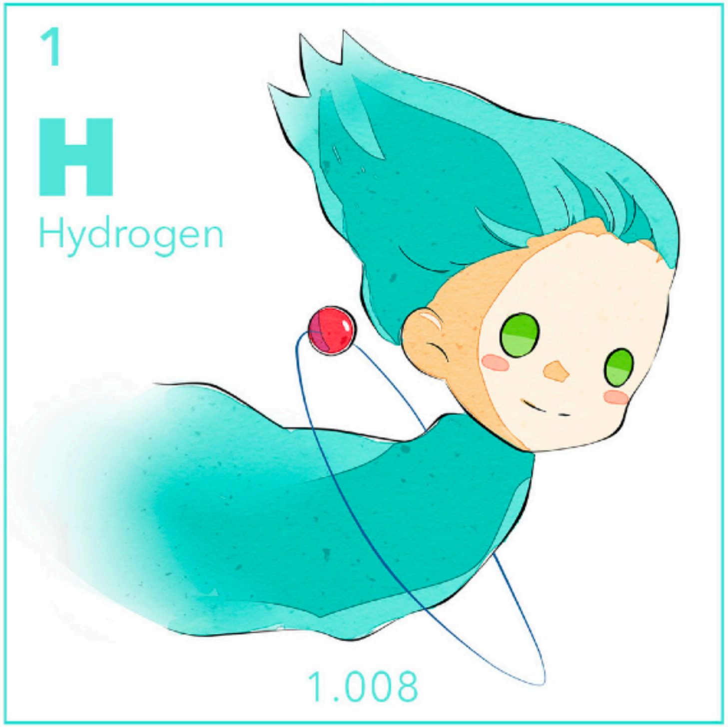
Atomic Physics

Chapter 2

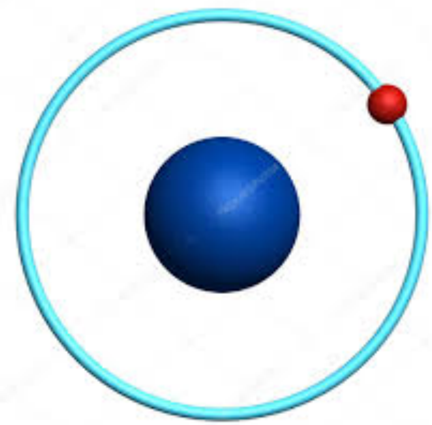
Bohr's Model of the Hydrogen



The Classical Atomic Model

The force of attraction on the electron due to the nucleus is

$$\vec{F} = \frac{-e^2}{4\pi\varepsilon_0}\frac{\vec{r}}{r^3}$$



The electron's radial acceleration

$$a_r = \frac{v^2}{r}$$

where v is the tangential velocity of the electron and Newton's second law now gives

$$\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2} = \frac{mv^2}{r}$$

and

$$v = \frac{e}{\sqrt{4\pi\varepsilon m r}}$$

The Classical Atomic Model

The total mechanical energy is

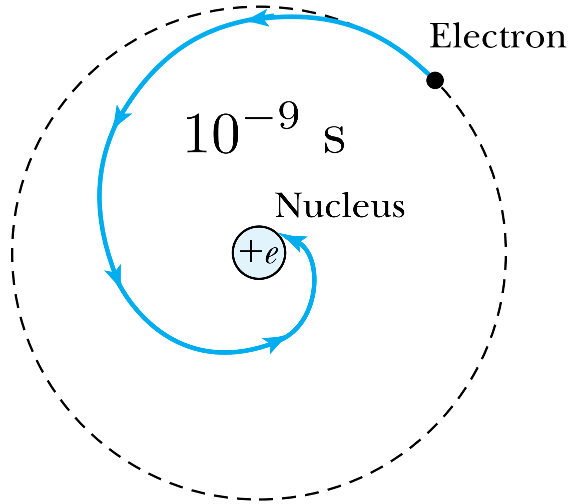
$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

with the equation about v, we have

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

The total energy is negative, indicating a bound system.

An accelerated electric charge continuously radiates energy in the form of electromagnetic radiation!



Bohr's general assumptions

A. Certain "stationary states" exist in atoms, which differ from the classical stable states in that the orbiting electrons do not continuously radiate electromagnetic energy. The stationary states are states of definite total energy.

B. The emission or absorption of electromagnetic radiation can occur only in conjunction with a transition between two stationary states. The frequency of the emitted or absorbed radiation is proportional to the difference in energy of the two stationary states (1 and 2):

$$E = E_1 - E_2 = h\nu$$

where h is Planck's constant.

Bohr's general assumptions

C. the angular momentum of the system in a stationary state being an integral multiple of $\hbar = h/2\pi$

$$L = mvr = n\hbar$$

where n is an integer called the principal quantum number.

The velocity can be solved

$$v = \frac{n\hbar}{mr}$$

with Newton's second law

$$v^2 = \frac{e^2}{4\pi\varepsilon_0 mr} = \frac{n^2\hbar^2}{m^2r^2}$$

Bohr model

Only certain values of radii are allowed

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

where the Bohr radius a_0 is given by

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$
$$= 0.53 \times 10^{-10} \text{ m}$$

The atomic radius is now quantized. The quantization of various physical values arises because of the principal quantum number n.

Bohr model

Electron's velocity in Bohr model

$$v_n = \frac{n\hbar}{mr_n} = \frac{n\hbar}{mn^2a_0} = \frac{1}{n}\frac{\hbar}{ma_0}$$

or

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

and

$$v_1 = \frac{\hbar}{ma_0} = 2.2 \times 10^6 \text{ m/s}$$

We define the dimensionless quantity ratio of v_1 to c as

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

This ratio is called the fine structure constant. It appears often in atomic structure calculations.

Bohr model

The energies of the stationary states

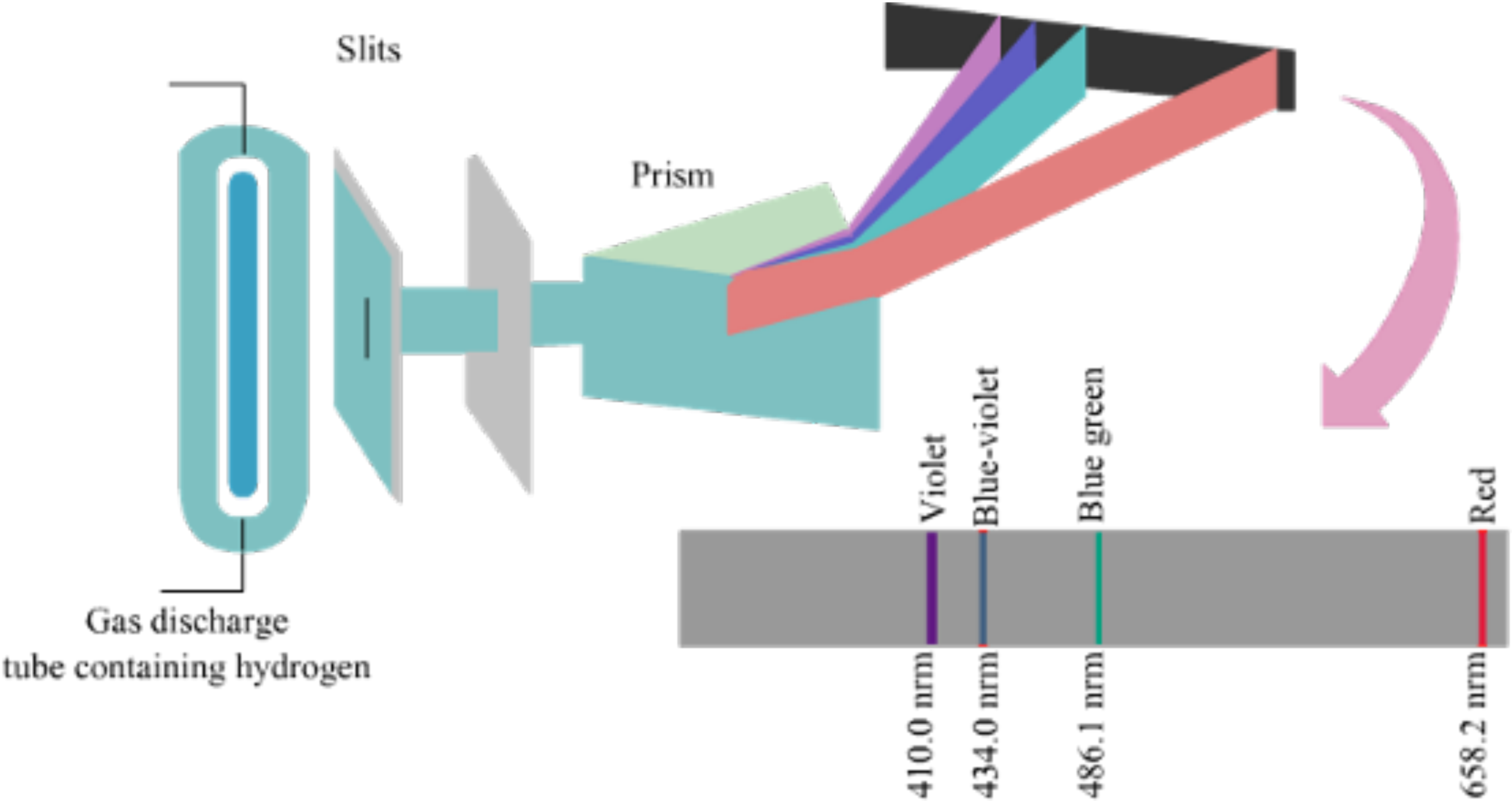
$$E_n = -\frac{e^2}{8\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2}$$

The lowest energy state (n=1) is $E_1 = -E_0$, where

$$E_0 = \frac{e^2}{8\pi\varepsilon_0 a_0} = \frac{e^2}{8\pi\varepsilon_0}\frac{me^2}{4\pi\varepsilon_0\hbar^2} = 13.6 \text{ eV}$$

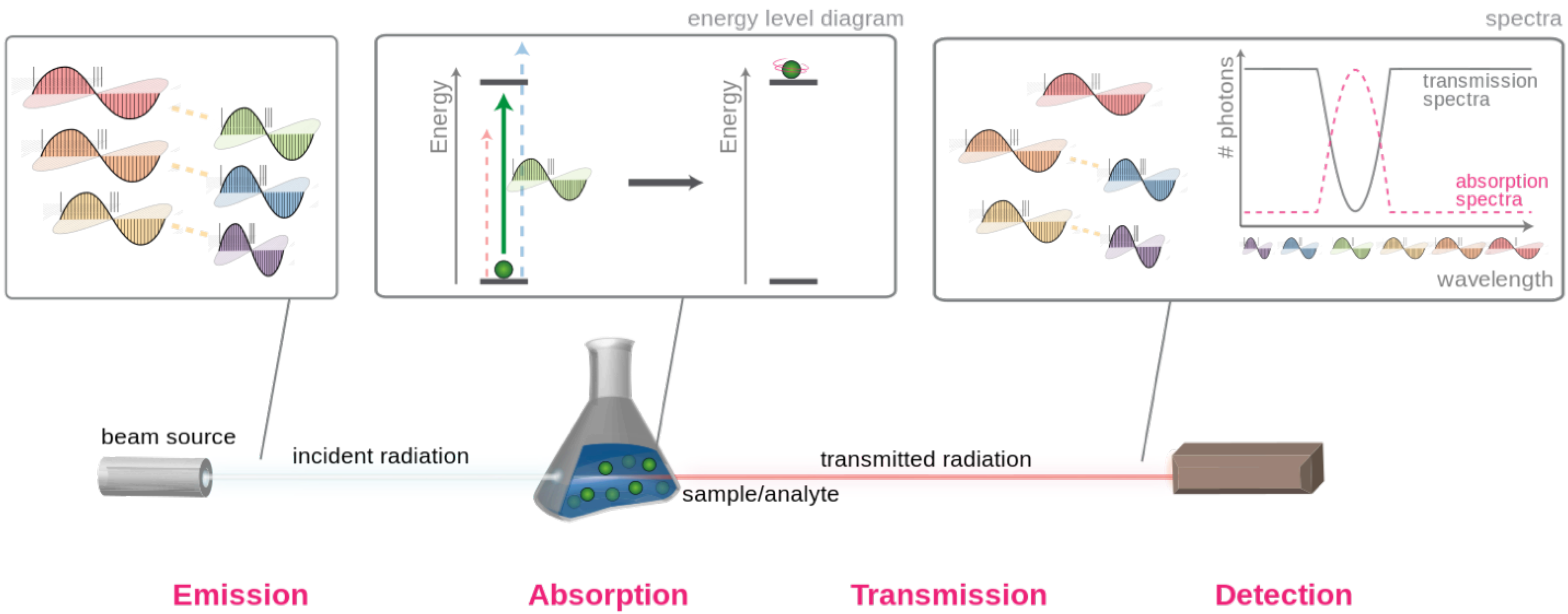
This is the experimentally measured ionization energy of the hydrogen atom. Bohr's assumption C imply that the atom can exsit only in "stationary state" with define, quantized energies E_n.

Line spectra



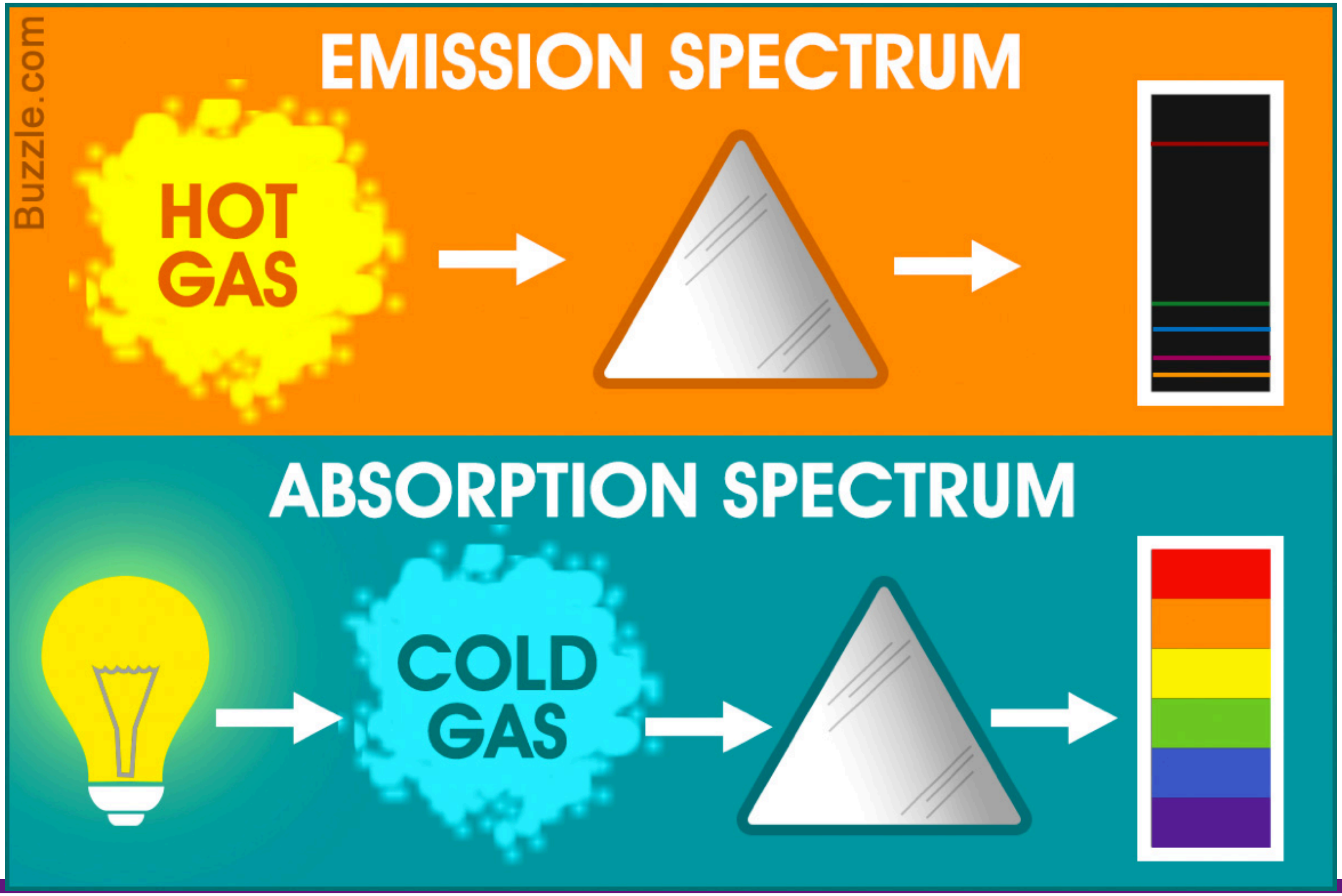
The absorption spectrum

When we pass white light (composed of all visible photon frequencies) through atomic hydrogen gas, we find that certain frequencies are absent. This pattern of dark lines is called an **absorption spectrum**.



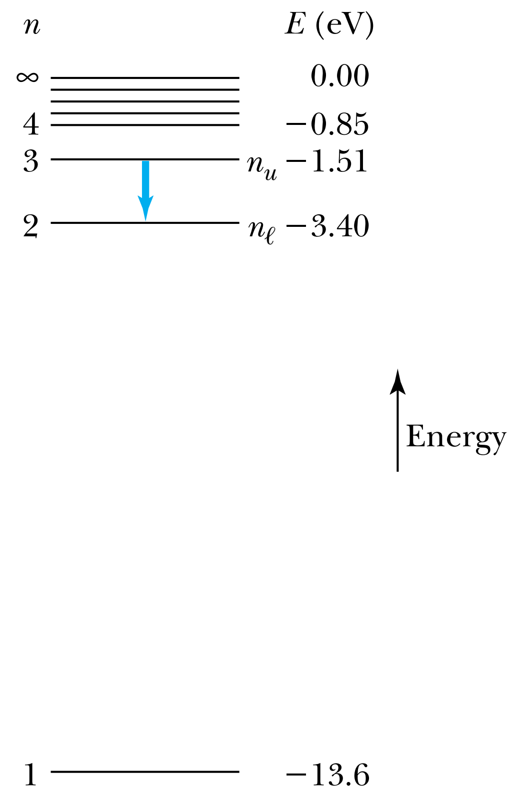
The emission spectrum

The missing frequencies are precisely the ones observed in the corresponding emission spectrum.



Bohr model

Emission of a quantum of light occurs when the atom is in an excited state (quantum number $n=n_u$) and decays to a lower energy state (quantum number $n=n_l$)



$$h\nu = E_u - E_l$$

where, v is the frequency of the emitted light quantum (photon). Because

$$\lambda\nu = c$$

we have

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_u - E_l}{hc}$$

$$= -\frac{E_0}{hc}\left(\frac{1}{n_u^2} - \frac{1}{n_l^2}\right) = \frac{E_0}{hc}\left(\frac{1}{n_l^2} - \frac{1}{n_u^2}\right)$$

Bohr model

where,

$$\frac{E_0}{hc} = \frac{me^4}{4\pi c\hbar^3(4\pi\varepsilon_0)^2} \equiv R_\infty$$

is called the **Rydberg constant** (for an infinite nuclear mass)

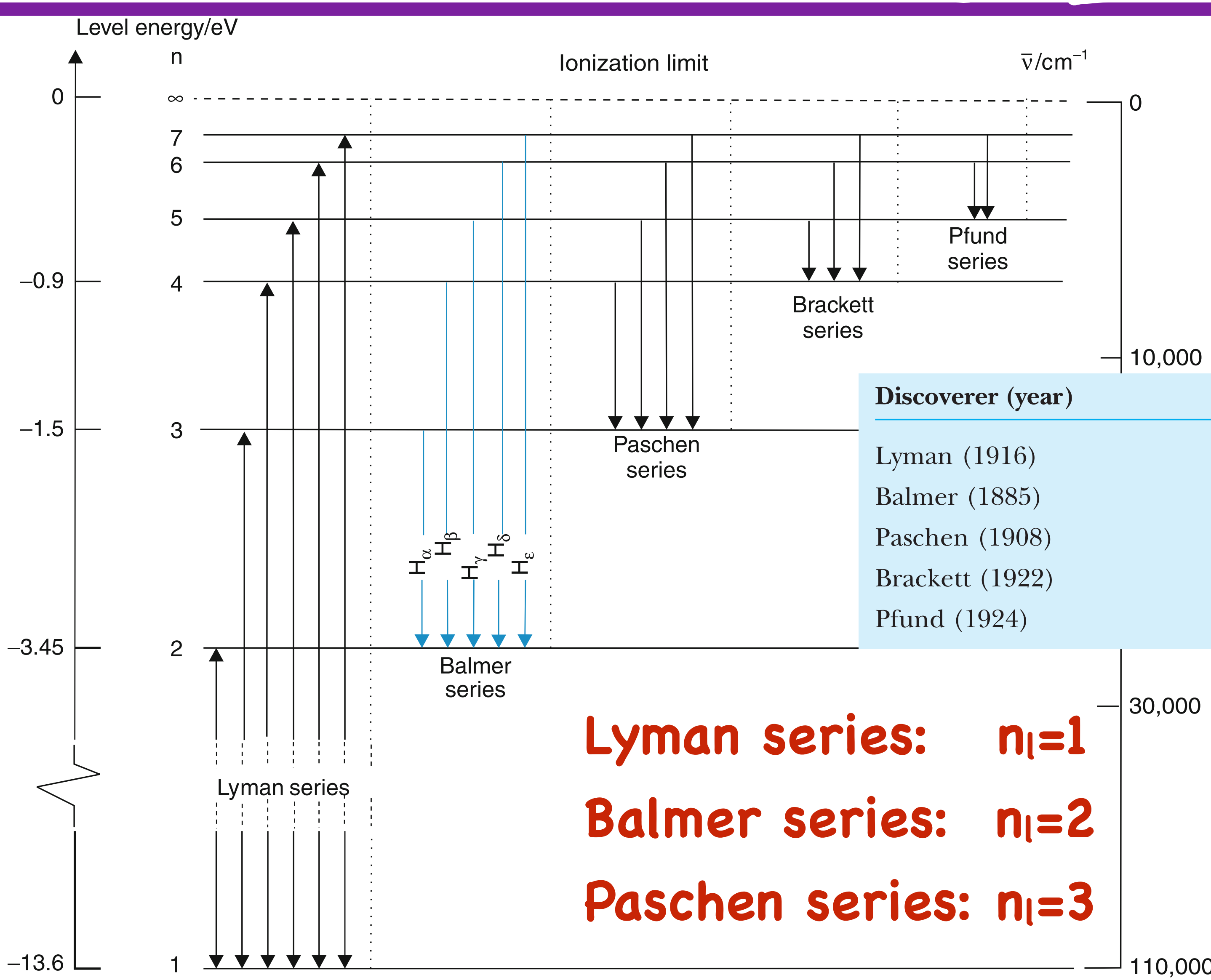
and

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

which was found by J. Rydberg.

Bohr's model predicts the frequencies (and wavelengths) of all possible transitions in atomic hydrogen.

The spectrum of hydrogen



Discoverer (year)	Wavelength
Lyman (1916)	Ultraviolet
Balmer (1885)	Visible, ultraviolet
Paschen (1908)	Infrared
Brackett (1922)	Infrared
Pfund (1924)	Infrared

Lyman series: $n_l=1$

Balmer series: $n_l=2$

Paschen series: $n_l=3$

The Correspondence Principle

Bohr's correspondence principle: In the limits where classical and quantum theories should agree, the quantum theory must reduce to the classical result.

To illustrate this principle, let us examine the predictions of the radiation law.

Classically the frequency of the radiation emitted is equal to the orbital frequency ν_{orb} of the electron around the nucleus:

$$\nu_{\text{classical}} = \nu_{\text{orb}} = \frac{\omega}{2\pi} = \frac{1}{2\pi}\frac{v}{r}$$

The Correspondence Principle

With Newton's second law:

$$\nu_{\text{classical}} = \frac{1}{2\pi}\sqrt{\frac{e^2}{4\pi\varepsilon_0 m r^3}} \qquad r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{me^2} \equiv n^2 a_0$$

Using Bohr model, the classical frequency in terms of fundamental constants and the principal quantum number n

$$\nu_{\text{classical}} = \frac{me^4}{4\varepsilon_0^2 h^3}\frac{1}{n^3}$$

In the Bohr model, the frequency of the transition from n+1 to n is

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

The Correspondence Principle

It becomes for large n

$$\nu_{\text{Bohr}} \approx \frac{2nE_0}{hn^4} = \frac{2E_0}{hn^3}$$

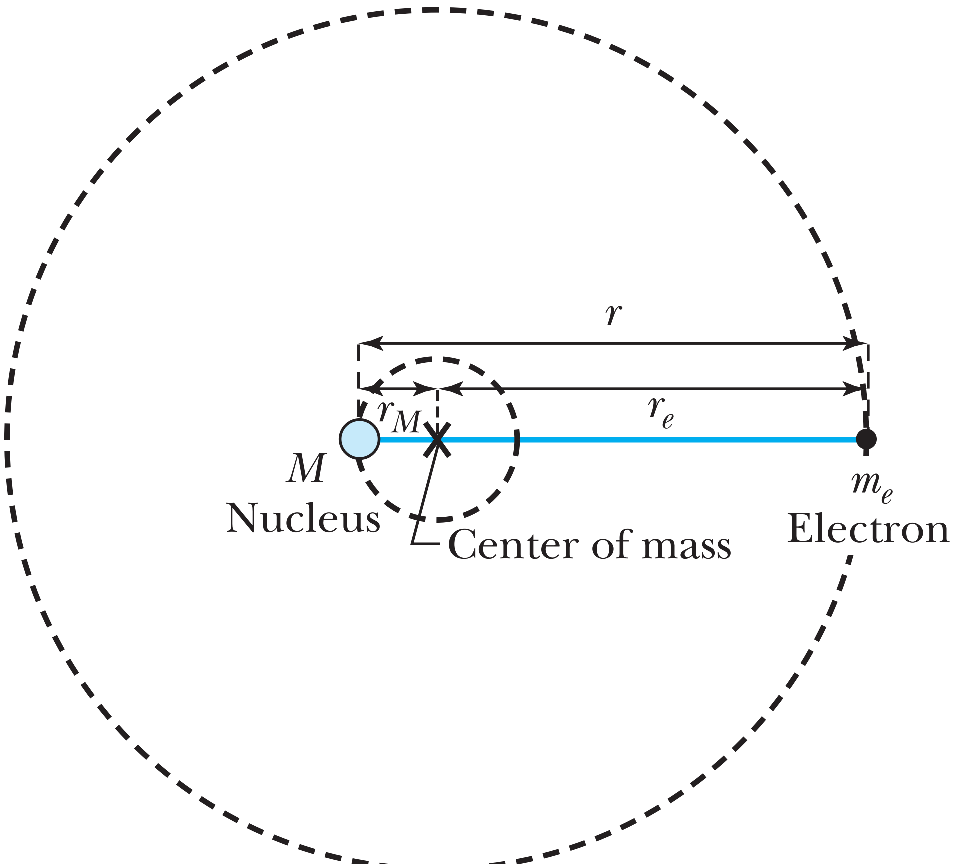
When the E_0 is substituted, the result is

$$\nu_{\text{Bohr}} = \frac{me^4}{4\epsilon_0^2 h^3} \frac{1}{n^3} = \nu_{\text{classical}}$$

so the frequencies of the radiated energy agree between classical theory and the Bohr model for large values of the quantum number n. Bohr's correspondence principle is verified for large orbits, where classical and quantum physics should agree.

The Successes of Bohr Model

A straightforward analysis derived from classical mechanics shows that this two-body problem can be reduced to an equivalent one-body problem



The Successes of Bohr Model

Reduced mass

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

and M is the mass of the nucleus. In the case of the hydrogen atom, M is the proton mass, and the correction for the hydrogen atom is

$$\mu_e = 0.999456 m_e$$

This difference can be measured experimentally. The Rydberg constant for infinite nuclear mass should be replaced by,

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

The Successes of Bohr Model

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The Rydberg constant for hydrogen is

$$R_{\mathrm{H}} = 1.096776 \times 10^{7}\ \mathrm{m}^{-1}$$

The Bohr model may be applied to any single-electron atom (hydrogen-like) even if the nuclear charge is greater than 1 proton charge (+e), for example He^{+} and Li^{++}.

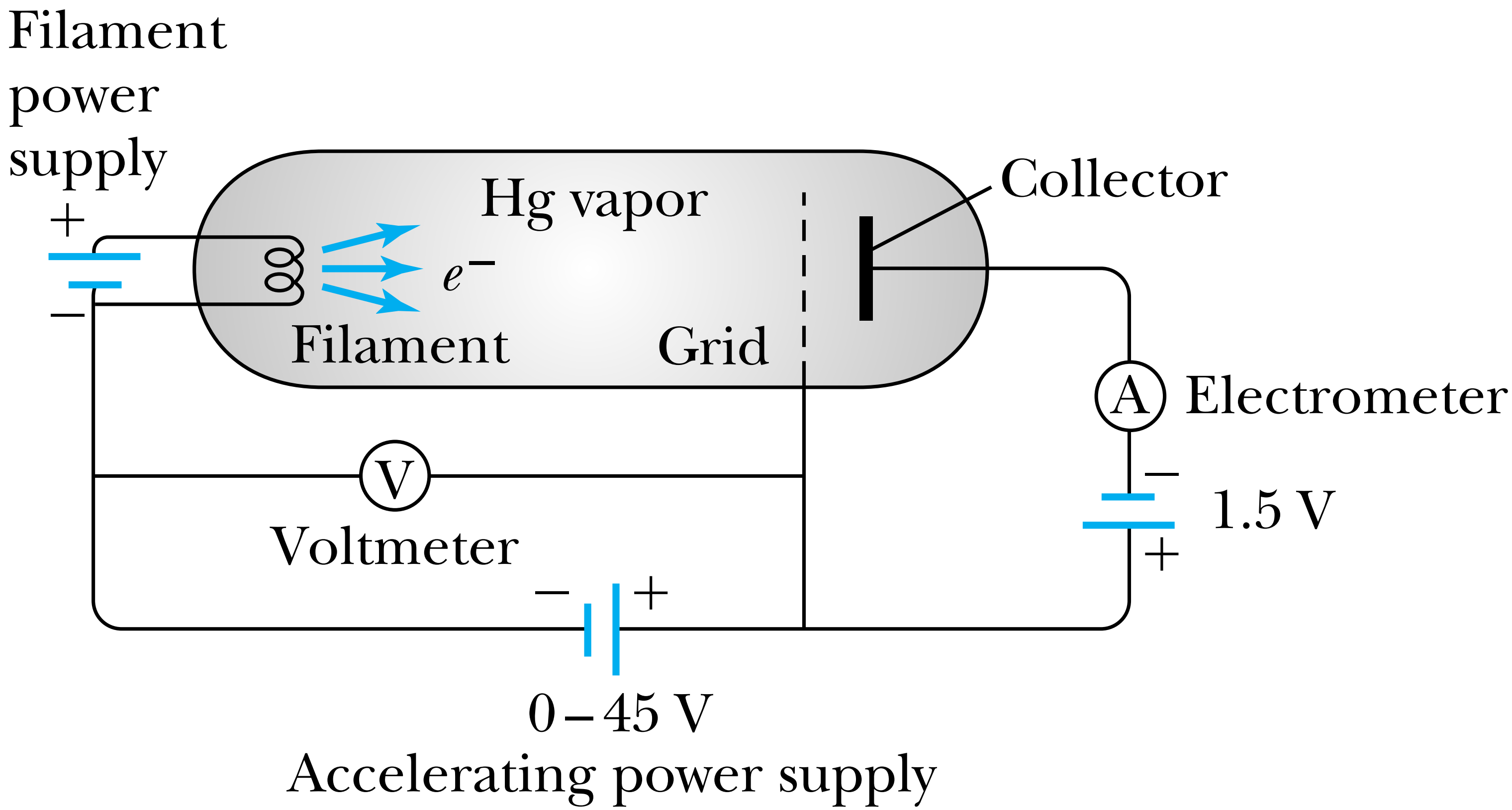
The Rydberg equation becomes

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

Z is the nuclear charge. This equation is valid only for single-electron atoms. Charged atoms, such as He^{+}, Li^{+}, and Li^{++}, are called ions

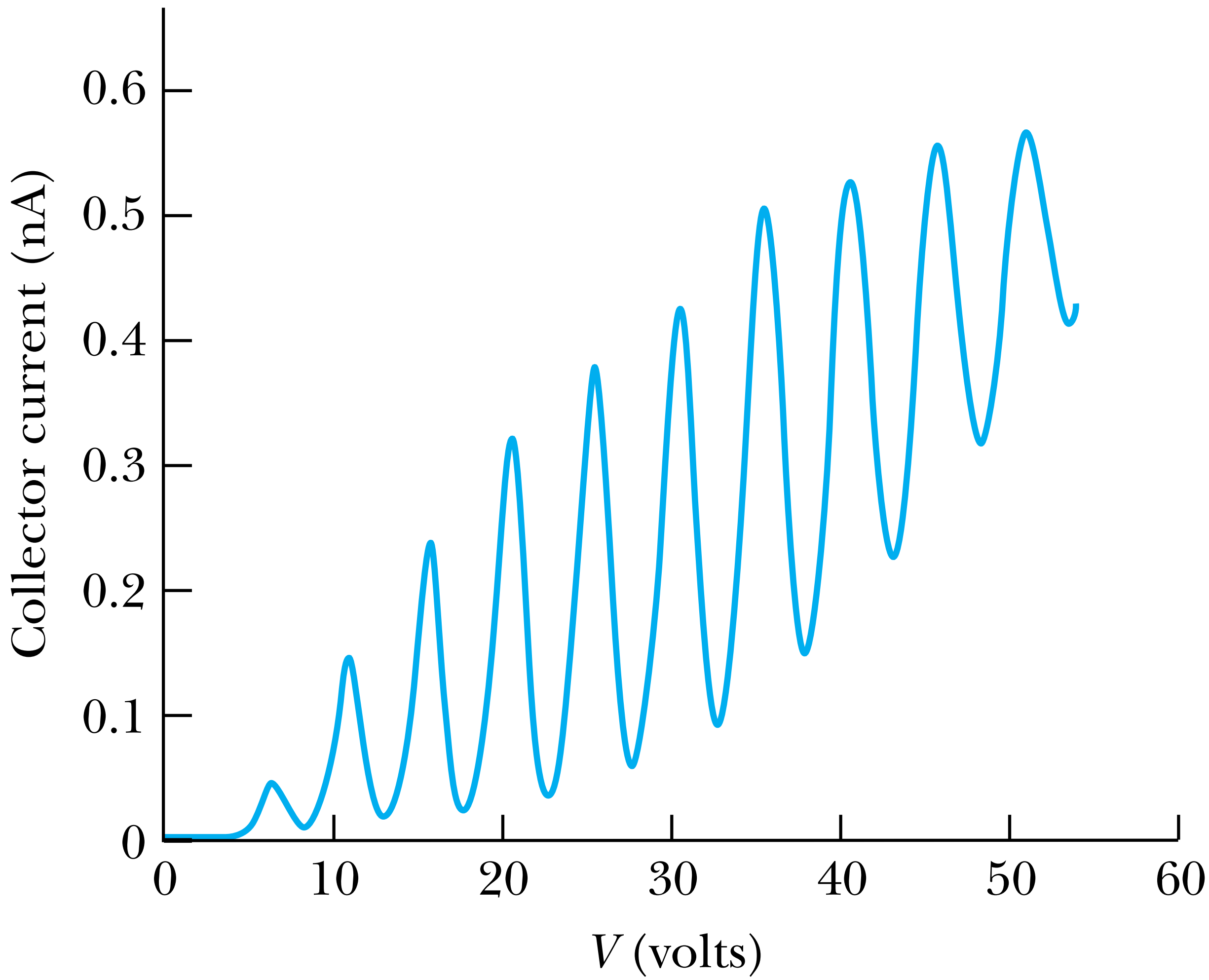
Atomic Excitation by Electrons

The German physicists James Franck and Gustav Hertz decided to study electron bombardment of gaseous vapors to study the phenomenon of ionization.



Atomic Excitation by Electrons

Data from Franck- Hertz experiment



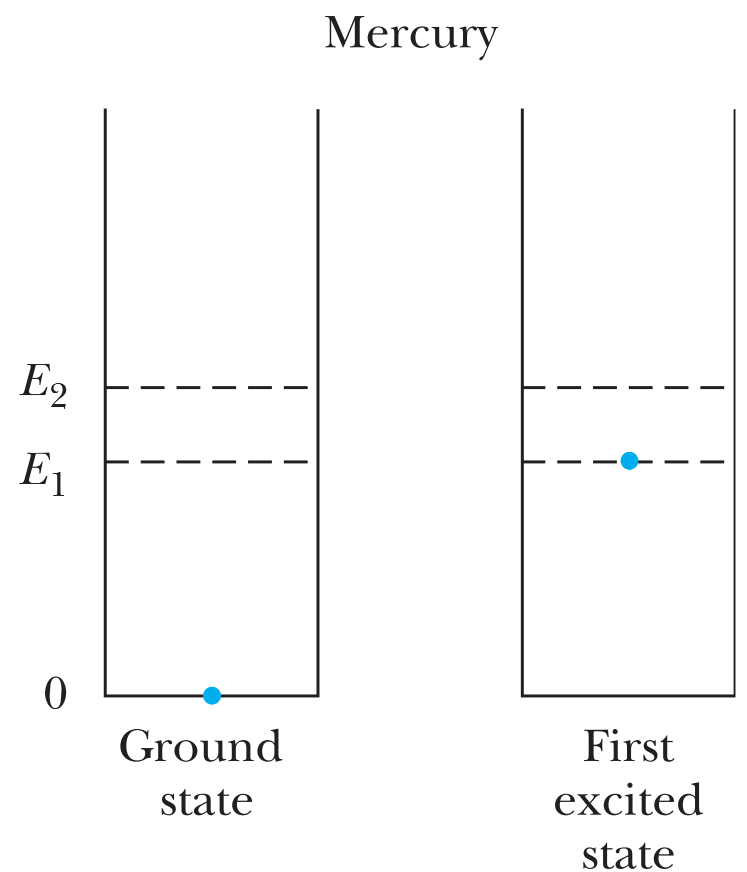
Atomic Excitation by Electrons

We can explain the experimental results of Franck and Hertz within the context of Bohr's picture of quantized atomic energy levels.

In the most popular representation of atomic energy states, we say that the atom, when all the electrons are in their lowest possible energy states, is the ground state. The first quantized energy state above the ground state is called the first excited state.

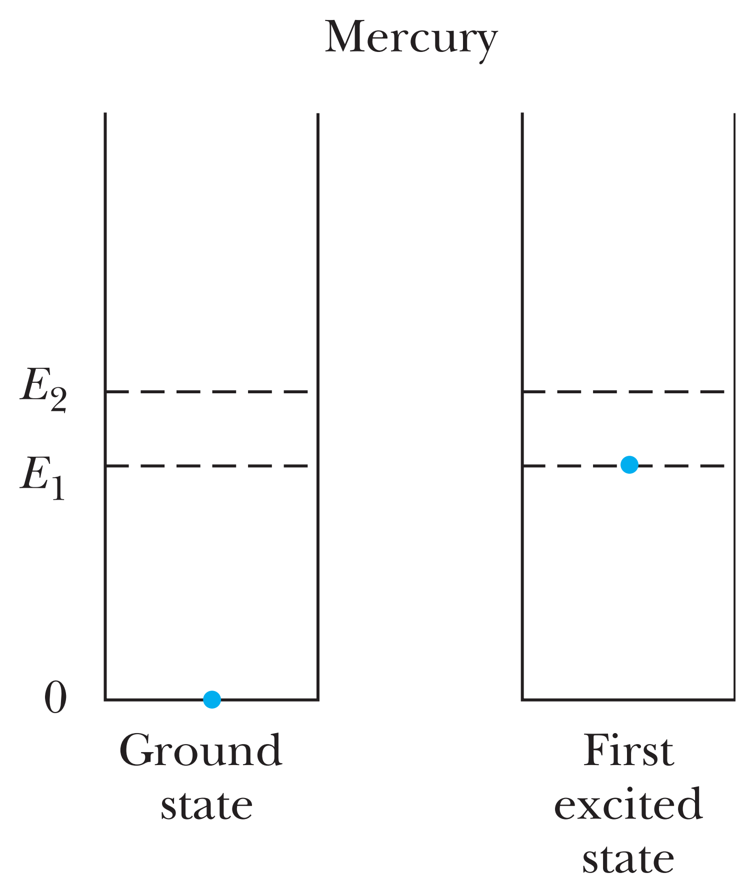
Atomic Excitation by Electrons

The first excited state of Hg is at an excitation energy of 4.88 eV. As long as the accelerating electron's kinetic energy is below 4.88 eV, no energy can be transferred to Hg because not enough energy is available to excite an electron to the next energy level in Hg



Atomic Excitation by Electrons

When the accelerating voltage is increased to 7 or 8 V, even electrons that have already made an inelastic collision have enough remaining energy to reach the collector. However, when the accelerating voltage reaches 9.8 V, the electrons have enough energy to excite two Hg atoms in successive inelastic collisions, losing 4.88 eV in each

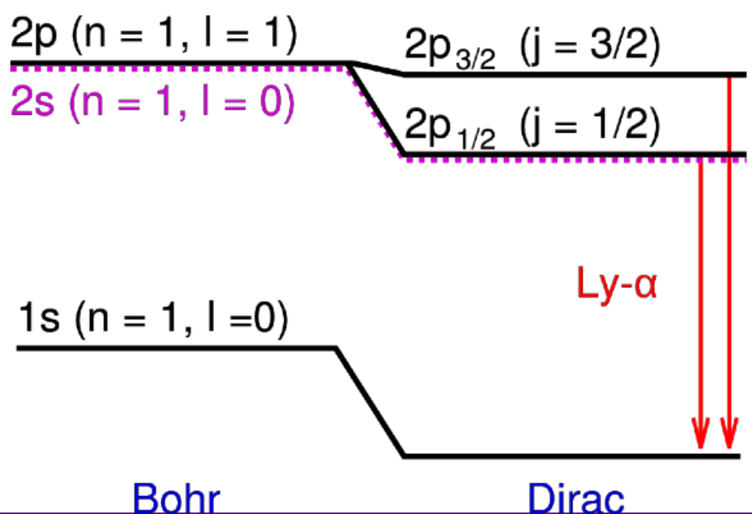


The limitations of Bohr Model

1. It could be successfully applied only to single-electron atoms (H, He^{+}, Li^{++}, and so on).

2. It was not able to account for the intensities or the fine structure of the spectral lines.

3. Bohr's model could not explain the binding of atoms into molecules.



The extension of Bohr model

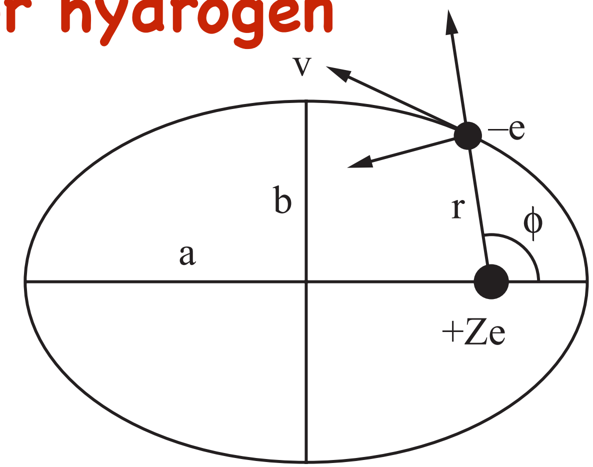
Sommerfeld succeeded partially in explaining the observed fine structure of spectral lines by introducing the following main modifications in Bohr's theory:

1. Sommerfeld suggested that the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of the foci.

2. Sommerfeld took into account the relativistic variation of the mass of the electron with velocity. Hence this model of the atom is called the relativistic atom model.

The extension of Bohr model

Elliptical orbits for hydrogen



Two quantization conditions are

$$\oint p_\phi \, d\phi = n_\phi h$$

$$\oint p_r \, dr = n_r h$$

where n_ϕ and n_r are the two quantum numbers introduced by Sommerfeld and

$$n_r + n_\phi = n$$

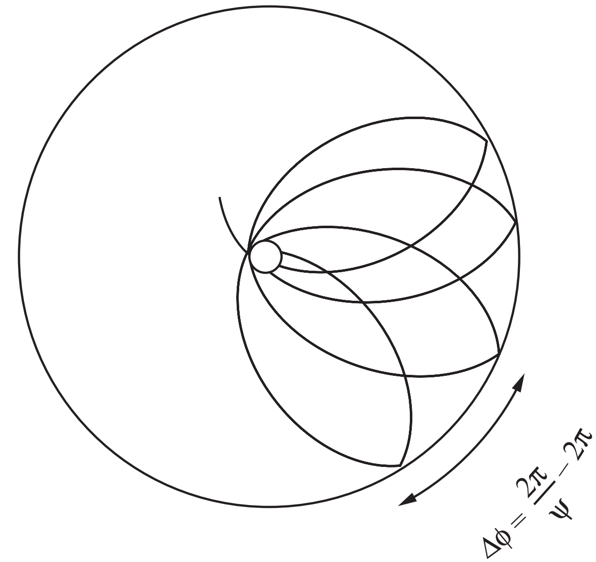
The extension of Bohr model

The energies for hydrogen with elliptical orbits

$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2}\left[\frac{1}{n_r + n_\phi}\right]^2$$

which is identical with the expression for the energy of the electron in a circular orbit of quantum number n. Thus, the introduction of elliptical orbits does not result in the production of new energy terms. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition.

The extension of Bohr model



Sommerfeld, including the relativistic correction in the treatment of elliptical orbits, showed that equation of the path of the electron was not simply that for an ellipse but was of the form

$$\frac{1}{r} = \frac{1}{a}\frac{1 + \epsilon \cos \gamma\phi}{1 - \epsilon^2}$$

where,

$$1 - \epsilon^2 = \frac{n_\phi^2 - \alpha^2 Z^2}{\left[n_r + \sqrt{n_\phi^2 - \alpha^2 Z^2}\right]}$$

and ε is the eccentricity , and the path of the electron is, therefore, a rosette .

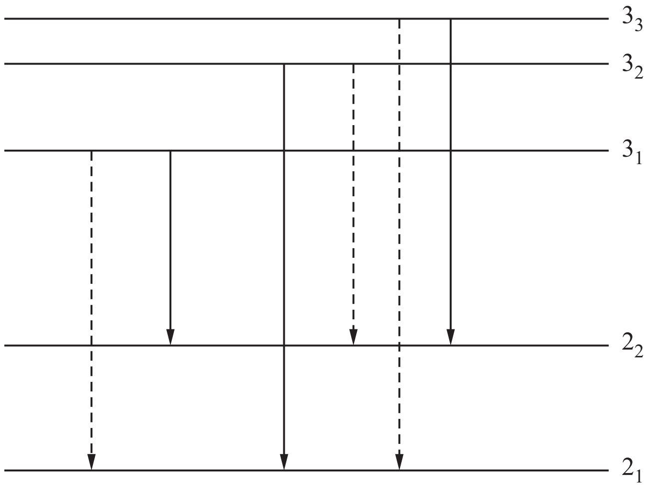
The extension of Bohr model

It can be shown that the total energy with a principal quantum number n in the relativistic theory is

$$E_{n, n_\phi} = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} - \frac{mZ^2e^4\alpha^2}{8\varepsilon_0^2h^2}\left[\frac{n}{n_\phi} - \frac{3}{4}\right]\frac{1}{n^4}$$

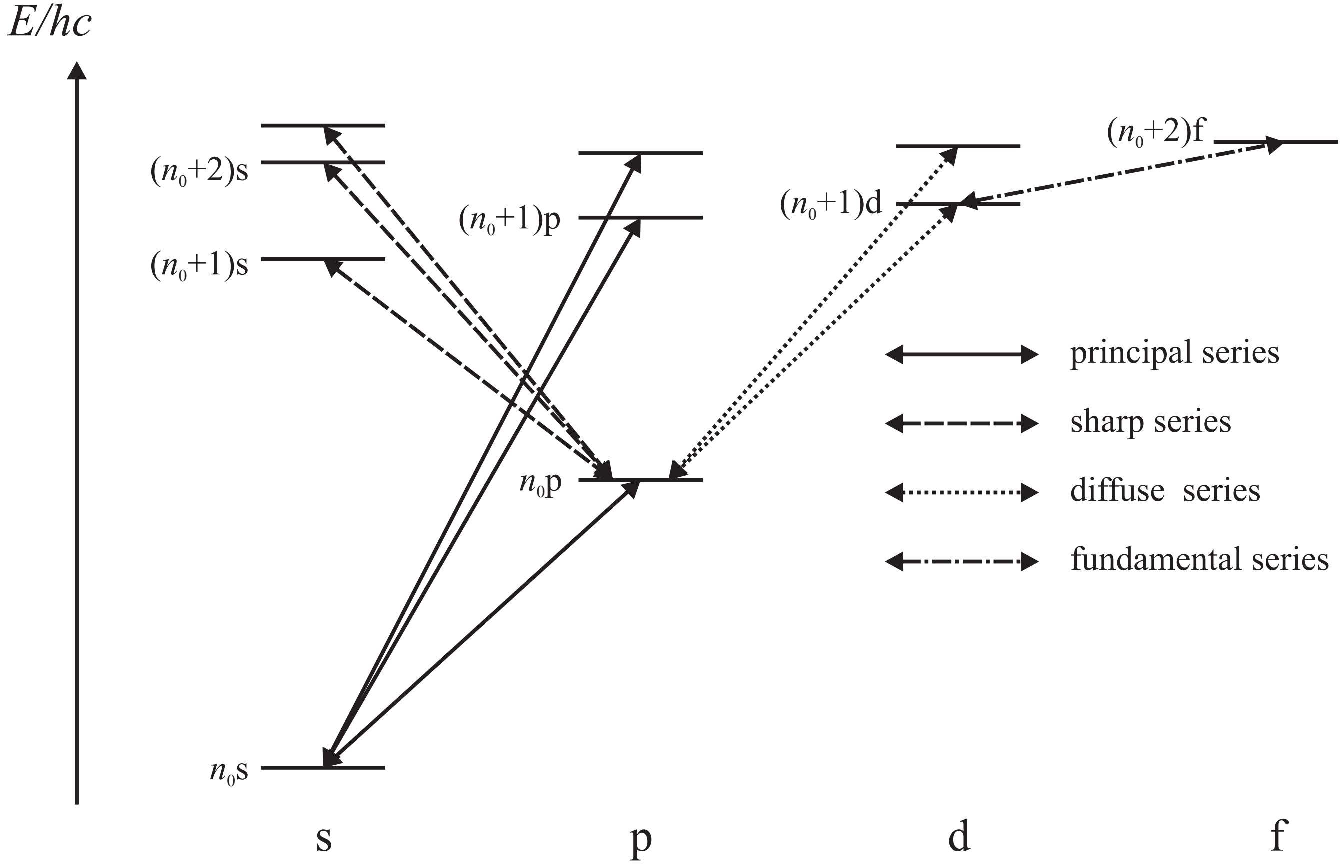
The second term is Sommerfeld's relativity correction arising from the rosette motion of the electron orbit with principal quantum number n and azimuthal quantum number n_ϕ.

H_α line is due to the transition from n = 3 state to n = 2 state of hydrogen atom.



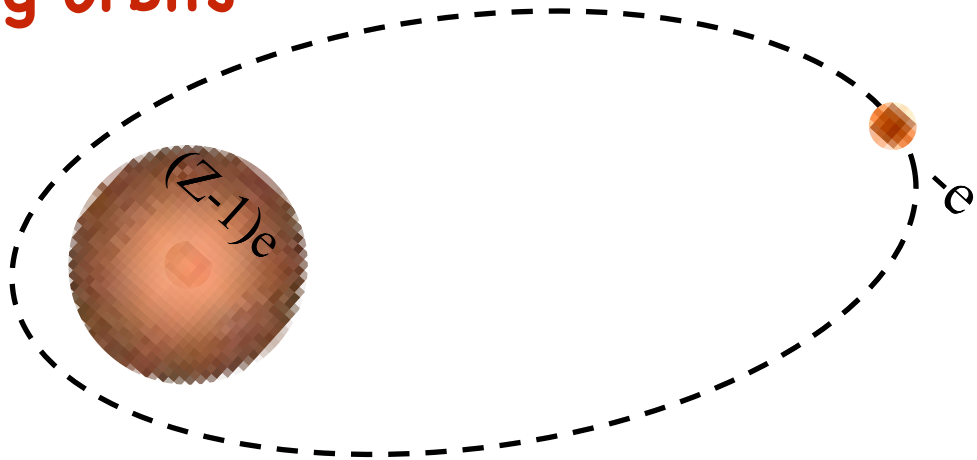
Alkali Atom

The alkali atoms have a weakly bound outer electron, the so-called valence electron, and all other (Z-1) electrons are in closed shells.

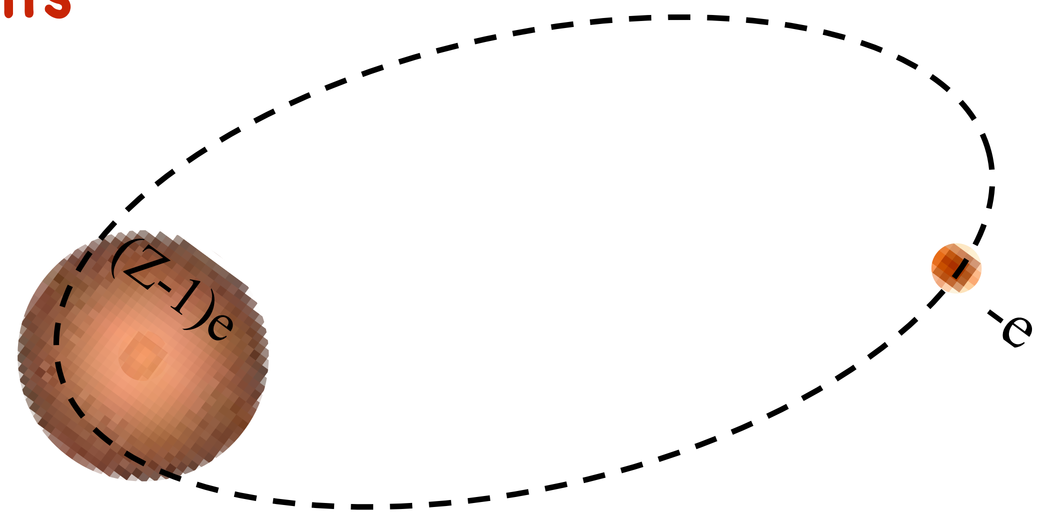


Penetrating effect

Non-Penetrating orbits

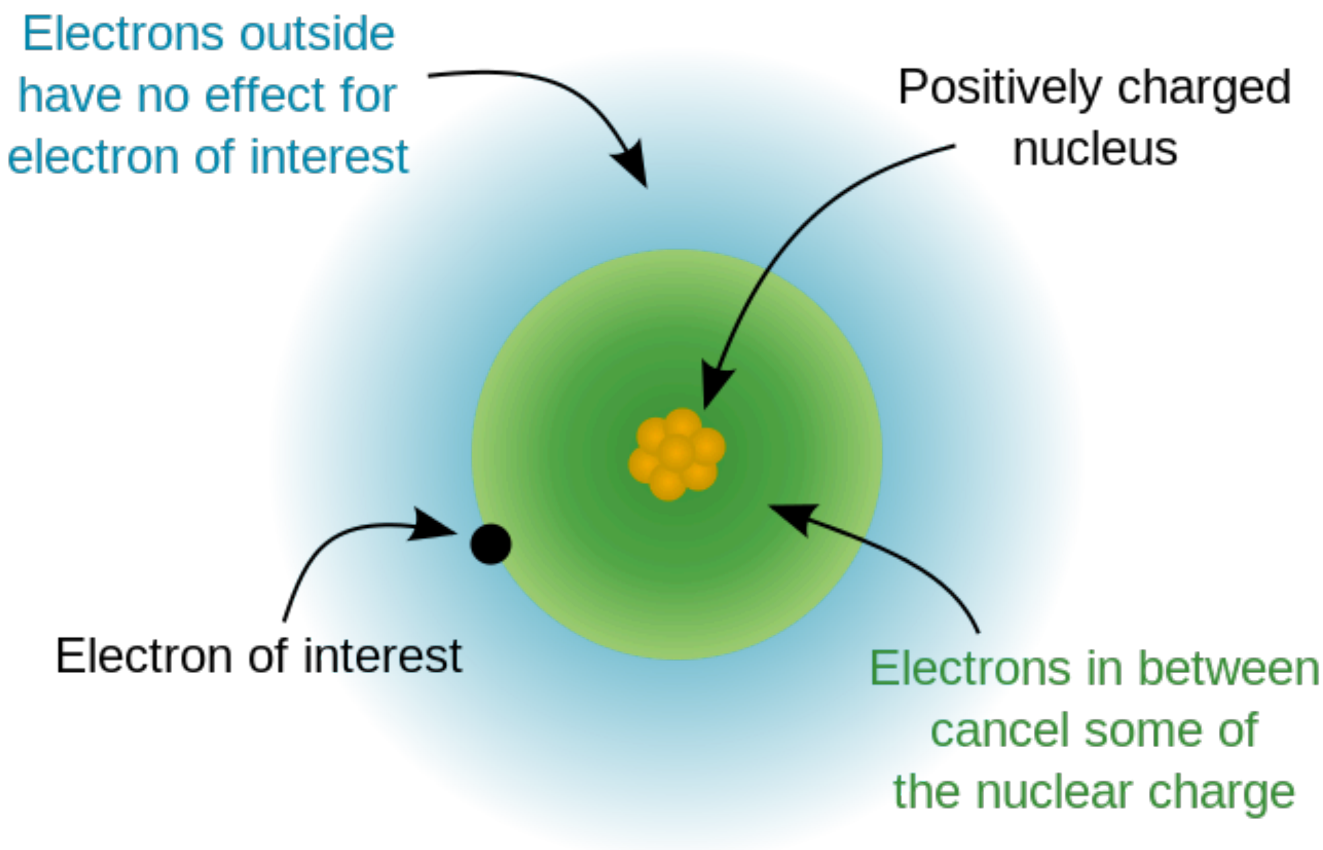


Penetrating orbits



Effective nuclear charge

The effective nuclear charge (often symbolized as Z_{eff}) is the net positive charge experienced by an electron in a multi-electronic atom.

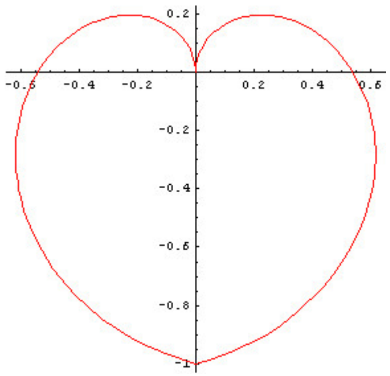


Effective nuclear charge

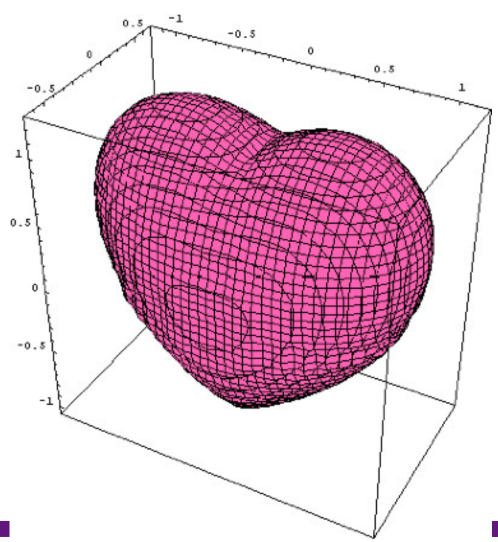
	H							**He**
Z	1							2
1s	1.00							1.69
	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Z	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Z	11	12	13	14	15	16	17	18
1s	10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
2s	6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
2p	6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
3s	2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
3p			4.07	4.29	4.89	5.48	6.12	6.76

Heart curve

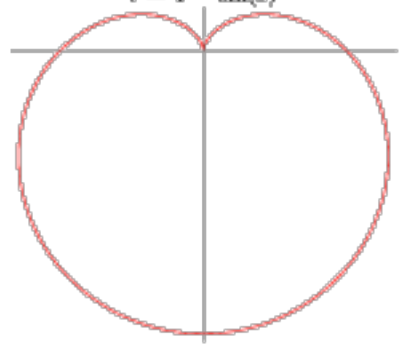
$$r = \sqrt{\mathrm{Sin}\,(0.5\,(x - 1.5\,\pi)) + 1}\,,\ \{x,\ -0.5\,\pi,\ 1.5\,\pi\}$$



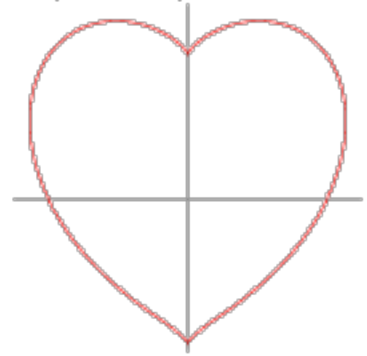
$$\left(x^2 + \frac{9}{4}\,y^2 + z^2 - 1\right)^3 - x^2 * z^3 - \frac{9}{80}\,y^2 * z^3$$



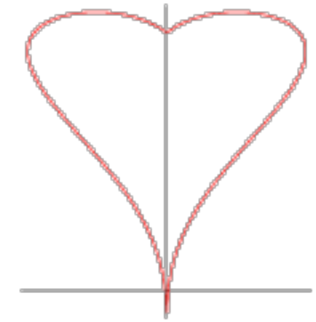
$$r = 1 - \sin(\theta)$$



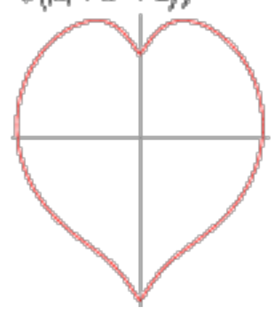
$$\left(x^2 + y^2 - 1\right)^3 - x^2\,y^3 = 0$$



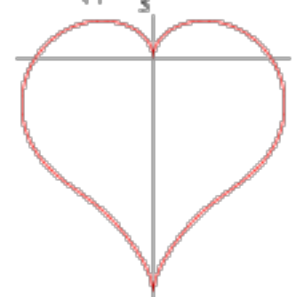
$$x = \sin(t)\cos(t)\log(|t|)$$
$$y = |t|^{0.3}\sqrt{\cos(t)}$$



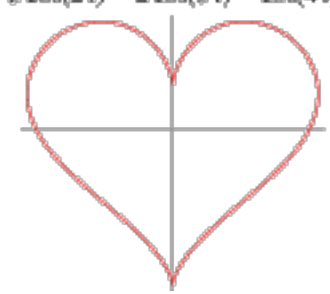
$$\left(y - \frac{2\left(|x| + x^2 - 6\right)}{3\left(|x| + x^2 + 2\right)}\right)^2 + x^2 = 36$$



$$r = \frac{\sin(t)\sqrt{|\cos(t)|}}{\sin(t) + \frac{7}{5}} - 2\sin(t) + 2$$



$$x = 16\sin^3(t)$$
$$y = 13\cos(t) - 5\cos(2\,t) - 2\cos(3\,t) - \cos(4\,t)$$



Homework

The Physics of Atoms and Quanta

8.1, 8.2, 8.3, 8.6, 8.8, 8.18

Exercise class

1. Determine the longest and shortest wavelengths observed in the Paschen series for hydrogen. Which are visible?

Exercise class

1.Determine the longest and shortest wavelengths observed in the Paschen series for hydrogen. Which are visible?

Solution: We insert the values of n into Rydberg equation to obtain

$$\frac{1}{\lambda_{\text{max}}} = (1.0974 \times 10^7)\left(\frac{1}{3^2} - \frac{1}{4^2}\right) = 5.335 \times 10^5\ \text{m}^{-1}$$

$$\lambda_{\text{max}} = 1875\ \text{nm}$$

and

$$\frac{1}{\lambda_{\text{min}}} = (1.0974 \times 10^7)\left(\frac{1}{3^2} - \frac{1}{\infty^2}\right) = 1.219 \times 10^6\ \text{m}^{-1}$$

$$\lambda_{\text{min}} = 820\ \text{nm}$$

The minimum and maximum wavelengths are both not visible and are both in the infrared.

Exercise class

2.Calculate the wavelength for the n_u=3 to n_l=2 transition (called the H_α line) for the atoms of hydrogen, deuterium, and tritium.

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Solution: The masses of proton, deuteron and triton are

$$\text{Proton} = 1.007276\ \text{u}$$

$$\text{Deuteron} = 2.013553\ \text{u}$$

$$\text{Triton (tritium nucleus)} = 3.015500\ \text{u}$$

Exercise class

2.Calculate the wavelength for the $n_u=3$ to $n_l=2$ transition (called the H_α line) for the atoms of hydrogen, deuterium, and tritium.

The corresponding Rydberg constants are

$$R_H = \frac{1}{1 + \frac{0.0005486}{1.00728}} R_\infty = 0.99946 R_\infty \quad \text{Hydrogen}$$

$$R_D = \frac{1}{1 + \frac{0.0005486}{2.01355}} R_\infty = 0.99973 R_\infty \quad \text{Deuterium}$$

$$R_T = \frac{1}{1 + \frac{0.0005486}{3.01550}} R_\infty = 0.99982 R_\infty \quad \text{Tritium}$$

The wavelengths are

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 0.13889 R$$

$$\lambda(H_\alpha, \text{hydrogen}) = 656.47 \text{ nm}$$

$$\lambda(H_\alpha, \text{deuterium}) = 656.29 \text{ nm}$$

$$\lambda(H_\alpha, \text{tritium}) = 656.23 \text{ nm}$$

Exercise class

3. Calculate the shortest wavelength that can be emitted by the Li^{++} ion.

Exercise class

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Solution: We used the Rydberg equation for Li^{++}

$$\frac{1}{\lambda} = (3)^2 R\left(\frac{1}{1^2} - \frac{1}{\infty}\right) = 9R$$

$$\lambda = \frac{1}{9R} = 10.1 \text{ nm}$$

Exercise class

4. An atom with one electron has the energy levels $E_n = -a/n^2$. Its spectrum has two neighboring lines with $\lambda_1 = 97.5$nm and $\lambda_2 = 102.8$nm in Lyman series. What is the value of the constant a and which atomic element belongs to this spectrum?

Exercise class

4. An atom with one electron has the energy levels $E_n = -a/n^2$. Its spectrum has two neighboring lines with $\lambda_1 = 97.5nm$ and $\lambda_2 = 102.8nm$ in Lyman series. What is the value of the constant a and which atomic element belongs to this spectrum?

Solution: The photon energies are then

$$h\nu_n = a\left(1 - \frac{1}{n^2}\right)$$

$$h\nu_{n+1} = a\left(1 - \frac{1}{(n+1)^2}\right)$$

$$\frac{\lambda_1}{\lambda_2} = \frac{\nu_{n+1}}{\nu_n} = \frac{1 - 1/(n+1)^2}{1 - 1/n^2}$$

so

$$n = 3$$

$$\frac{1}{\lambda_3} = Z^2 R_A \left(1 - \frac{1}{3^2}\right)$$

$$Z = 1$$