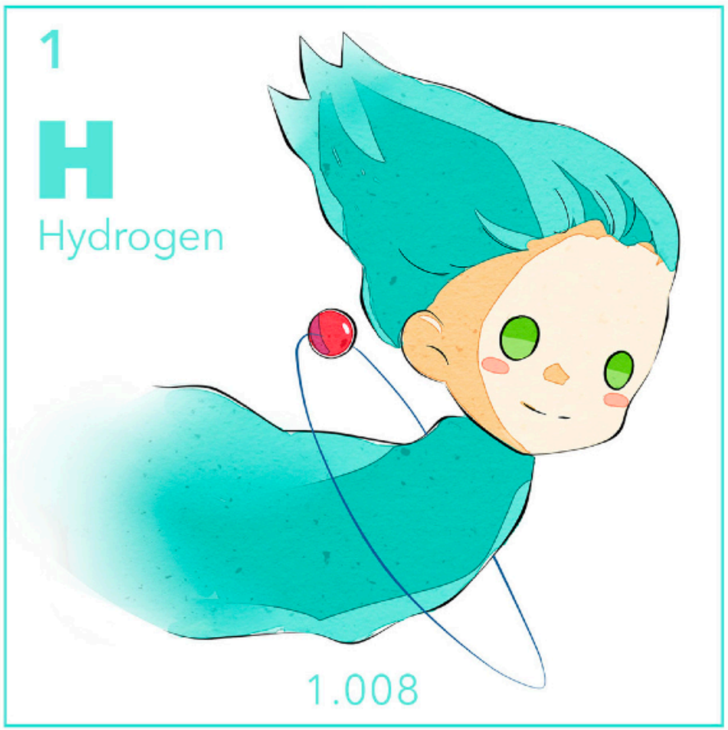
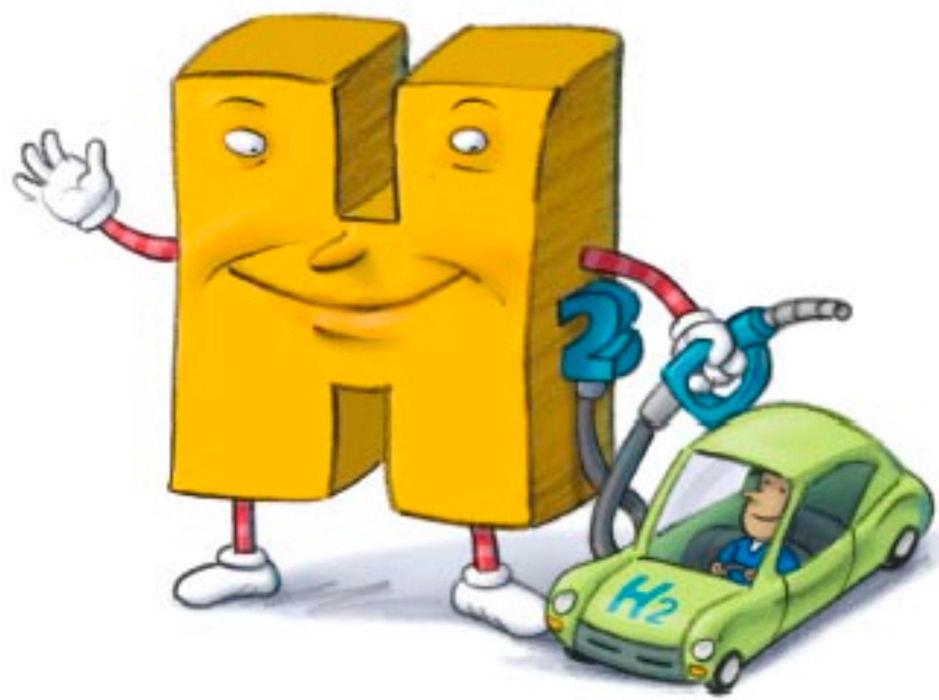
Atomic Physics

Chapter 2

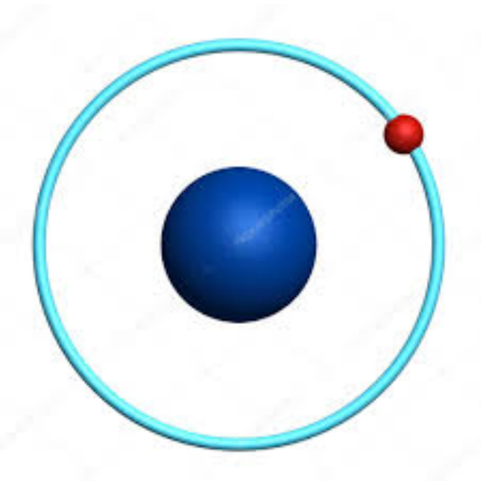
Bohr's Model of the Hydrogen





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 total mechanical energy is

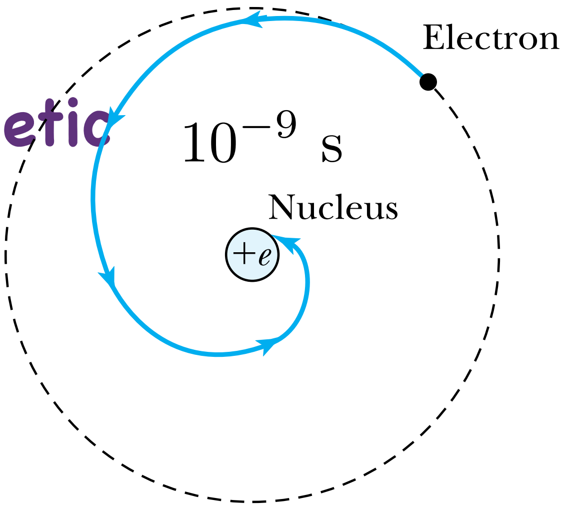
$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

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!



$$\frac{dU}{dt} = -\frac{2e^6}{3r^4 m_0^2 c^3} = -\frac{2}{3}\frac{r_0^3}{r^4} m_0 c^3. \quad t_{\text{fall}} = \frac{a_0^3}{4r_0^2 c}.$$

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.

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

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

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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

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

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

Electron's velocity in Bohr model

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

or

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

and

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

We define the dimensionless quantity ratio of v_1 to c as

$$\alpha \equiv \frac{v_1}{c} = \frac{\hbar}{ma_0 c} = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$$

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

The energies of the stationary states

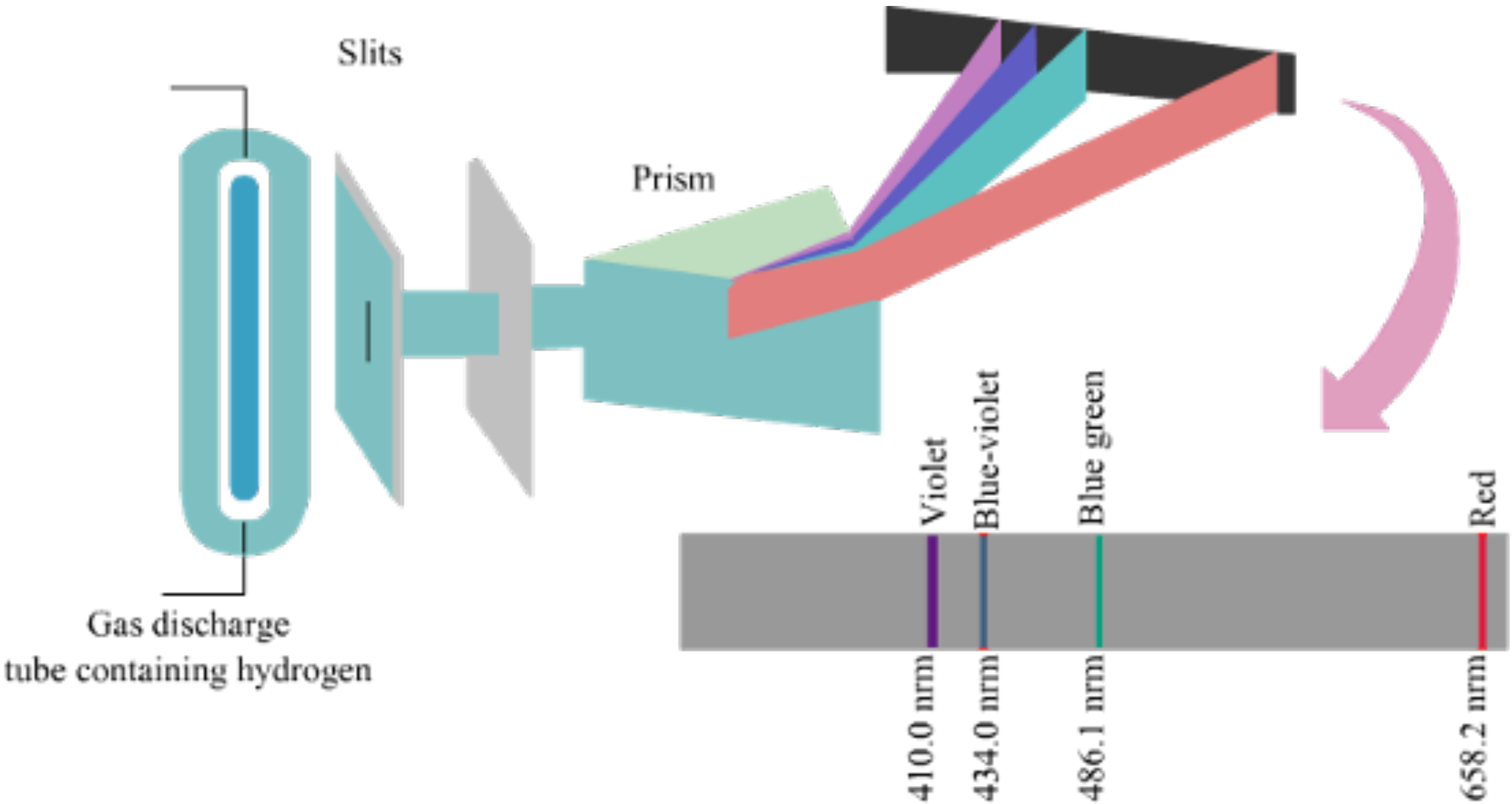
$$E_n = -\frac{e^2}{8\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2}$$

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



Line spectra

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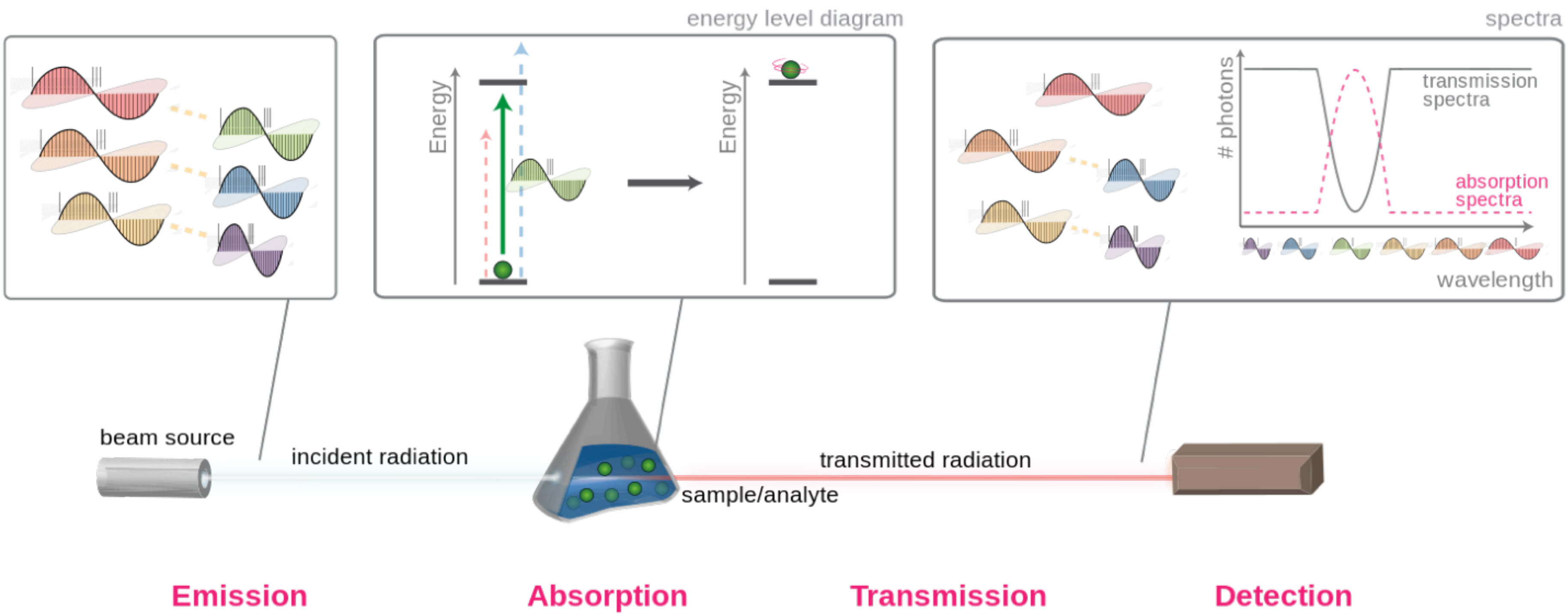
In 1859 Gustav Kirchhoff and Robert Bunsen had already found, through joint research, that atoms only absorb or emit light at certain discrete wavelengths λ_i .

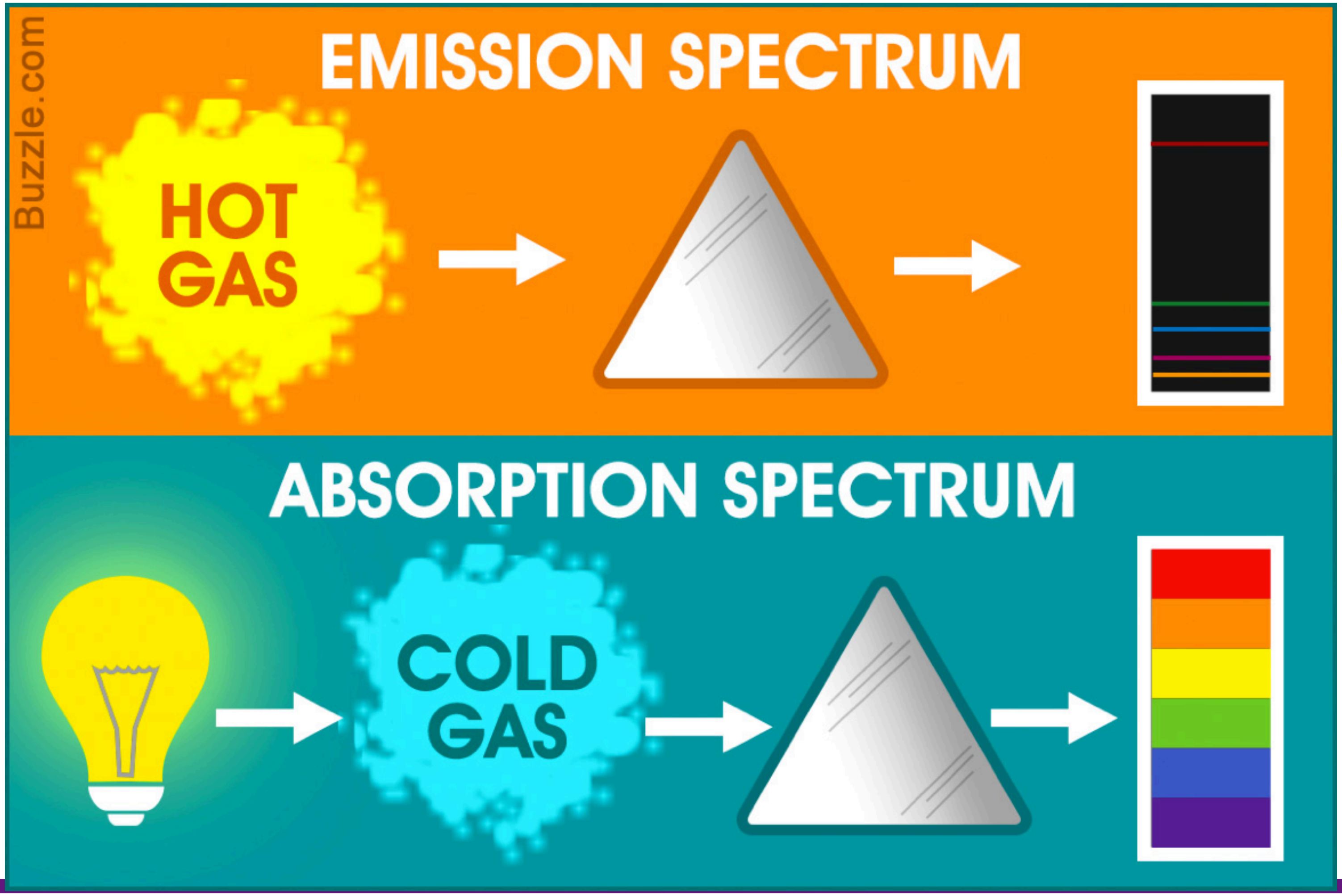
These specific wavelengths that are characteristic of each chemical element, are called the absorption or emission spectra of the atom.

These spectra are like a fingerprint of the atom, since every atomic species can be unambiguously recognized by its 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.

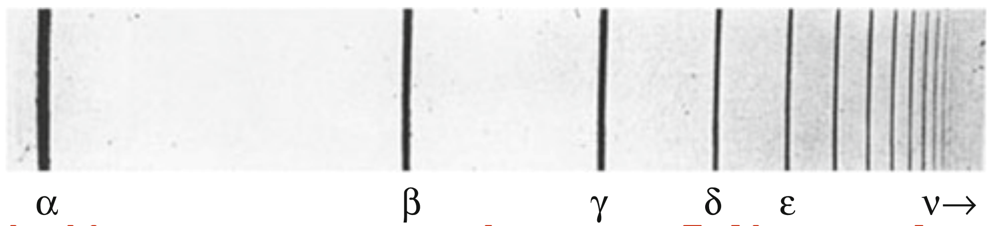


The missing frequencies are precisely the ones observed in the corresponding emission spectrum.



The Rydberg formula

The most simple of all atoms is the H atom, consisting of only one proton and one electron. Its emission spectrum was measured in 1885 by Johann Jakob Balmer.



He could fit the wave numbers of its emission lines by the simple formula

$$\bar{\nu}_K = Ry\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

where the integer numbers n_1, n_2 take the values $n_1 = 2$ and $n_2 = 3,4,5,.....$ The constant Ry = 109,678cm^{-1} is the Rydberg constant, which is historically given by spectroscopists in units of inverse centimeters cm^{-1}

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 $n=n_l$)

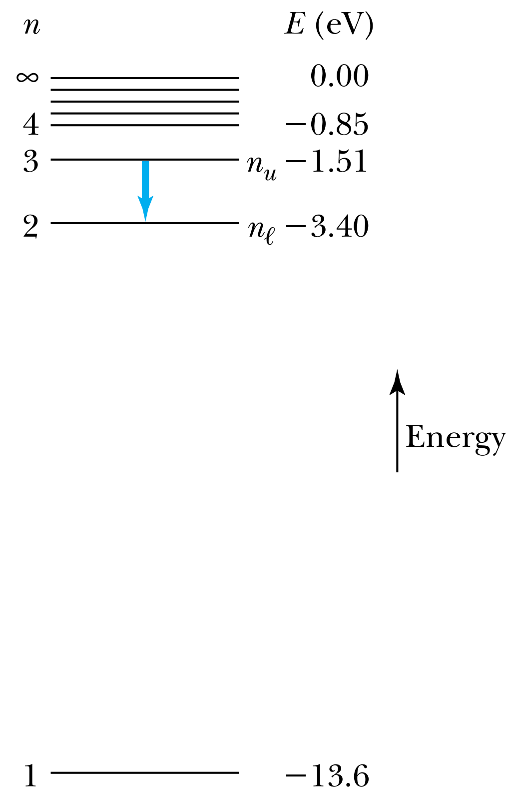
$$h\nu = E_u - E_l$$

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

$$\lambda\nu = c$$

we have

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



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)

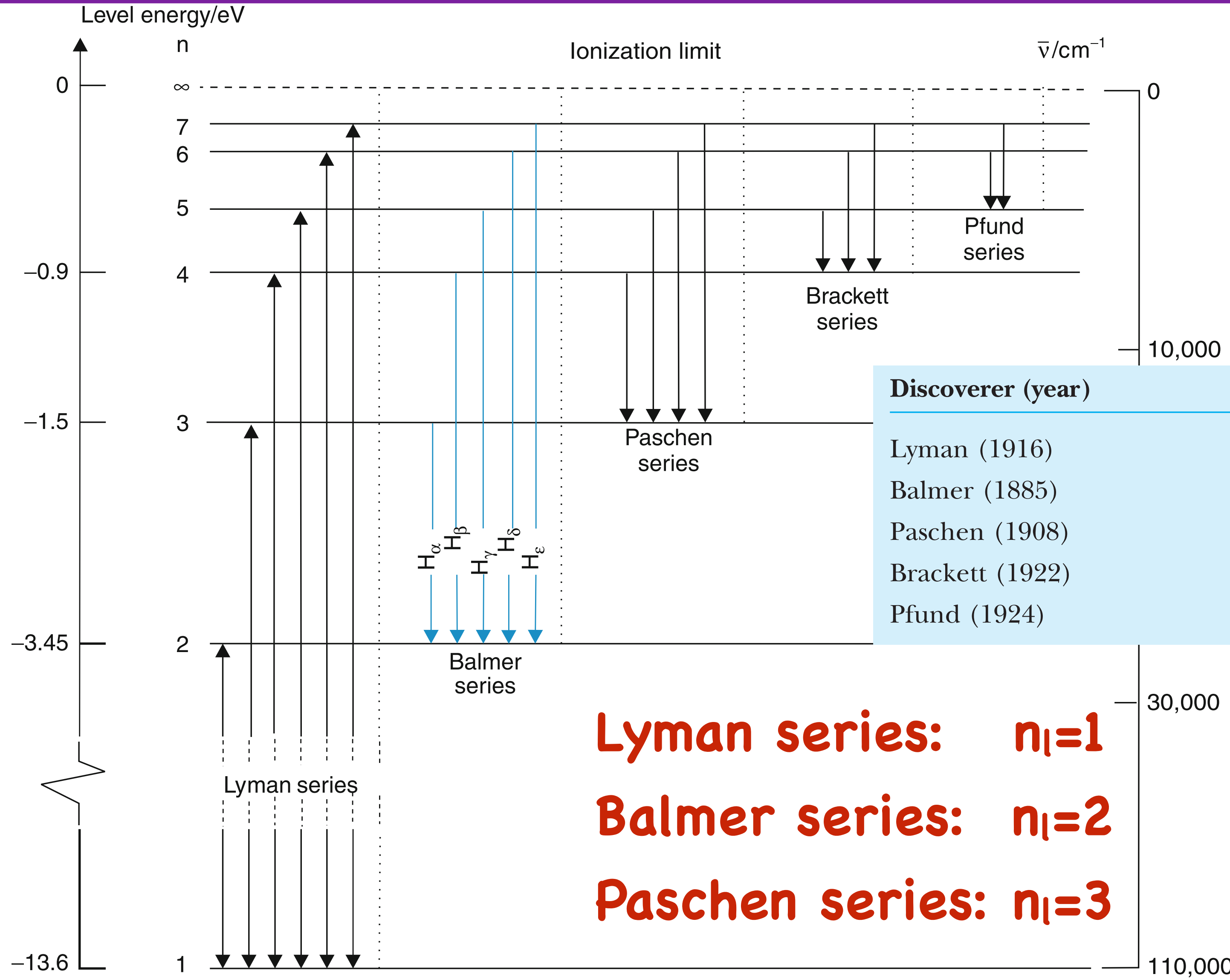
and

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

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

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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:

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

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

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

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

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

n	ν_{QM}	ν_{cla}	Difference (%)
5	$5.26 \cdot 10^{13}$	$7.38 \cdot 10^{13}$	29
10	$6.57 \cdot 10^{12}$	$7.72 \cdot 10^{12}$	14
100	$6.578 \cdot 10^{9}$	$6.677 \cdot 10^{9}$	1.5
1000	$6.5779 \cdot 10^{6}$	$6.5878 \cdot 10^{6}$	0.15
10,000	$6.5779 \cdot 10^{3}$	$6.5789 \cdot 10^{3}$	0.015

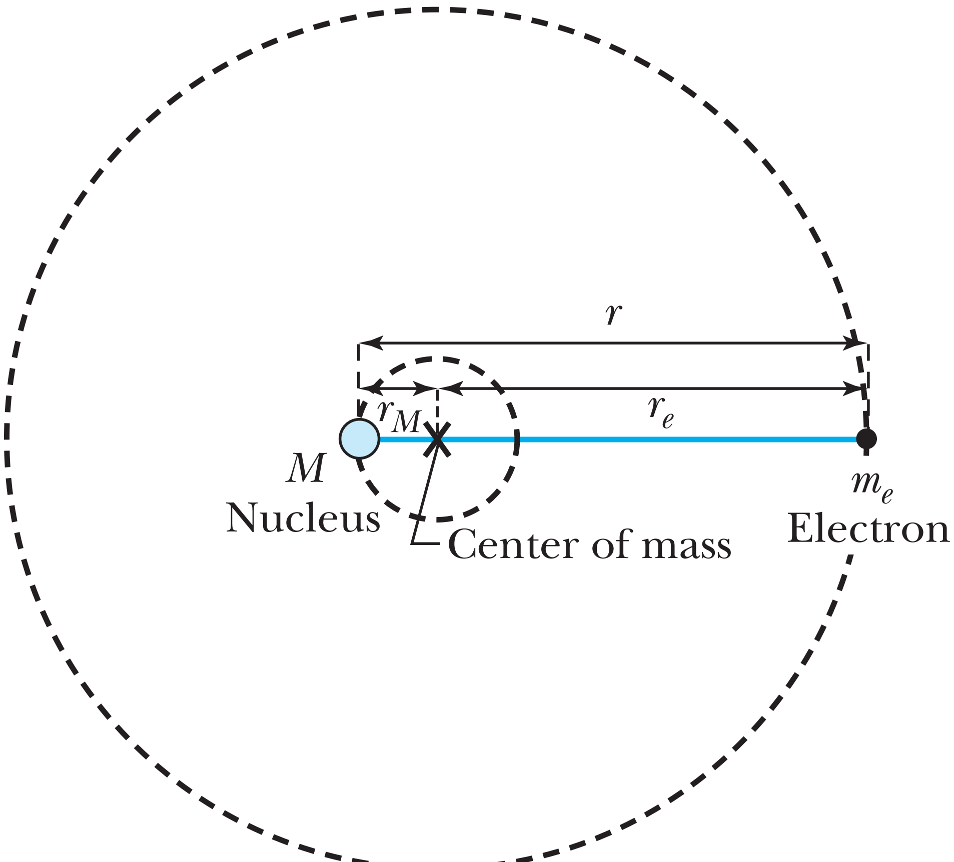
so the frequencies of the radiated energy agree between classical theory and the Bohr model for large values of the quantum number n. Bohr's correspondence principle is verified for large orbits, where classical and quantum physics should agree.

Angular momentum

Black-body radiation

The probability of particle in the Harmonic oscillator

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



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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 Rydberg constant for hydrogen is

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

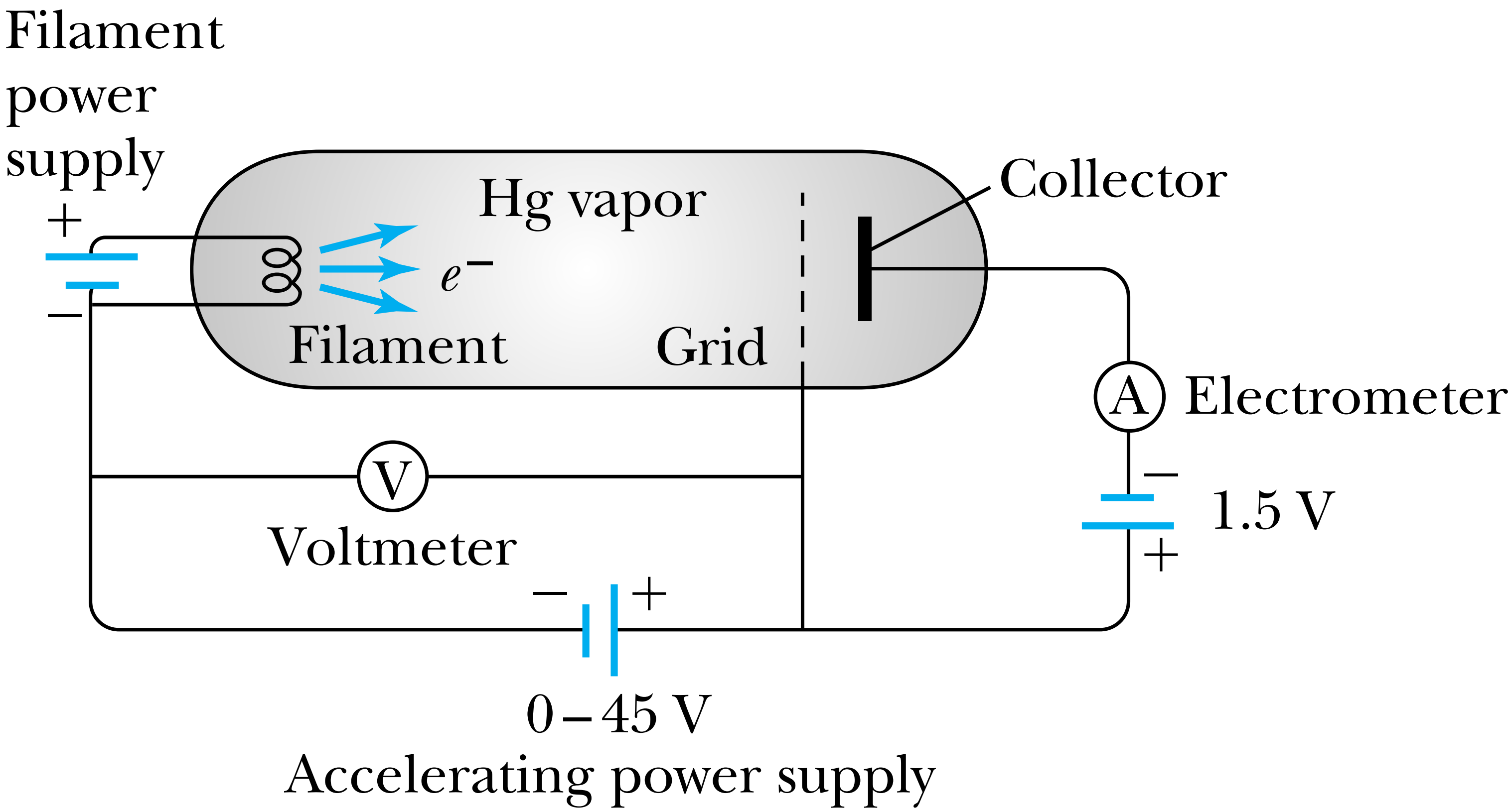
The Bohr model may be applied to any single-electron atom (hydrogen-like) even if the nuclear charge is greater than 1 proton charge (+e), for example He^{+} and Li^{++}.

The Rydberg equation becomes

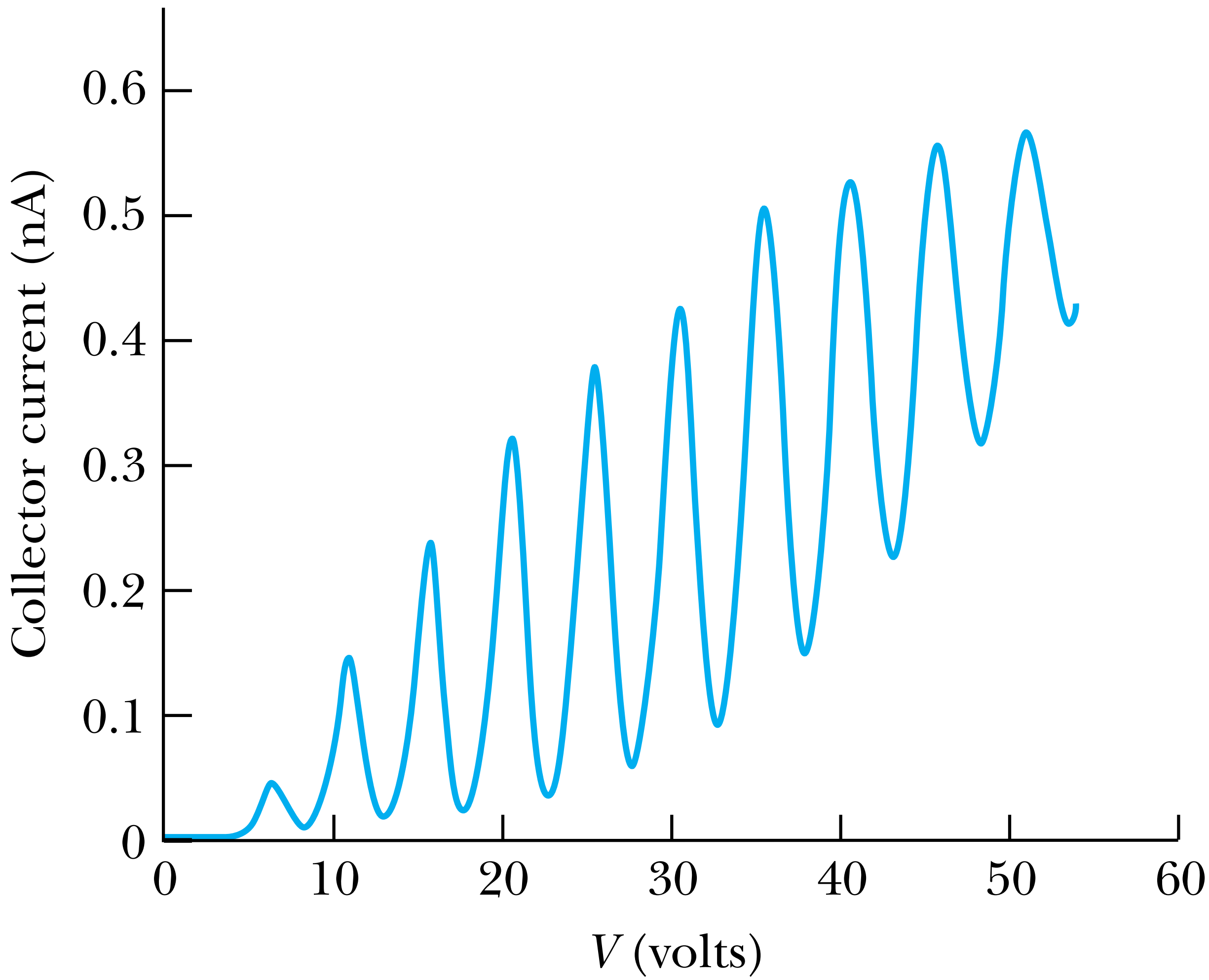
$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

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

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



Data from Franck- Hertz experiment



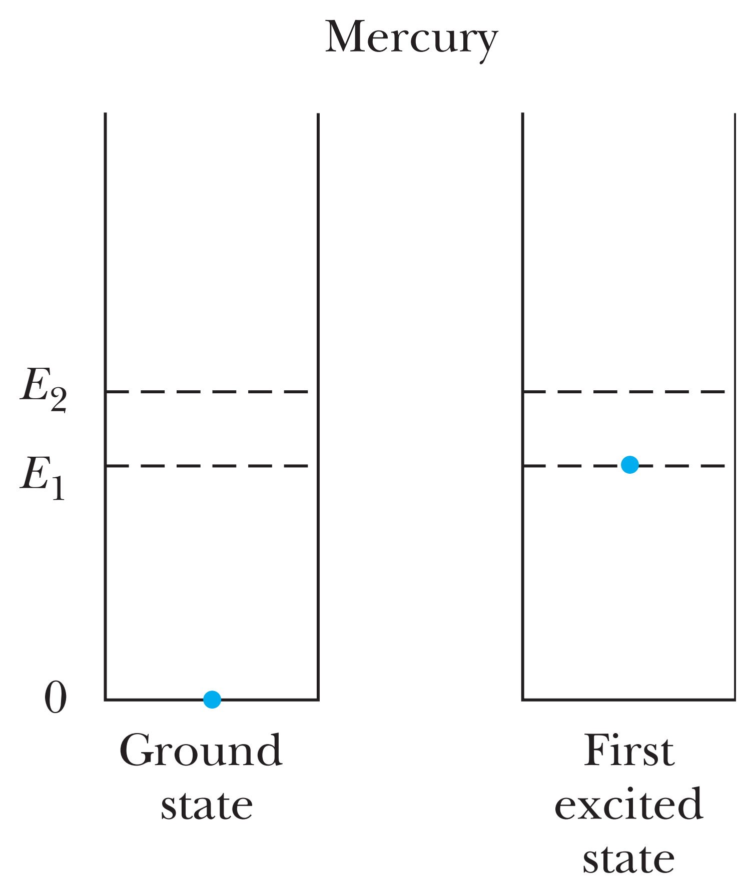
Atomic Excitation by Electrons

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

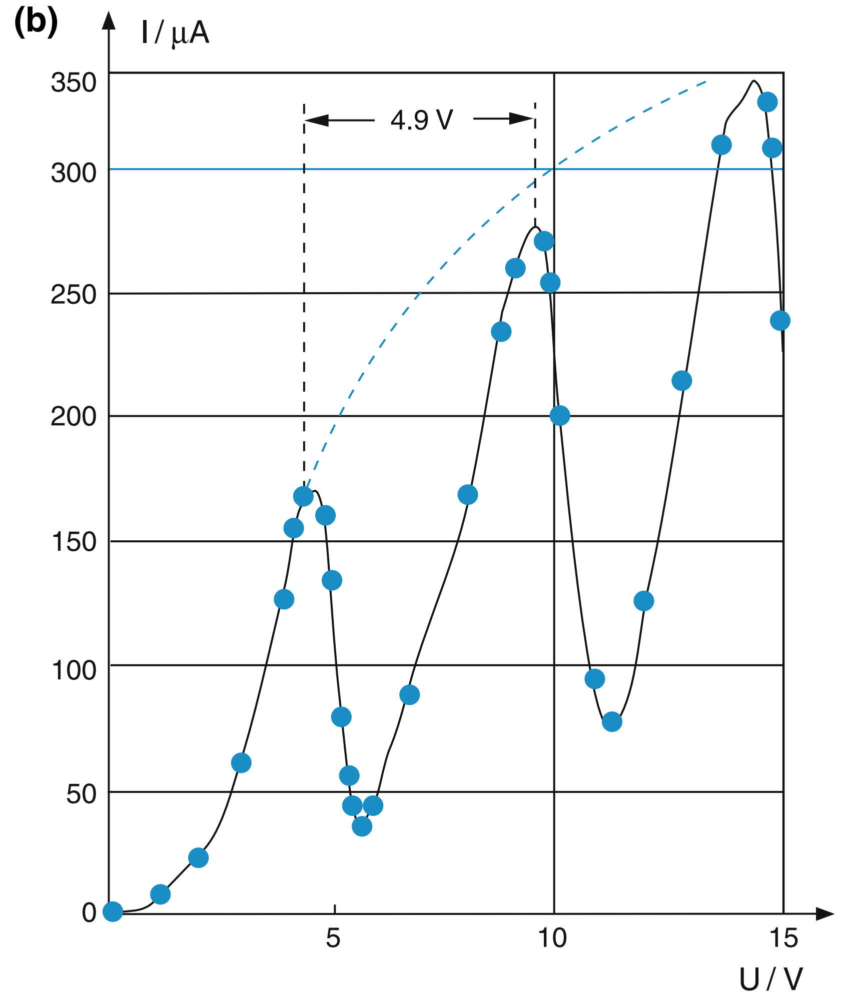
The first excited state of Hg is at an excitation energy of 4.88 eV. As long as the accelerating electron's kinetic energy is below 4.88 eV, no energy can be transferred to Hg because not enough energy is available to excite an electron to the next energy level in Hg



The electrons suffer elastic and inelastic collisions with the Hg atoms. In inelastic collisions,

$$e^{-}(E_{\mathrm{kin}}) + \mathrm{Hg} \rightarrow \mathrm{Hg}^{*}(E_{\mathrm{a}}) + e^{-}(E_{\mathrm{kin}} - E_{\mathrm{a}})$$

the electrons excite the Hg atoms and transfer the amount $\Delta E_{kin} = E_{kin} - E_a$ of their kinetic energy to the excitation energy E_a of the atom.



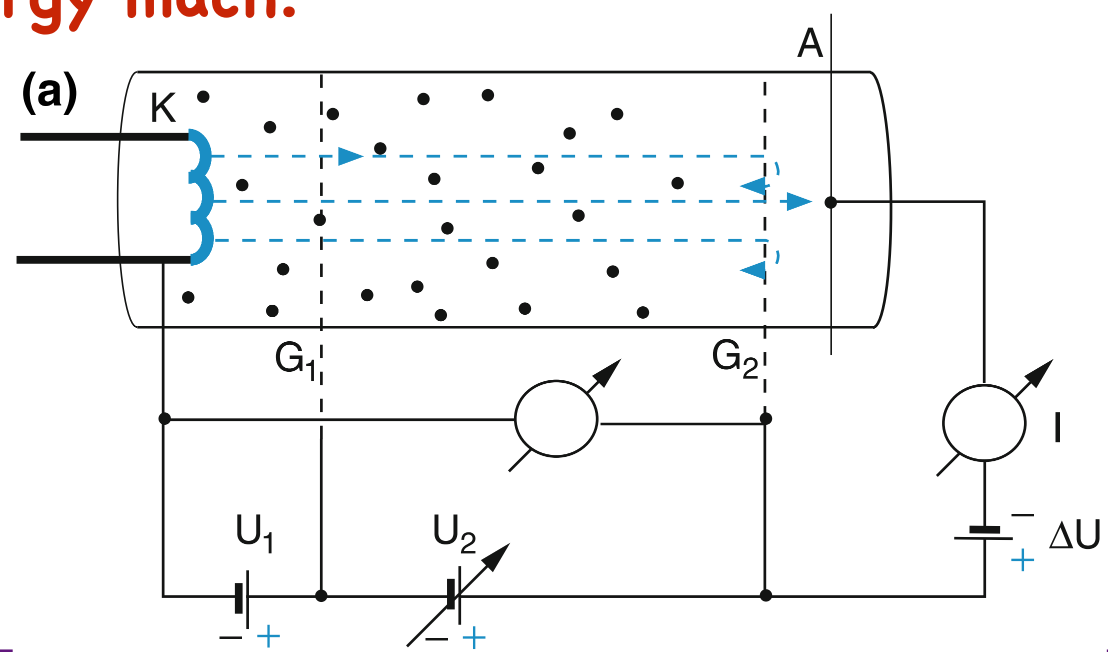
The further maxima and minima in the actually measured current I (U_A) are due to the fact that at sufficiently large voltages U the electron can regain, after n inelastic collisions, the minimum required kinetic energy eΔU during its flight path to the grid for overcoming the bias voltage but has not enough energy for the (n + 1)th inelastic collision

The exact form of the curve I (U) is determined by

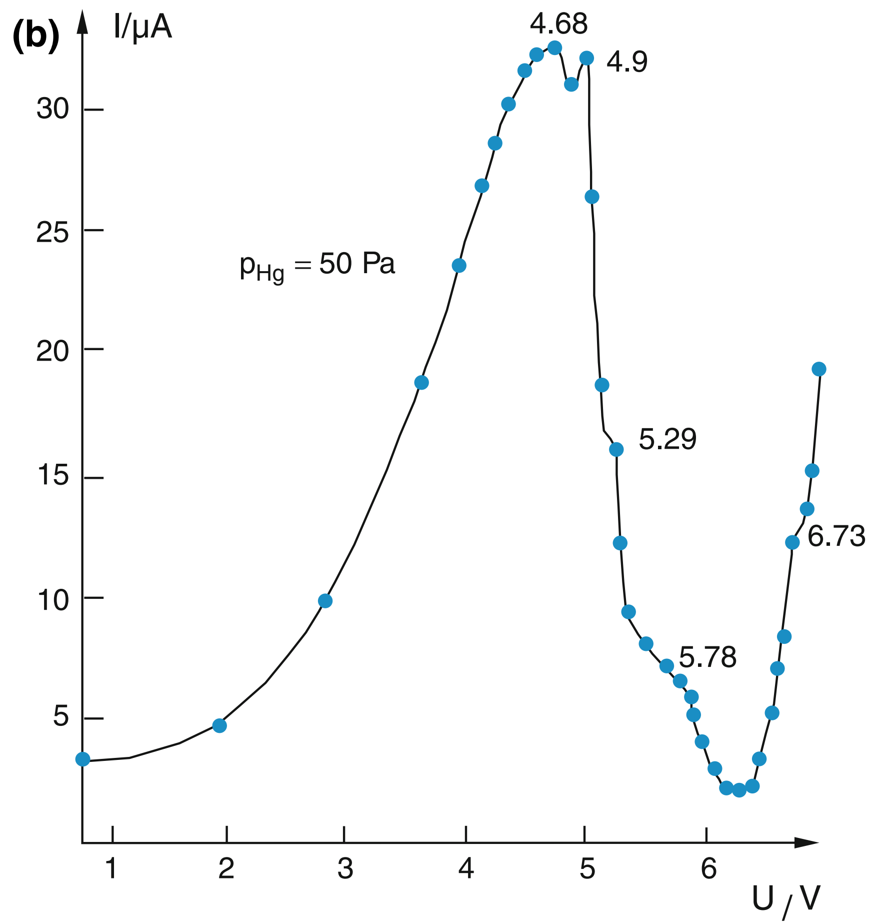
1. The energy dependence of the excitation probability
2. The energy distribution of the electrons emitted from the hot cathode.

Atomic Excitation by Electrons

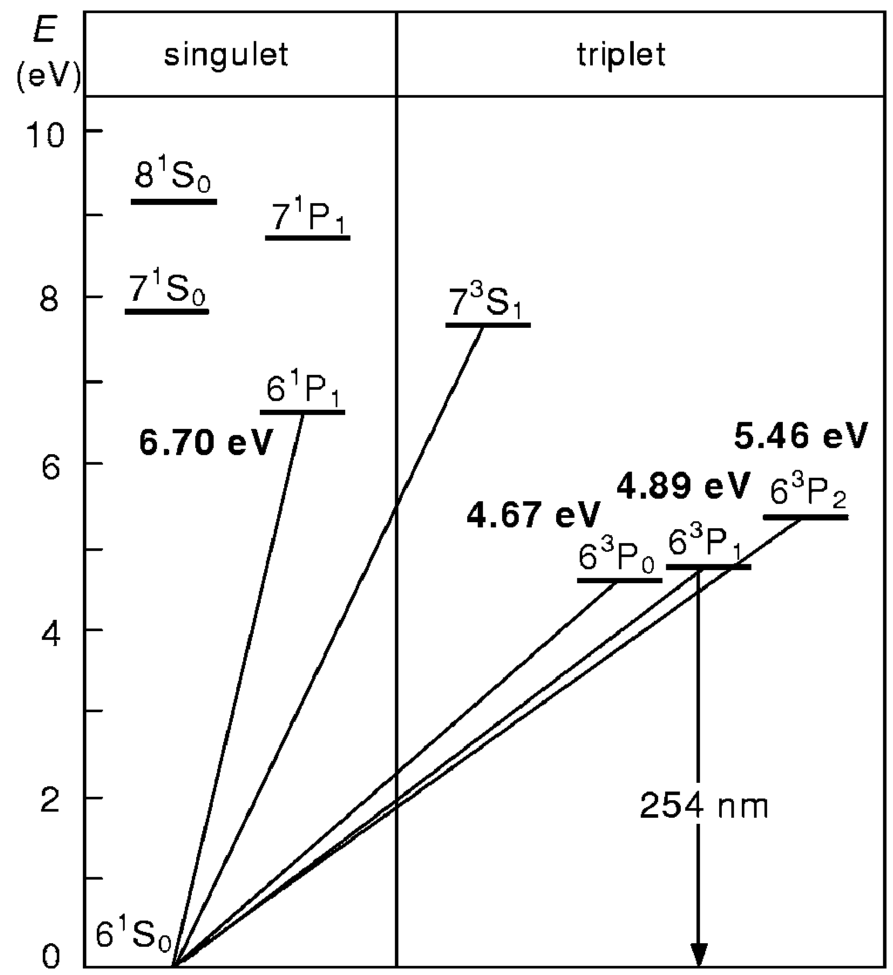
With the improved experimental setup, the energy resolution could be substantially improved. Here, two grids are used and the acceleration of the electrons is essentially restricted to the short flight path between K and G_1, while the small adjustable voltage U_2 between G_2 and G_1 does not change the electron energy much.



Atomic Excitation by Electrons



$$6^1S_0 \rightarrow 6^3P_{0,1,2}$$

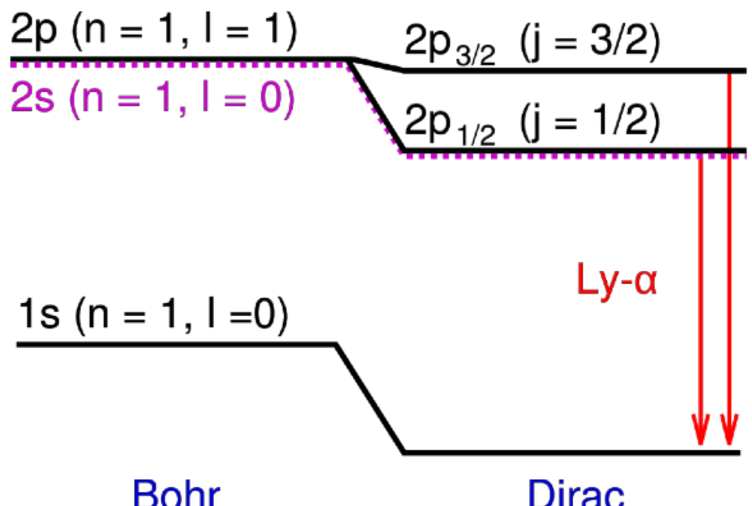


The limitations of Bohr Model

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.



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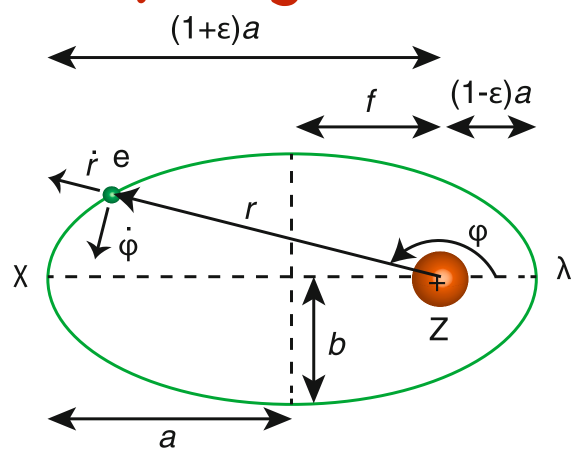
Sommerfeld succeeded partially in explaining the observed fine structure of spectral lines by introducing the following main modifications in Bohr's theory:

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

$$\oint p_\phi r\, d\phi = n_\phi h \qquad \oint p_r\, dr = n_r h.$$

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

$$n = n_r + n_\phi$$

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To integrate the second condition about the radial direction, one notes that

$$p_r = m_r \frac{dr}{dt} = m_r \frac{dr}{d\phi}\frac{d\phi}{dt} = \frac{1}{r^2}\left(m_r r^2 \frac{d\phi}{dt}\right)\frac{dr}{d\phi} = \frac{L}{r^2}\frac{dr}{d\phi},$$

so that

$$\oint p_r\, dr = \oint \frac{L}{r^2}\left(\frac{dr}{d\phi}\right)^2 d\phi = n_r h.$$

In the equation of the ellipse:

$$r = \frac{b^2}{a(1 + e\cos\phi)} = \frac{a(1-e^2)}{1 + e\cos\phi},$$

where

$$e = \sqrt{1 - b^2/a^2}$$

To integrate the second condition about the radial direction, one notes that

$$p_r = m_r \frac{dr}{dt} = m_r \frac{dr}{d\phi}\frac{d\phi}{dt} = \frac{1}{r^2}\left(m_r r^2 \frac{d\phi}{dt}\right)\frac{dr}{d\phi} = \frac{L}{r^2}\frac{dr}{d\phi},$$

so that

$$\oint p_r\, dr = \oint \frac{L}{r^2}\left(\frac{dr}{d\phi}\right)^2 d\phi = n_r h.$$

In the equation of the ellipse:

$$r = \frac{b^2}{a(1+e\cos\phi)} = \frac{a(1-e^2)}{1+e\cos\phi},$$

where $e = \sqrt{1-b^2/a^2}$ is the eccentricity of the ellipse.

Therefore

$$n_r h = e^2 L \int_0^{2\pi} \frac{\sin^2\phi \, d\phi}{(1 + e\cos\phi)^2} = 2\pi L\left(\frac{1}{\sqrt{1-e^2}} - 1\right),$$

and substituting

$$L = n_\phi \hbar$$

then leads to

$$\sqrt{1-e^2} = \frac{n_\phi}{n_r + n_\phi} = \frac{b}{a}.$$

Thus, the only allowed orbits are those with (quantized) eccentricity given by

$$e_{nm} = \sqrt{1 - \frac{m^2}{n^2}},$$

where

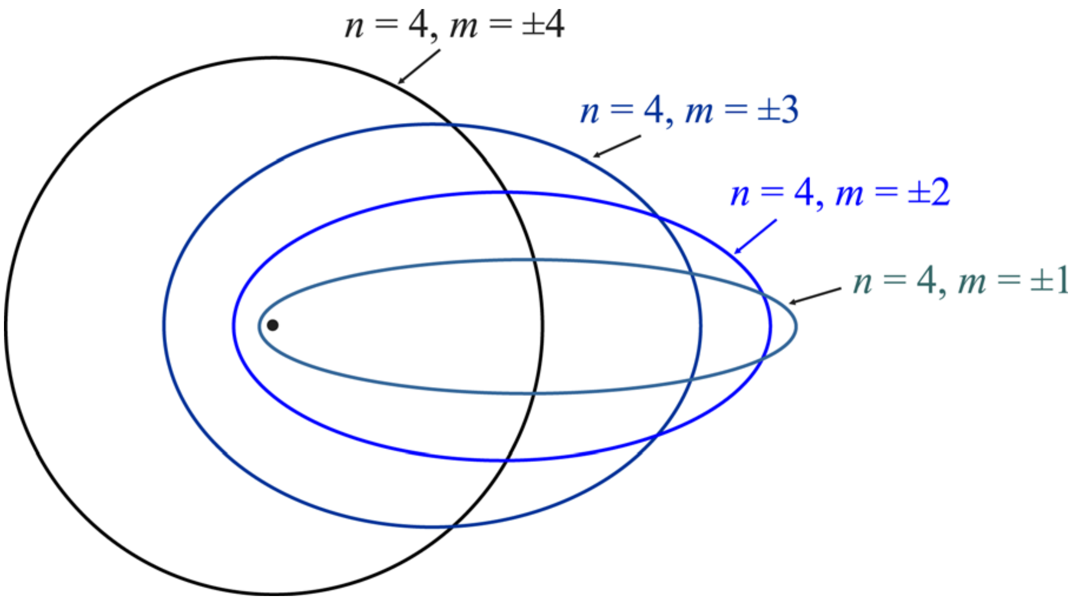
$$m = \pm n_\phi$$

We can find the (quantized) energy, angular momentum, and the semi-major and minor axes as a function of the quantum numbers n and m:

$$E_{nm} = -\frac{m_r \kappa^2}{2\hbar^2}\frac{1}{n^2}, \qquad \kappa = Ze^2/4\pi\epsilon_0$$

$$a_{nm} = \frac{\hbar^2}{m_r \kappa} n^2,$$

$$b_{nm} = \frac{m}{n} a_n = mn \frac{\hbar^2}{m_r \kappa}.$$



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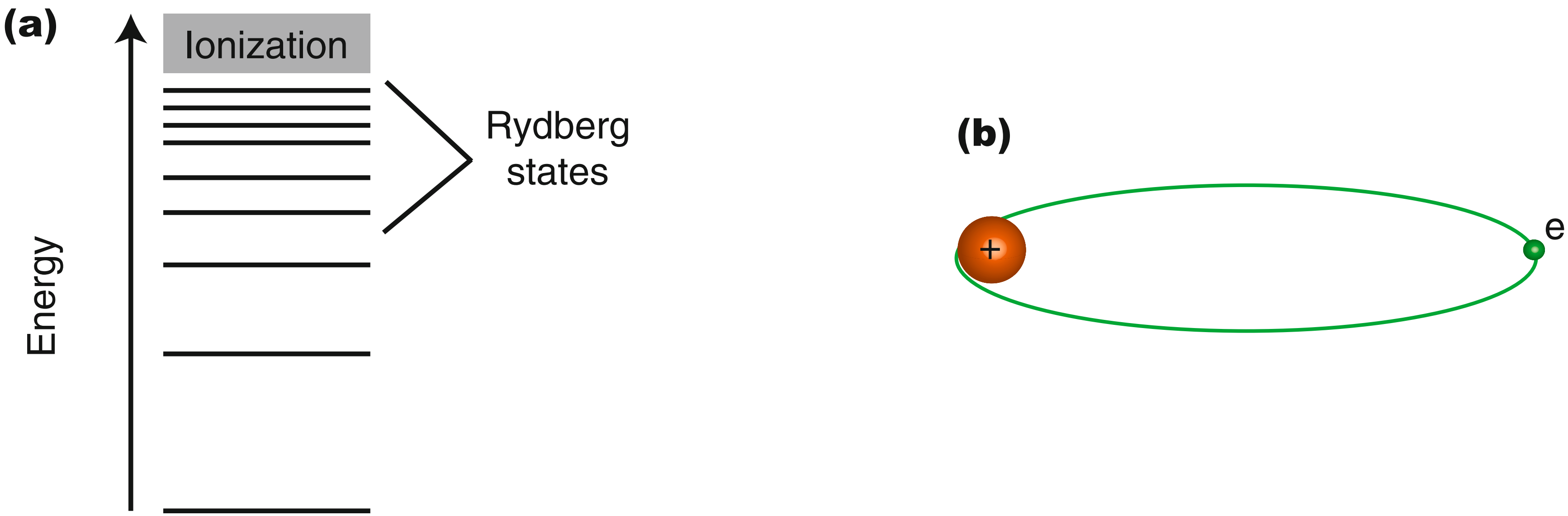
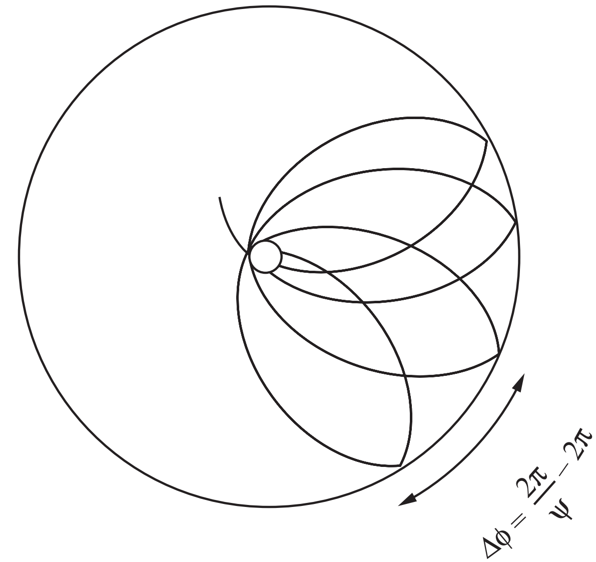
Any atom in a highly excited state with high principal quantum number n is defined as a Rydberg atom



In particular, the Rydberg electron feels the attractive force of a positively charged ionic core, and as a consequence, the electron describes an elliptical orbit around the ionic core.

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,

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

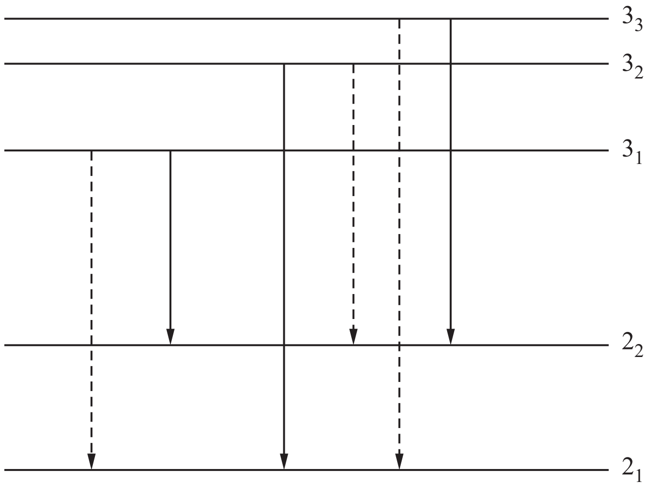
and ε is the eccentricity (离心率) and the path of the electron is, therefore, a rosette (玫瑰花结).

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

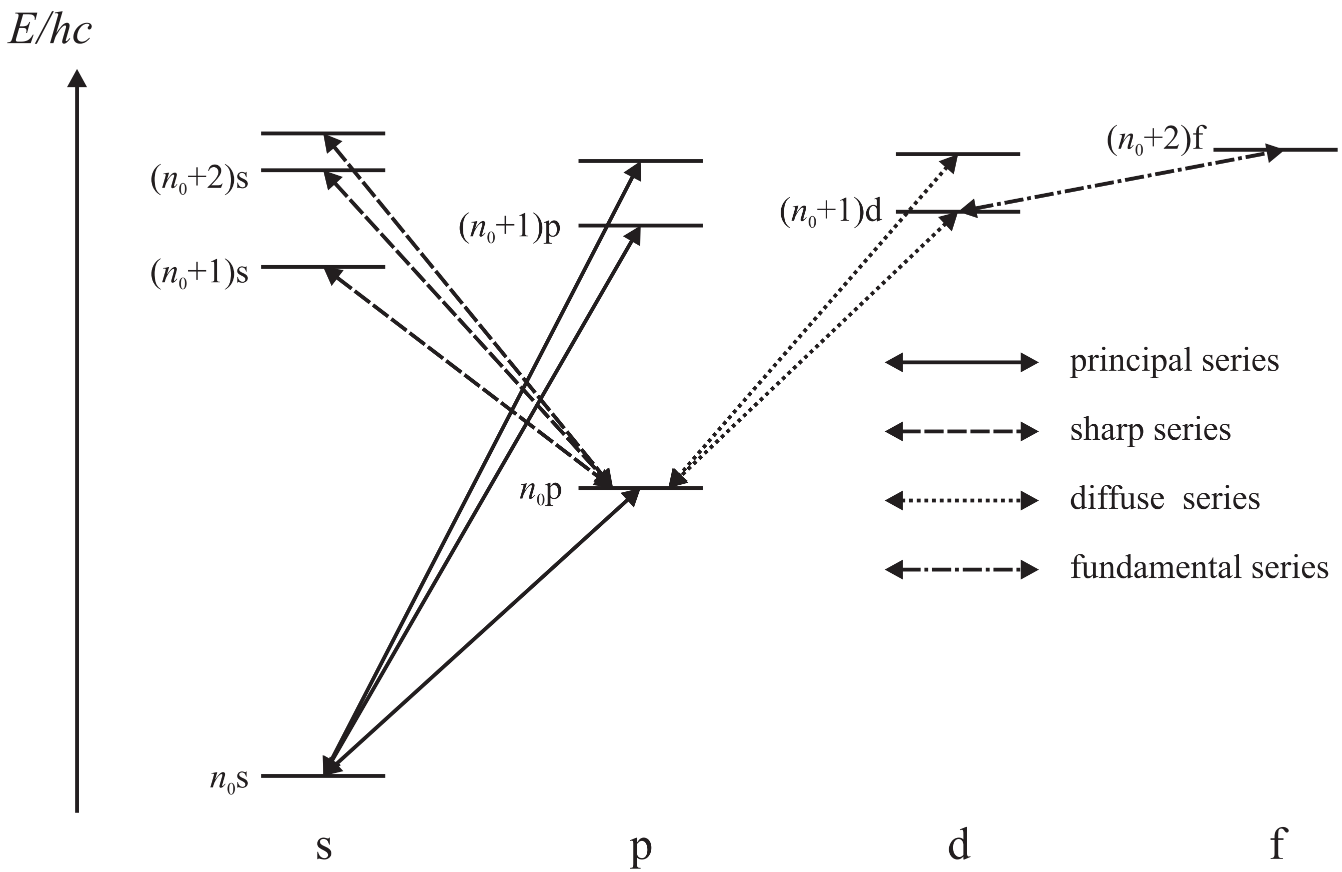
$$E_{n},\, n_{\phi} = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} - \frac{mZ^2e^4\alpha^2}{8\varepsilon_0^2h^2}\left[\frac{n}{n_\phi} - \frac{3}{4}\right]\frac{1}{n^4}$$

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.



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



Muonic Atoms

A muonic atom consists of the atomic nucleus, a negatively charged muon μ^- and the electron shell with (Z-p) electrons.

Because of the large muon mass $m_\mu = 206.76\ m_e$ the lowest possible Bohr orbit (n = 1) of the muon is for a nuclear charge Z e with Z = 30 only,

$$r_1(\mu^-) = 7.7 \times 10^{-15}\ \mathrm{m},$$

which is of the same order of magnitude as the nuclear radius. The muonic atom levels are very much influenced by the spatial distribution of the nuclear charge.the muonic atom levels are very much influenced by the spatial distribution of the nuclear charge

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Since the mean lifetime of μ^- is 2.2 μs muonic atoms are unstable even in their ground state. For light atoms ($Z < 10$) the μ^- decays according to the scheme

$$\mu^- \rightarrow e^- + \overline{\nu}_{\mathrm{e}} + \nu_\mu$$

into an electron, an electron antineutrino and a muon neutrino. For heavy atoms ($Z > 10$) the lowest μ^- orbit is already within the nucleus. In this case the muon induces the nuclear reaction

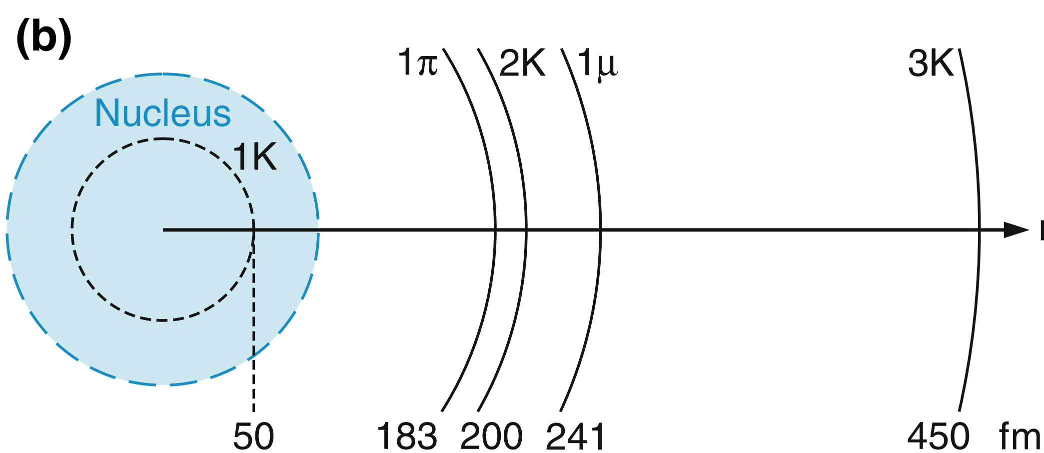
$$\mu^- + p \rightarrow n + \nu_\mu ,$$

where a proton in the nucleus is converted into a neutron.

Pionic and Kaonic Atoms

Instead of the muon, a negative π^- meson can also be captured by a neutral atom. The energy released by this capture process is sufficient to eject one or several electrons from the atomic electron shell

The nucleons (protons and neutrons) in the atomic nucleus interact with the π^- meson not only through Coulomb forces but also through the short range, but much stronger, nuclear force.



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Exotic atoms with heavier negative mesons (K^-, η^-) allows probing of charge and mass distribution at even smaller distances from the center of the nucleus.

Particle	e^-	μ^-	π^-	K^-
m/m_e	1	207	273	967
Bohr radius r_1 in fm	$\frac{5.3}{Z} \cdot 10^4$	$\frac{256}{Z}$	$\frac{194}{Z}$	$\frac{54.8}{Z}$
Term energy for $n = 1, Z = 1$	$-13.6\,\mathrm{eV}$	$-2.79\,\mathrm{keV}$	$-3.69\,\mathrm{keV}$	$-13.1\,\mathrm{keV}$
$\Delta E(n = 2 \to 1)$ for $Z = 20$	$4.1\,\mathrm{keV}$	$837\,\mathrm{keV}$	$1.1\,\mathrm{MeV}$	$3.9\,\mathrm{MeV}$
Mean lifetime of free particle τ/s	∞	$2.2 \cdot 10^{-6}$	$2.6 \cdot 10^{-8}$	$1.2 \cdot 10^{-8}$
Fine structure splitting 2^2P for $Z = 20, n = 2$	$6.6\,\mathrm{eV}$	$1.3\,\mathrm{keV}$	$1.8\,\mathrm{keV}$	$6.4\,\mathrm{keV}$

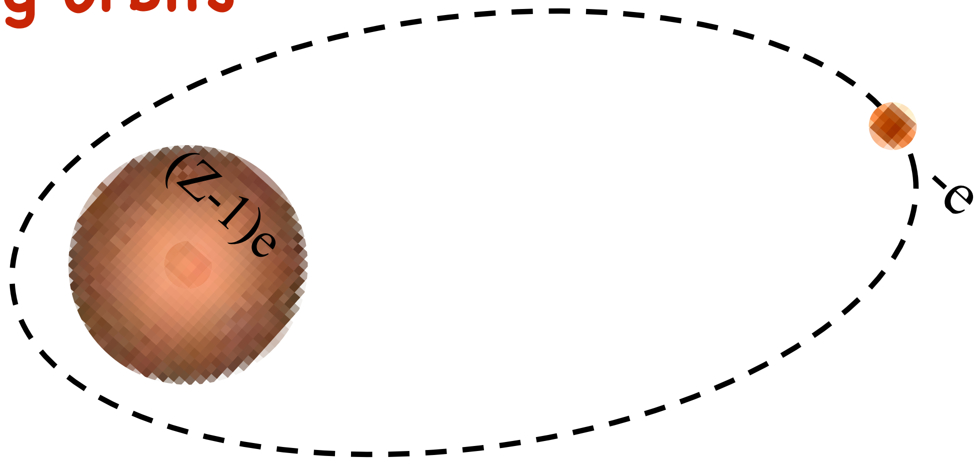
Positronium is a hydrogen-like system consisting of an electron e and a positron e^+ . Its investigation gives very interesting information about a pure leptonic system of two light particles with equal masses, which have opposite charges and magnetic moments.

Positronium is one of the few systems where the lifetime of the ground state is smaller than that of excited states because the particles can come into contact and annihi- late by the process

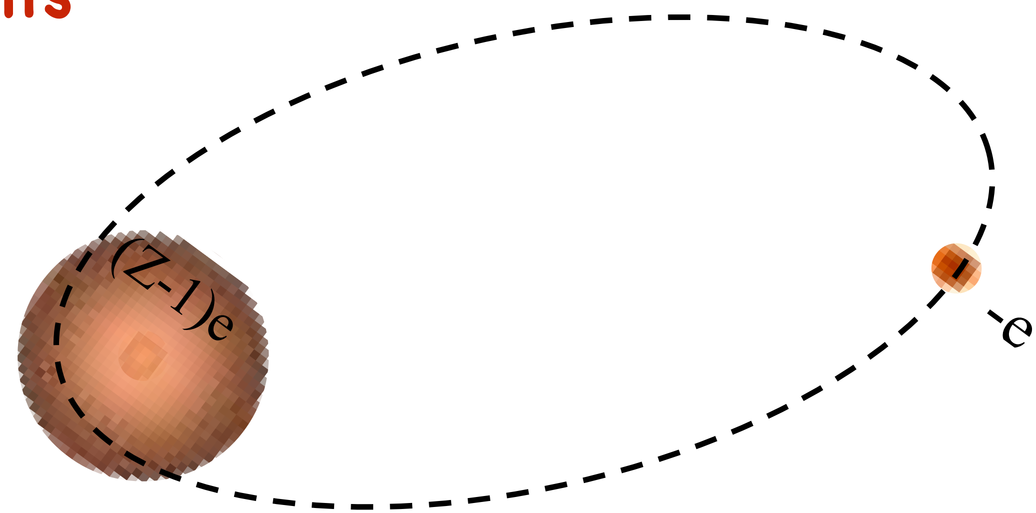
$$e^+ + e^- \to 2\gamma .$$

Penetrating effect

Non-Penetrating orbits

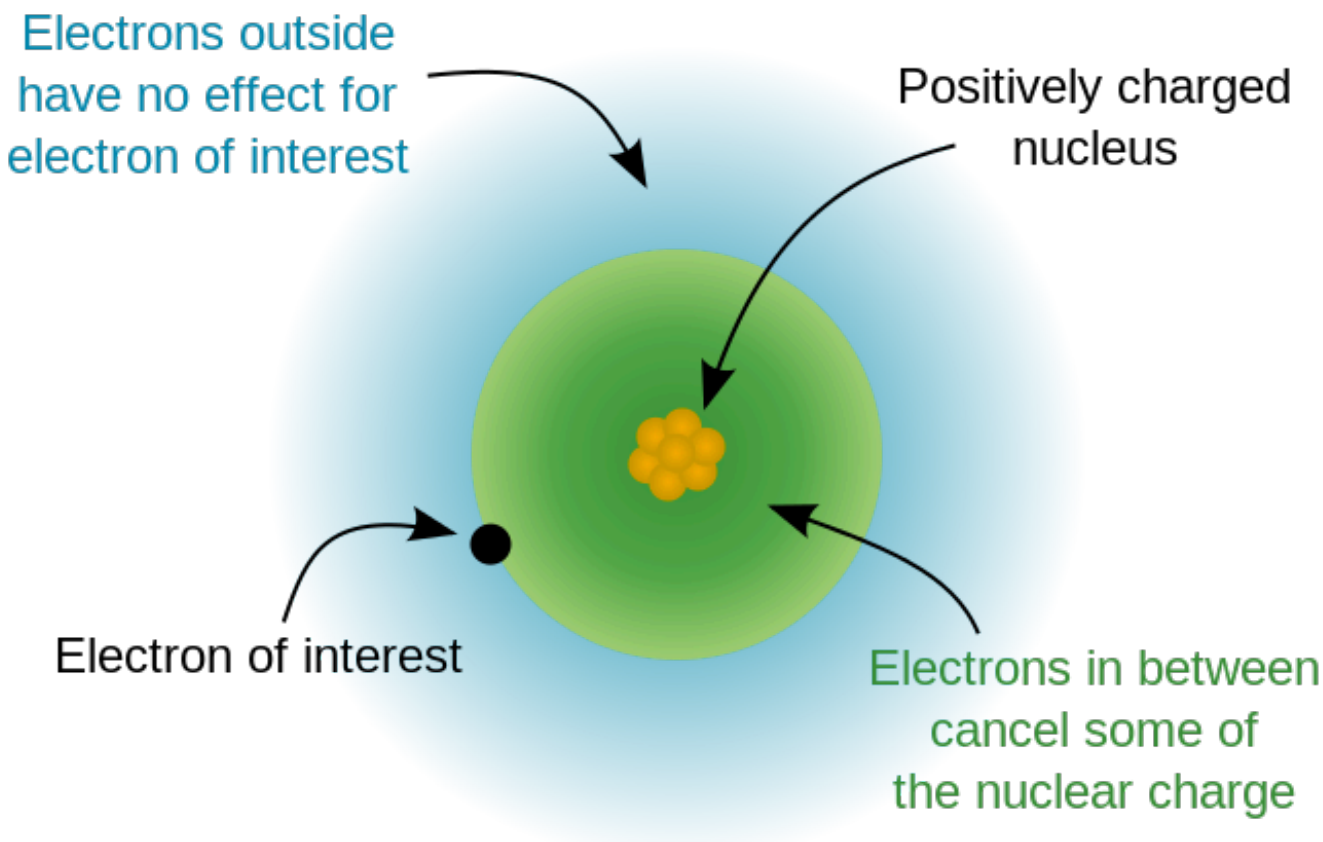


Penetrating orbits



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

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	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

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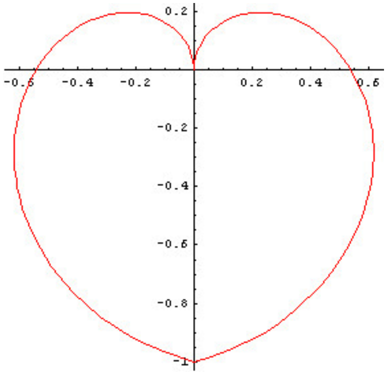
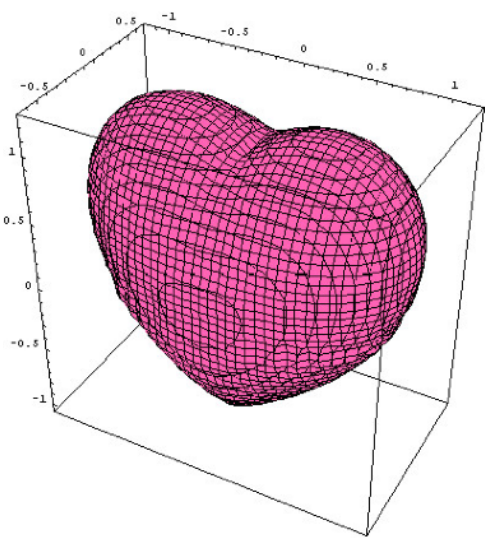
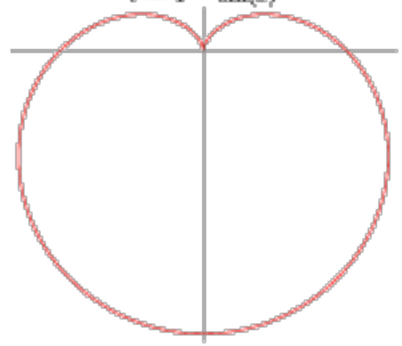
$$r = \sqrt{\mathrm{Sin}\,(0.5\,(x - 1.5\,\pi)) + 1}\,,\ \{x,\ -0.5\,\pi,\ 1.5\,\pi\}$$



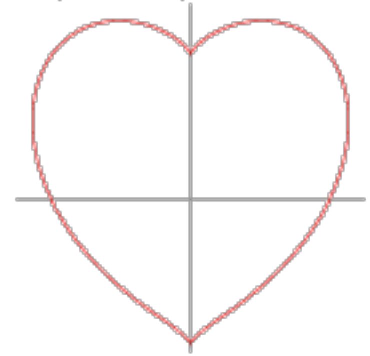
$$\left(x^2 + \frac{9}{4}\,y^2 + z^2 - 1\right)^3 - x^2 * z^3 - \frac{9}{80}\,y^2 * z^3$$



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

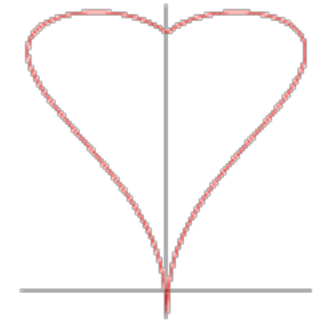


$(x^2 + y^2 - 1)^3 - x^2 y^3 = 0$

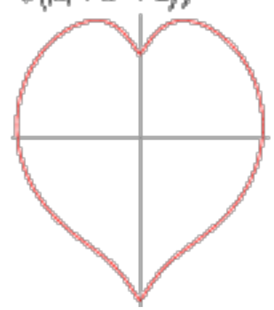


$x = \sin(t)\cos(t)\log(|t|)$

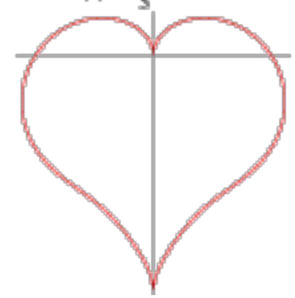
$y = |t|^{0.3}\sqrt{\cos(t)}$



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

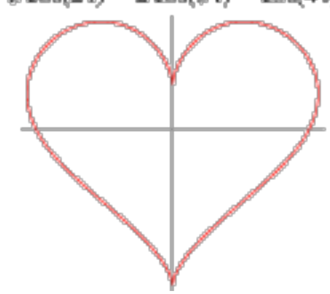


$$r = \frac{\sin(t)\sqrt{|\cos(t)|}}{\sin(t) + \frac{7}{5}} - 2\sin(t) + 2$$



$x = 16\sin^3(t)$

$y = 13\cos(t) - 5\cos(2t) - 2\cos(3t) - \cos(4t)$



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The Physics of Atoms and Quanta

8.1, 8.2, 8.3, 8.6, 8.8, 8.18