lambda_K} = R(Z-1)^2\left(\frac{1}{1^2} - \frac{1}{n^2}\right) = R(Z-1)^2\left(1 - \frac{1}{n^2}\right)$$

$$\Downarrow$$

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

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.

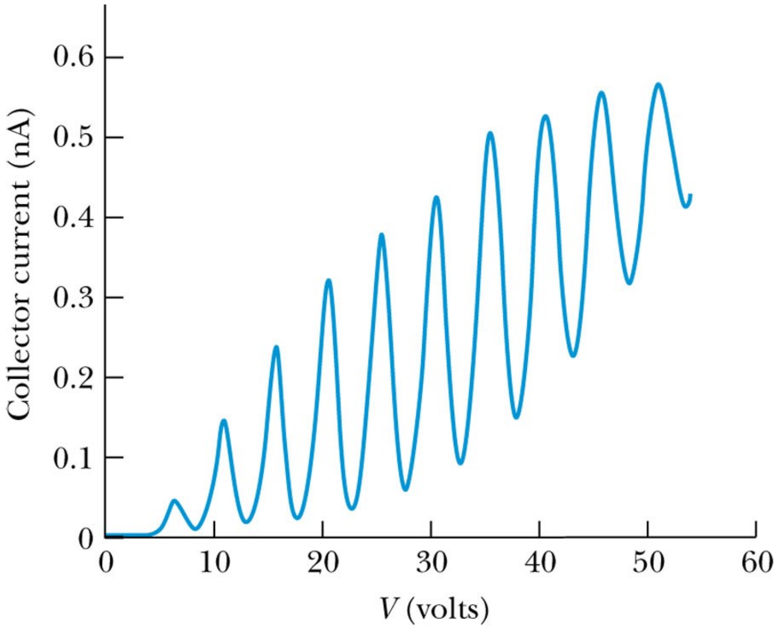
→ sudden drop in the current.

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.