

PHYS 3313 – Section 001

Lecture #14

Monday, March 6, 2017

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- The Classic Atomic Model
- Bohr Radius
- Bohr's Hydrogen Model and Its Limitations
- Characteristic X-ray Spectra



Announcements

- Midterm Exam
 - In class this Wednesday, March. 8
 - Covers from CH1.1 through what we learn today, CH4.7 plus the math refresher in the appendices
 - **Please do NOT miss the exam! You will get an F if you miss it.**
 - BYOF: You may bring a one 8.5x11.5 sheet (front and back) of handwritten formulae and values of constants for the exam
 - No derivations, word definitions or solutions of any problems!
 - No additional formulae or values of constants will be provided!
- Mid-term grade discussions
 - Monday March 20 and Wednesday, March 22
 - Monday we will have class for the first 45min..
 - Wednesday we will replace the class with your grade discussion



The Classical Atomic Model

As suggested by the Rutherford Model, an atom consisted of a small, massive, positively charged nucleus surrounded by moving electrons. This then suggested consideration of a planetary model of the atom.

Let's consider atoms in a planetary model.

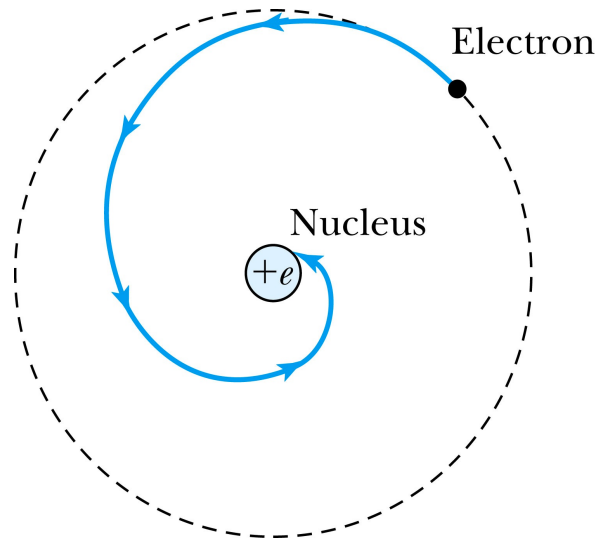
- The force of attraction on the electron by the nucleus and Newton's 2nd law give
$$\vec{F}_e = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \hat{e}_r = -\frac{mv^2}{r} \hat{e}_r$$

where v is the tangential speed of an electron.

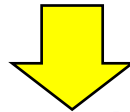
- The total energy is
$$E = K + V = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r}$$

The Planetary Model is Doomed

- From the 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.

The Bohr Model of the Hydrogen Atom – The assumptions

- “Stationary” states or orbits must exist in atoms, i.e., orbiting electrons **do not radiate** energy in these orbits. These orbits or stationary states are of a fixed definite energy E .
- The emission or absorption of electromagnetic radiation can occur only in conjunction with a transition between two stationary states. The frequency, f , of this radiation is proportional to the *difference* in energy of the two stationary states:
 - $$E = E_1 - E_2 = hf$$
 - *where h is Planck's Constant*
 - *Bohr thought this has to do with the fundamental length of order $\sim 10^{-10}m$*
- Classical laws of physics do not apply to transitions between stationary states.
- The mean kinetic energy of the electron-nucleus system is quantized as $K = nhf_{\text{orb}}/2$, where f_{orb} is the frequency of rotation. This is equivalent to the angular momentum of a stationary state to be an integral multiple of $h/2\pi$

How did Bohr Arrived at the angular momentum quantization?

- The mean kinetic energy of the electron-nucleus system is quantized as $K = nhf_{\text{orb}}/2$, where f_{orb} is the frequency of rotation. This is equivalent to the angular momentum of a stationary state to be an integral multiple of $h/2\pi$.
- Kinetic energy can be written $K = \frac{nhf}{2} = \frac{1}{2}mv^2$
- Angular momentum is defined as $|\vec{L}| = |\vec{r} \times \vec{p}| = mvr$
- The relationship between linear and angular quantifies $v = r\omega$; $\omega = 2\pi f$
- Thus, we can rewrite $K = \frac{1}{2}mvr\omega = \frac{1}{2}L\omega = \frac{1}{2}2\pi Lf = \frac{nhf}{2}$

$$2\pi L = nh \Rightarrow L = n \frac{h}{2\pi} = n\hbar, \text{ where } \hbar = \frac{h}{2\pi}$$

Bohr's Quantized Radius of Hydrogen

- The angular momentum is $|\vec{L}| = |\vec{r} \times \vec{p}| = mvr = n\hbar$
- So the speed of an orbiting e can be written $v_e = \frac{n\hbar}{m_e r}$
- From the Newton's law for a circular motion

$$F_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{m_e v_e^2}{r} \Rightarrow v_e = \frac{e}{\sqrt{4\pi\epsilon_0 m_e r}}$$

- So from the above two equations, we can get

$$v_e = \frac{n\hbar}{m_e r} = \frac{e}{\sqrt{4\pi\epsilon_0 m_e r}} \Rightarrow r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e e^2}$$

Bohr Radius

- The radius of the hydrogen atom for the n^{th} stationary state is

$$r_n = \frac{4\pi\epsilon_0\hbar^2 n^2}{m_e e^2} = a_0 n^2$$

Where the **Bohr radius** for a given stationary state is:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \cdot (9.11 \times 10^{-31} \text{ kg}) \cdot (1.6 \times 10^{-19} \text{ C})^2} = 0.53 \times 10^{-10} \text{ m}$$

- The smallest diameter of the hydrogen atom is

$$d = 2r_1 = 2a_0 \approx 10^{-10} \text{ m} \approx 1 \text{ \AA}$$

– OMG!! The fundamental length!!

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

Ex. 4.6 Justification for non-relativistic treatment of orbital e

- Are we justified for the non-relativistic treatment of the orbital electrons?
 - When do we apply relativistic treatment?

- When $v/c > 0.1$

- Orbital speed: $v_e = \frac{e}{\sqrt{4\pi\epsilon_0 m_e r}}$

- Thus

$$v_e = \frac{(1.6 \times 10^{-16}) \cdot (9 \times 10^9)}{\sqrt{(9.1 \times 10^{-31}) \cdot (0.5 \times 10^{-10})}} \approx 2.2 \times 10^6 \text{ (m/s)} < 0.01c$$

Uncertainties

- Statistical Uncertainty: A naturally occurring uncertainty due to the number of measurements
 - Usually estimated by taking the square root of the number of measurements or samples, $\sqrt{N}$
- Systematic Uncertainty: Uncertainty due to unintended biases or unknown sources
 - Biases made by personal measurement habits
 - Some sources that could impact the measurements
- In any measurement, the uncertainties provide the significance to the measurement

The Hydrogen Atom

- Recalling the total E of an e in an atom, the n^{th} stationary states E_n

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{E_1}{n^2} \quad E_0 = -\frac{e^2}{8\pi\epsilon_0 a_0} = \frac{-(8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \cdot (1.6 \times 10^{-19} \text{ C})^2}{2(0.53 \times 10^{-10} \text{ m})} = -13.6 \text{ eV}$$

where E_0 is the ground state energy

n	E (eV)
∞	0.00
4	-0.85
3	-1.51
2	-3.40

n_u (at $n=3$)
 n_ℓ (at $n=2$)

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

$$hf = E_u - E_l$$

↑
Energy

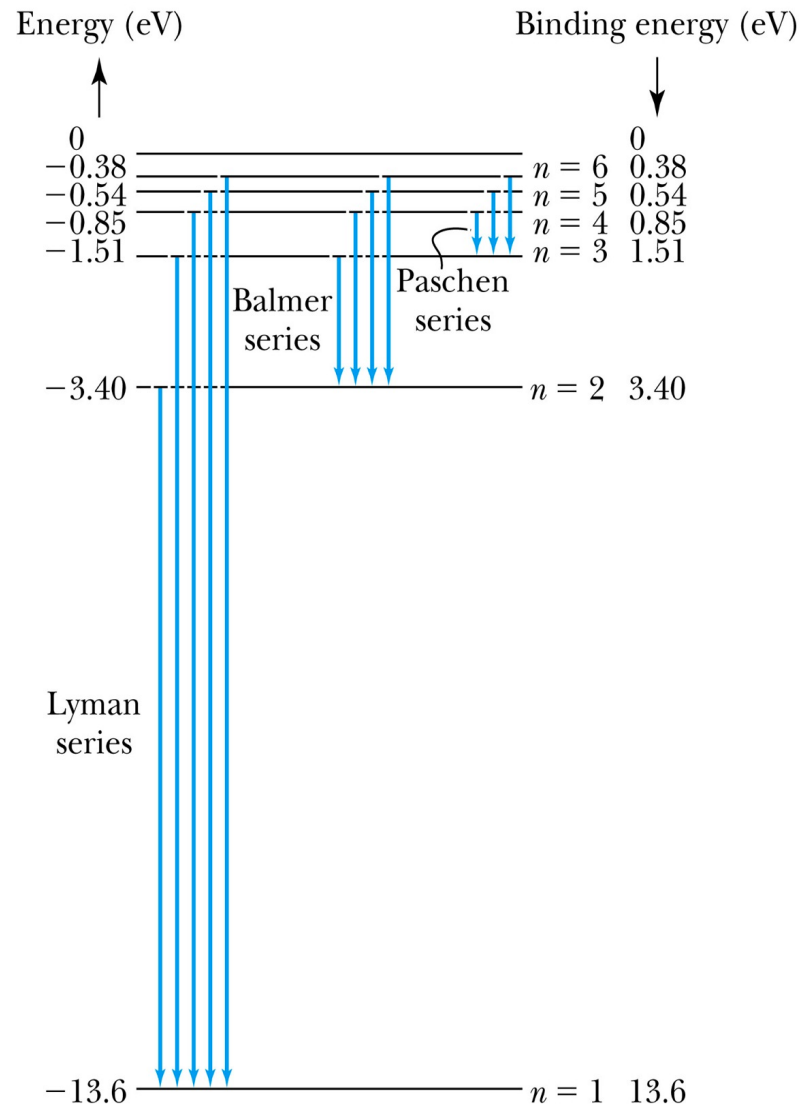
where f is the frequency of a photon.

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{E_u - E_l}{hc} = \frac{E_0}{hc} \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right) = R_\infty \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

1 ————— -13.6

R_∞ is the **Rydberg constant**. $R_\infty = E_0/hc$

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

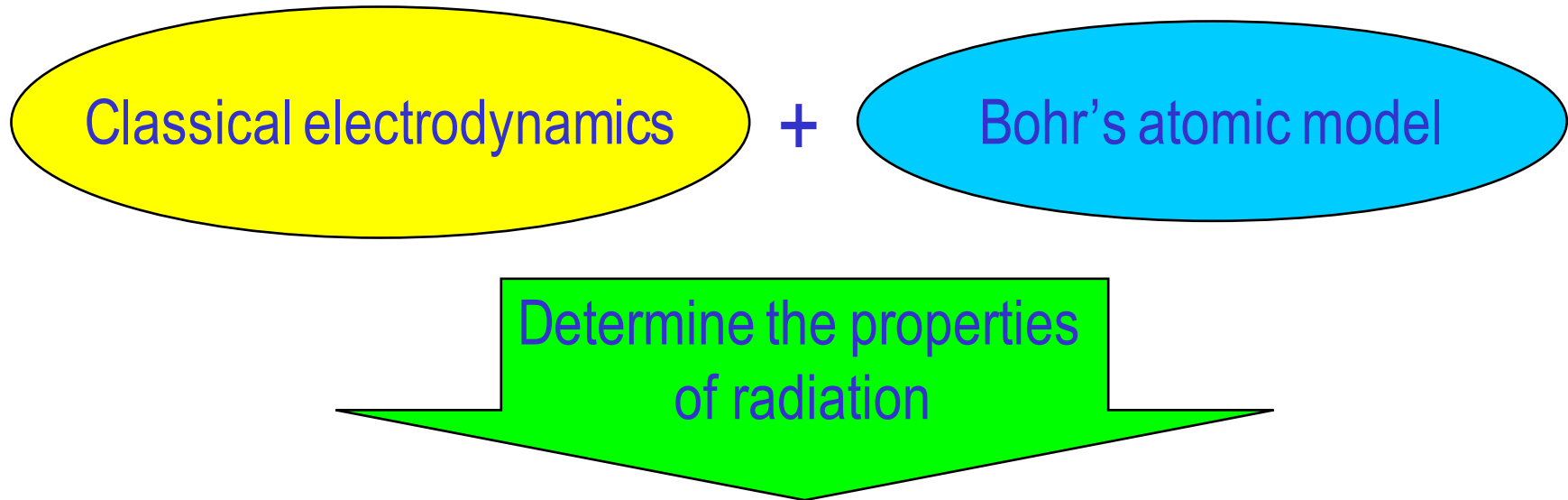
- The electron's speed on an orbit in the Bohr model:

$$v_e = \frac{n\hbar}{m_e r_n} = \frac{n\hbar}{m_e \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e e^2}} = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0 \hbar}$$

- On the ground state, $v_1 = 2.2 \times 10^6 \text{ m/s} \sim$ less than 1% of the speed of light
- The ratio of v_1 to c is the **fine structure constant, α** .

$$\alpha \equiv \frac{v_1}{c} = \frac{\hbar}{ma_0 c} = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{(8.99 \times 10^9 \text{ N} \cdot \text{m}^2 / \text{C}^2) \cdot (1.6 \times 10^{-19} \text{ C})^2}{(1.055 \times 10^{-34} \text{ J} \cdot \text{s}) \cdot (3 \times 10^8 \text{ m/s})} \approx \frac{1}{137}$$

The Correspondence Principle



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

Bohr's correspondence principle

In the limits where classical and quantum theories should agree, the quantum theory must produce the classical results.

The Correspondence Principle

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

$$f_{\text{classical}} = f_{\text{orb}} = \frac{\omega}{2\pi} = \frac{1}{2\pi} \frac{v}{r} = \frac{1}{2\pi r} \frac{e}{\sqrt{4\pi\epsilon_0 m_e r}} = \frac{1}{2\pi} \left(\frac{e^2}{4\pi\epsilon_0 m_e r^3} \right)^{1/2} = \frac{m_e e^4}{4\epsilon_0^2 h^3} \frac{1}{n^3}$$

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

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

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

Substitute E_0 :

$$f_{\text{Bohr}} = \frac{2E_0}{hn^3} = \frac{2}{hn^3} \left(\frac{e^2}{8\pi\epsilon_0 a_0} \right) = \frac{m_e e^4}{4\epsilon_0^2 h^3} \frac{1}{n^3} = f_{\text{Classical}}$$

So the frequency of the radiated E between classical theory and Bohr model agrees in large n case!!

The Importance of Bohr's Model

- Demonstrated the need for Plank's constant in understanding the atomic structure
- Assumption of quantized angular momentum which led to quantization of other quantities, r , v and E as follows

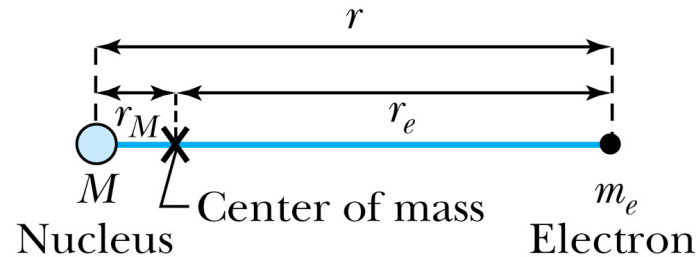
- Orbital Radius:
$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} n^2 = a_0 n^2$$

- Orbital Speed:
$$v = \frac{n\hbar}{mr_n} = \frac{\hbar}{ma_0} \frac{1}{n}$$

- Energy levels:
$$E_n = \frac{e^2}{8\pi\epsilon_0 a_0 n^2} = \frac{E_0}{n^2}$$

Successes and Failures of the Bohr Model

- The electron and hydrogen nucleus actually revolve about their mutual center of mass → reduced mass correction!!



- All we need is to replace m_e with atom's **reduced mass**.

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

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

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

$$\text{For H: } R_H = 1.096776 \times 10^7 \text{ m}^{-1}$$

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
 - Works even for ions → What would change?
 - The charge of the nucleus $\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$
- 2) Could not account for the intensities or the fine structure of the spectral lines
 - Fine structure is caused by the electron spin
 - Under a magnetic field, the spectrum splits by the spin
- 3) Could not explain the binding of atoms into molecules

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.

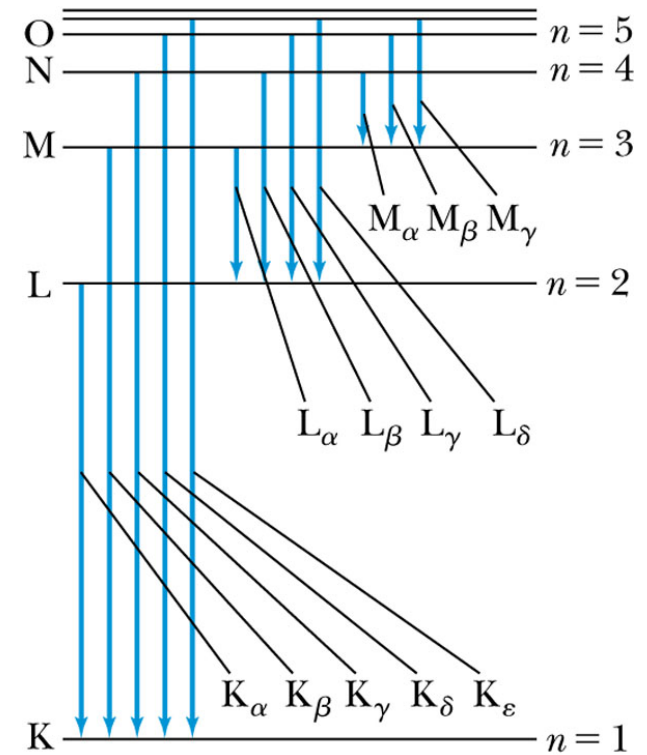
- When a transition occurs in a heavy atom, the radiation emitted is an **x ray**.
- It has the energy $E (\text{x ray}) = E_u - E_\ell$.

Atomic Number

L shell to K shell $\longrightarrow$ K_{α} x ray

M shell to K shell $\longrightarrow$ 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 .

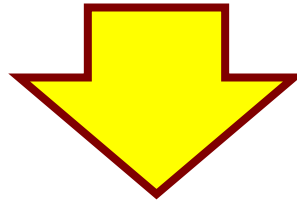
This holds for the K_{α} x ray

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

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

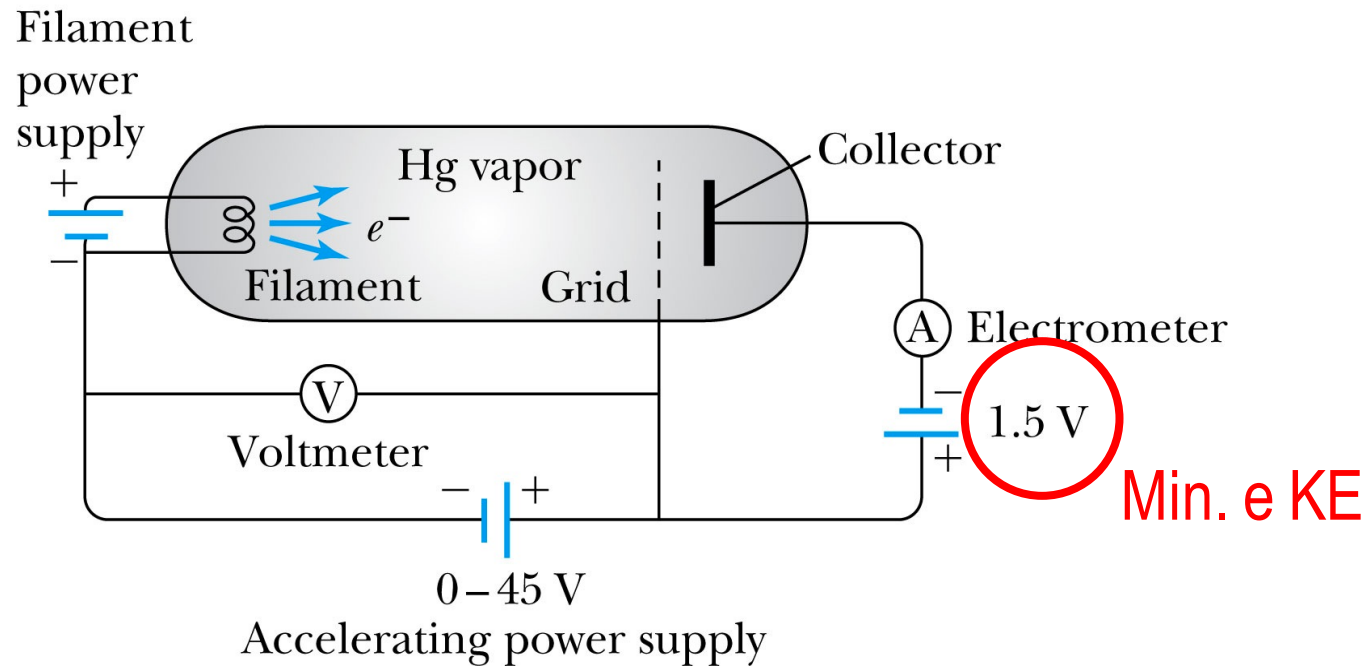
$$\frac{1}{\lambda_K} = R(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{n^2} \right) = R(Z - 1)^2 \left(1 - \frac{1}{n^2} \right)$$



- Moseley's research clarified the importance of the electron shells for all the elements, not just for hydrogen
 - Concluded correctly that atomic number Z , rather than the atomic weight, is the determining factor in ordering of the periodic table

Atomic Excitation by Electrons

- Franck and Hertz studied the phenomenon of ionization KE transfer from electrons to atoms.



When the accelerating voltage is below 5 V

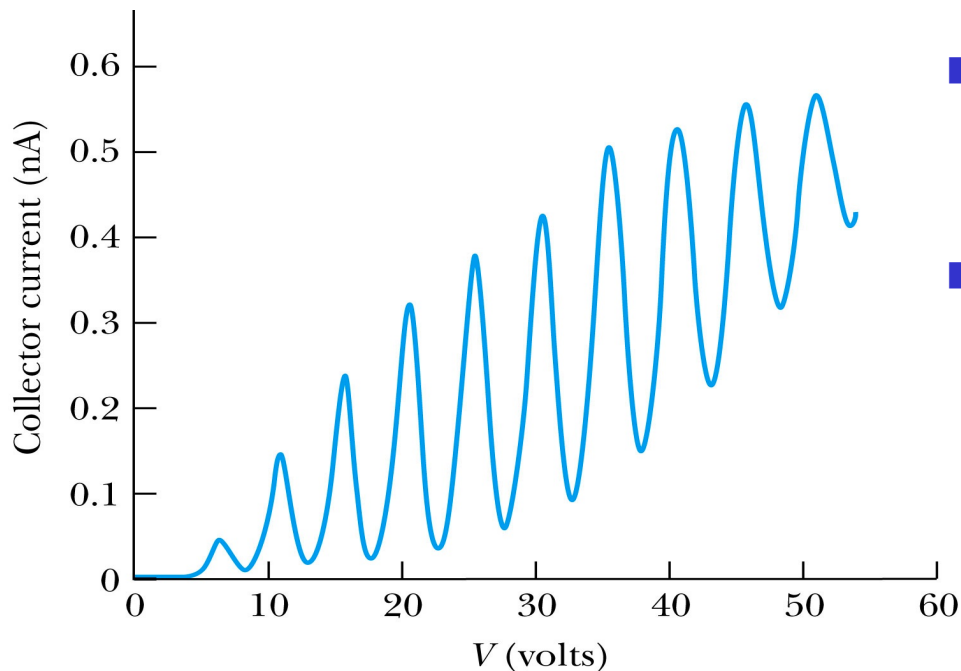
→ electrons did not lose energy going through the mercury vapor

When the accelerating voltage is above 5 V, 10V, etc..

→ sudden drop in the current

Atomic Excitation by Electrons

- Ground state has E_0 which can be considered as 0.
First excited state has E_1 .
The energy difference $E_1 - 0 = E_1$ is the **excitation energy**.



- Hg (mercury) 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 9.76 eV and so on.