Atomic Spectra

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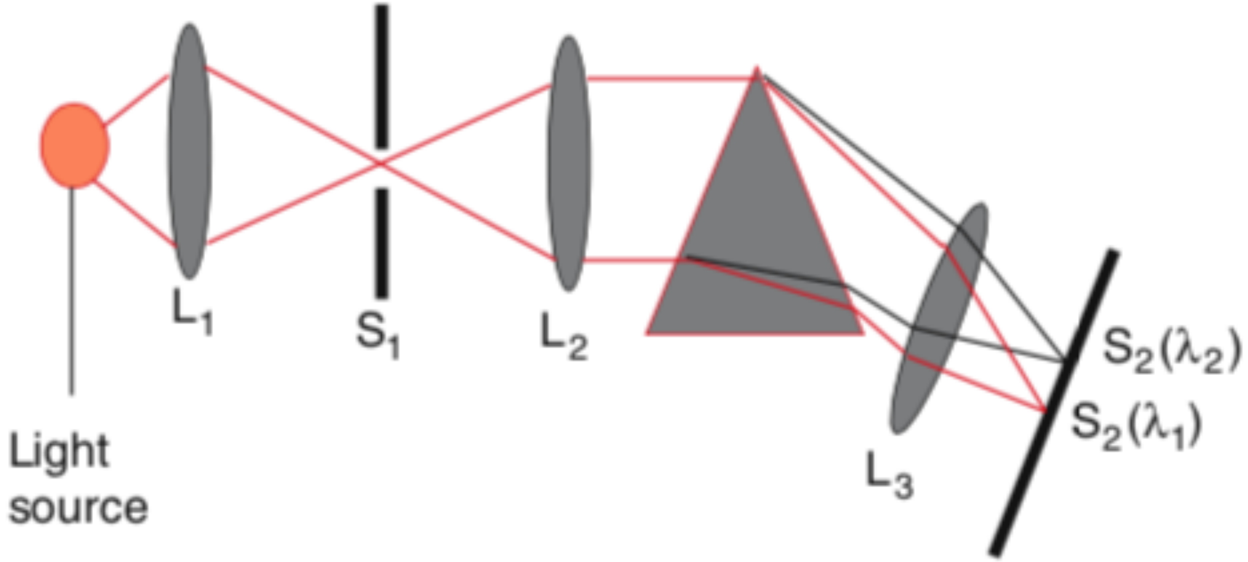
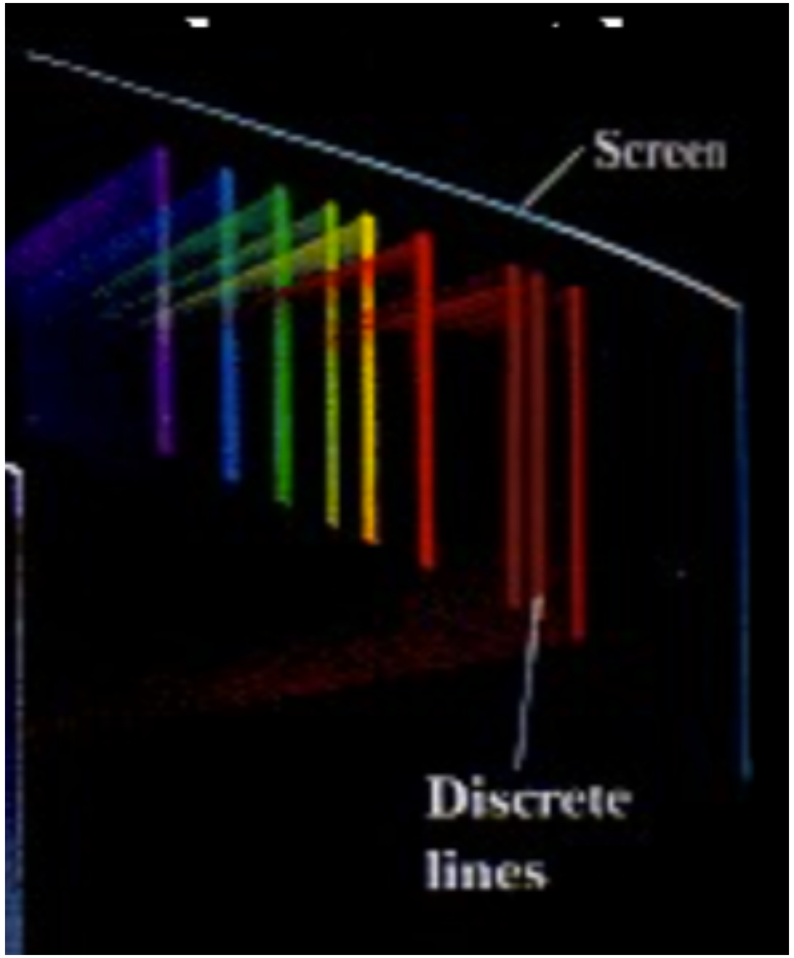
All objects emit electromagnetic waves. For a solid object, such as the hot filament of a light bulb, these waves have a continuous range of wavelengths, some of which are in the visible spectrum. The continuous range of wavelengths is a result of the entire collection of atoms that make up the solid.

In contrast, individual atoms, free of the strong interactions that are present in a solid, emit only certain specific wavelengths that are unique to those atoms.

In 1859 *Gustav Kirchhoff* (1824–1887) and *Robert Bunsen* (1811–1899) 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.

Measuring the emission spectrum





•Each wavelength observed in an absorption spectrum also appears in the emission spectrum of the same kind of atoms if the atoms have been excited into the emitting state by absorption of light or by collisional excitation.

The absorption and emission spectra are characteristic for specific atoms. They allow the unambiguous determination of the chemical element corresponding to these spectra. The spectral analysis therefore yields the composition of chemical elements in a sample. This is particularly important in astrophysics where the spectrum of the starlight gives information on the number and the composition of chemical elements in the atmosphere of the star.

• The spectral lines are not completely narrow, even if the spectral resolution of the spectrograph is extremely high. This means that the atoms do not emit strictly monochromatic radiation but show an intensity distribution $I(\lambda K)$ around each wavelength λK with a finite halfwidth $\Delta\lambda$.

Hydrogen atom emission spectrum

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* (1825– 1898). He could fit the wavenumbers $\bar{\nu}_K = 1/\lambda_K$ 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 $n_2 = 3,4,5,\ldots$. The constant $Ry = 109{,}678\,\text{cm}^{-1}$ is the Rydberg constant, which is historically given by spectroscopists in units of inverse centimeters cm^{-1}, since all wavenumbers $\bar{\nu}_K = 1/\lambda_K$ are measured in these units.

Later on *Theodore Lyman* (1874–1954) and *Fried- rich Paschen* (1865–1947) found further series in the emission and absorption spectrum of the H atom, which could all be described by the Balmer formula (3.80), but with $n_1 = 1$ (Lyman series) or $n_1 = 3$ (Paschen series)

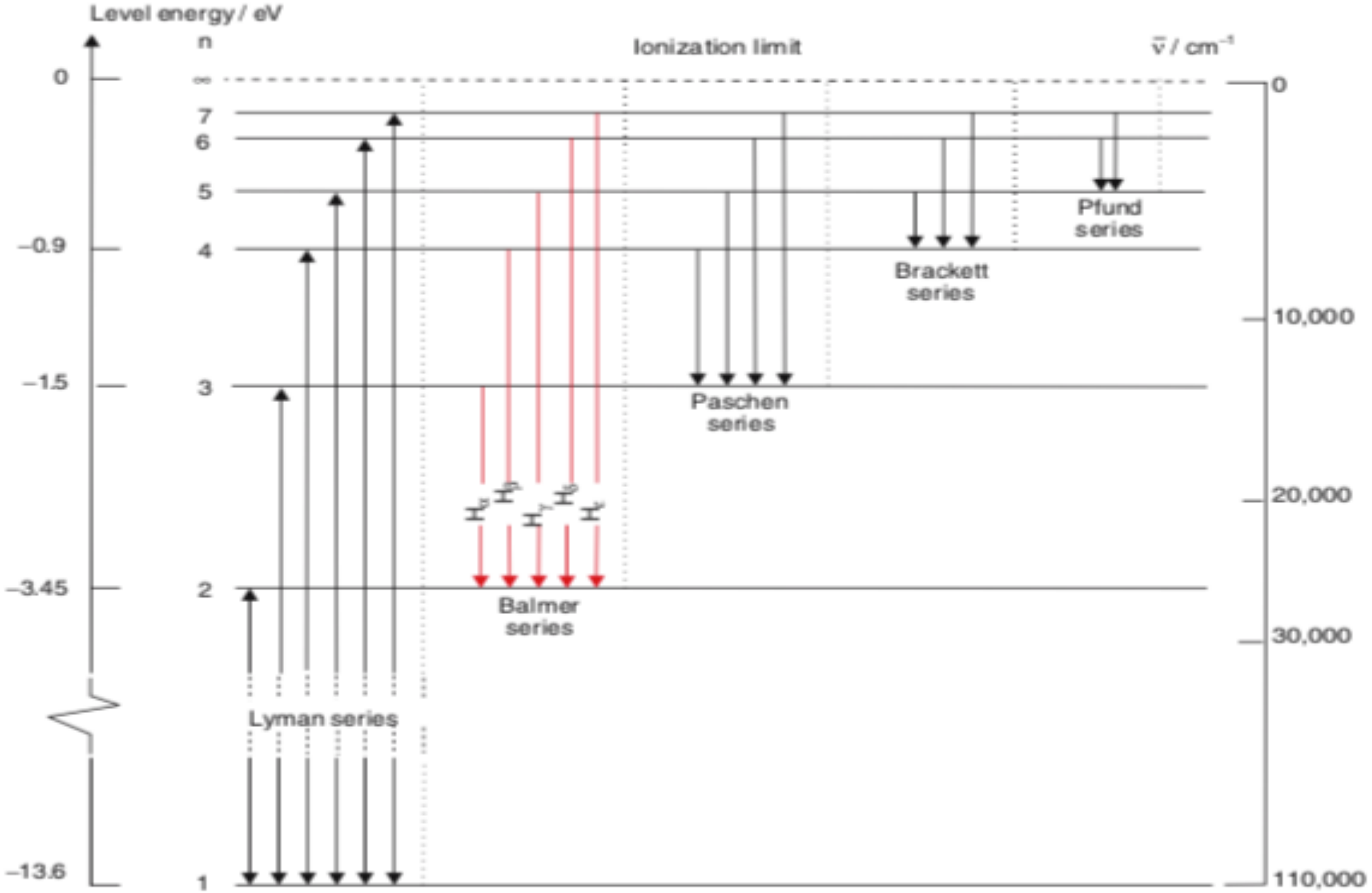


Fig. 3.40. Simplified level scheme of the hydrogen atom and the different absorption or emission series

Bohr's Atomic Theory

- The electron (mass m_e, charge $-e$) and the nucleus (mass m_N, charge $+Ze$) both move on circles with radius r_e or r_N, respectively, around their center of mass.

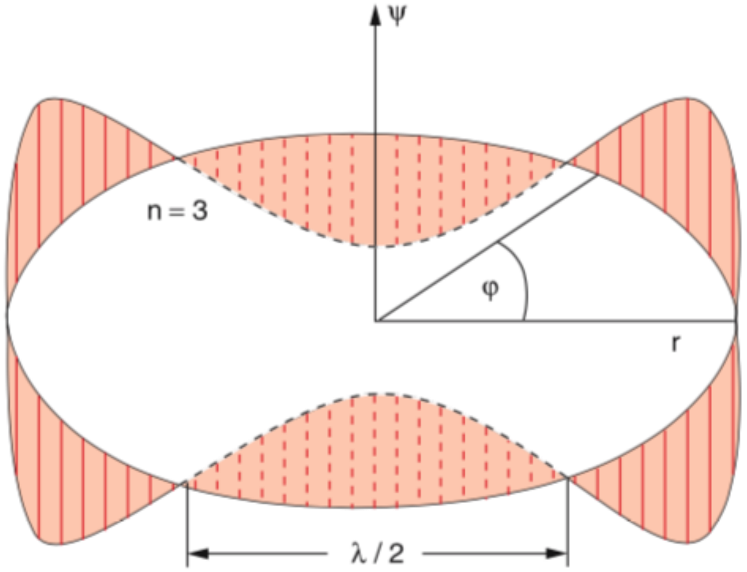
- This movement of two bodies can be described in the center of mass system by the movement of a single particle with reduced mass $\mu=(m_e m_N)/(m_e+m_N)\approx\mu_e$ in the Coulomb potential Epot(r) around the center r = 0, where r is the distance between electron and nucleus.

- The balance between Coulomb force and centripetal force yields the equation

$$\frac{\mu v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}, \quad \Rightarrow \quad r = \frac{Ze^2}{4\pi\varepsilon_0 \mu v^2}$$

As long as there are no further restrictions for the kinetic energy $(\mu/2)v^2$ any radius r is possible, according to previous equation.

If, however, the electron is described by its matter wave, $\lambda_{dB} = h/(\mu v)$ a stationary state of the atom must be described by a standing wave along the circle since the electron should not leave the atom.



This gives the quantum condition:

$$2\pi r = n\lambda_{dB} \quad (n = 1, 2, 3, \ldots),$$

which restricts the possible radii r to the discrete values (3.83). With the de Broglie wavelength $\lambda_{dB} = h/(\mu v)$ the relation between velocity and radius is obtained.

$$v = n\frac{h}{2\pi\mu r}$$

$$r_n = \frac{n^2 h^2 \varepsilon_0}{\pi\mu Z e^2} = \frac{n^2}{Z} a_0 ,$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi \mu e^2} = 5.2917 \times 10^{-11}\ \text{m} \approx 0.5\ \text{Å}$$

is the smallest radius of the electron ($n = 1$) in the hydrogen atom ($Z = 1$), which is named the Bohr radius.

The kinetic energy E_{kin} of the atom in the center of mass system

$$E_{kin} = \frac{\mu}{2} v^2 = \frac{1}{2} \frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{1}{2} E_{pot}$$

and equals −1/2 times its potential energy. The total energy

$$E = E_{kin} + E_{pot} = +\frac{1}{2} E_{pot} = -\frac{1}{2} \frac{Ze^2}{4\pi\varepsilon_0 r}$$

The total energy is negative and approaches zero for $r \to \infty$. Inserting the equation for r yields the possible energy values E_n of an electron moving in the Coulomb potential of the nucleus:

$$E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 h^2 n^2} = -Ry^* \frac{Z^2}{n^2}$$

$$Ry^* = hcRy = \frac{\mu e^4}{8\varepsilon_0^2 h^2}$$

expressed in energy units Joule.

This illustrates that the total energy of the atom in the center of mass system (which nearly equals the energy of the electron) can only have discrete values for stationary energy states, which are described by the quantum number n = 1, 2, 3. . . . (Fig. 3.40). Such a stationary energy state of the atom is called a quantum state. In Bohr's model, the quantum number n equals the number of periods of the standing de Broglie wave along the circular path of the electron.

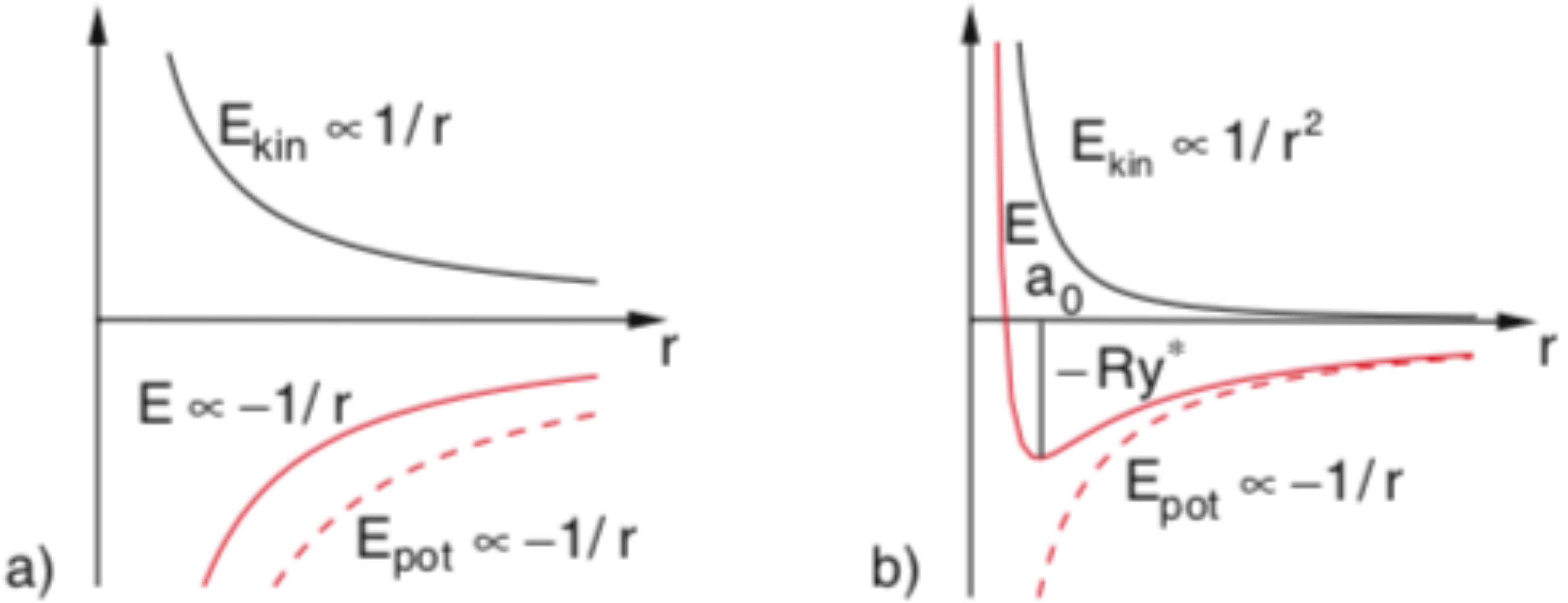


Fig. 3.43a,b. Radial dependence of kinetic, potential, and total energy of the electron in the Coulomb field of the nucleus. (**a**) Classical model (**b**) Quantum mechanical model

NOTES

1. The exact value of the Rydberg constant R_y depends, according to (3.89), on the reduced mass μ of the electron nucleus system. It differs, therefore, slightly for different masses of the nucleus. In order to have a unique definition, the Rydberg constant Ry_∞ for infinite nuclear mass $m_N = \infty \Rightarrow \mu = m_e$ is defined. Its numerical value is $R_{y\infty} = 109{,}737.31534\ \text{cm}^{-1}$.
The Rydberg constant for finite nuclear mass m_N is then:
$Ry = Ry_\infty \mu / m_e$.

2. Bohr's atomic model is a "semi-classical model", which treats the movement of the electron as that of a point mass on a classical path but adds an additional quantum condition (which is in fact a boundary condition for the de Broglie wavelength of the moving electron).

3. This quantum condition can also be formulated using the angular momentum $\boldsymbol{L}$ of the electron. Multiplying (3.84) by μr yields $\mu r v = |\boldsymbol{L}| = n$□ ,
where □ $= h/2\pi$.

This means that:

> The angular momentum of the electron on its path around the nucleus is quantized. The absolute value $n\hbar$ is an integer multiple of Planck's constant $\hbar$.

There are two identical conditions due to the boundary condition for the standing de Broglie wave :

a) The angular momentum of the atom in the center of mass system is $|\mathbf{L}| = n\hbar$
b) The circumference of the circular path of the electron $2\pi r = n\lambda_{dB}$ must be an integer multiple of the de Broglie wavelength

In order to explain the line spectra observed in absorption or emission, the following hypothesis is added to Bohr's model.

By absorption of a photon $h\nu$ the atom can be excited from a lower energy State E_i into a higher state E_k, if the energy conservationis fulfilled.

$$h\nu_{ik} = E_k - E_i$$

Using the above relation for the energies E_k, E_i yields the frequencies of the absorbed light.

$$E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 h^2 n^2} = -Ry^* \frac{Z^2}{n^2}$$

$$\Rightarrow$$

$$\nu_{ik} = \frac{Ry^*}{h} Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_k^2} \right)$$

If we substitute With the wave numbers $\bar{\nu} = \nu/c$ and $Ry^* = hc \cdot Ry$ we obtain for the hydrogen atom ($Z = 1$) exactly Balmer's formula for his observed spectra.

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

Summary the preceding results of Bohr's model of hydrogenic atoms with a single electron.

- The electron moves on circles around the nucleus with quantized radii

$$r_n = \frac{n^2}{Z^2} a_0 = \frac{n^2 h^2 \varepsilon_0}{\pi \mu Z e^2}$$

that increase quadratically with the integer quantum number n.

- The possible values r_n are inversely proportional to the nuclear charge Ze. For the He^+ ion with $Z = 2$ they are only half as large as in the hydrogen atom.

- In each quantum state the atom has a well-defined total energy

$$E_n = -Ry^* \frac{Z^2}{n^2}, \qquad E_{pot} = +2E_n,$$
$$E_{kin} = -E_n.$$

The energy $E_\infty = 0$ for $n = \infty$ and $r_n \to \infty$ is chosen as zero. In its lowest possible state the energy is $E_1 = -Ry^* Z^2$. Therefore the positive energy $-E_1$ is necessary to ionize the atom in its ground state (i.e., to bring the electron from $r = r_1$ to $r = \infty$). It is called the *ionization energy*. For the H atom the ionization energy is $E_{ion} = 13.6$ eV.

- By absorption of a photon $h\nu = E_k - E_i$ the atom can be excited from its lower energy state E_i into the higher state E_k. Emission of a photon by an excited atom causes a transition from E_k to E_i.

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Note:
The first excited state ($n = 2$) of the H atom already needs an excitation energy of about 10.2eV, which is 3/4 of the ionization energy.

Although Bohr's semi-classical atomic model explains the observed spectra very well, and also brings some esthetical satisfaction, because of its resemblance to the planetary system, it leaves several questions open. One essential point is that, according to classical electrodynamics, every accelerated charge should emit radiation. The electron on its circular path is such an accelerated charge. It should, therefore, loose energy by emitting radiation and should spiral down into the nucleus. Therefore, the Bohr model cannot explain the existence of stable atoms.

The Stability of Atoms

The stability of atoms is consistently explained by quantum theory. We will here give a conspicuous argument based on the uncertainty relation. It should be only regarded as a simple estimation that is not restricted to circular paths of the electron. If a is the mean radius of the atom, we can give the distance r of the electron from the nucleus with an uncertainty $\Delta r \leq a$, since we know that the electron has to be found somewhere within the atom. According to the uncertainty relation the uncertainty Δp_r of the radial component of the electron momentum p must be larger than $\hbar/a$. Therefore, we conclude for the uncertainty $\Delta p \geq \Delta p_r \geq \hbar/a$ (otherwise we could determine p within narrower limits than its component p_r). We find the relation $p > \Delta p \geq \hbar/a$. The mean kinetic energy of the electron is:

$$E_{\text{kin}} = \frac{p^2}{2m_e} \geq \frac{(\Delta p)^2}{2m_e} \geq \frac{\hbar^2}{2m_e a^2} .$$

Its potential energy at a distance a from the nucleus is:

$$E_{\text{pot}} = -\frac{e^2}{4\pi\varepsilon_0 a}$$

and its total energy $E = E_{kin} + E_{pot}$ at the distance a is:

$$E \geq \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\varepsilon_0 a}\ .$$

The largest probability of finding the electron is at a distance a_{min} where the total energy is minimum, i.e., where $dE/da = 0$. This gives

$$a_{min} = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = \frac{\varepsilon_0 h^2}{\pi\mu e^2} = a_0$$

which is identical to the Bohr radius a_0.

Therefore, a stable state exists with the minimum energy limit

$$E_{min} = -\frac{me^4}{2(4\pi\varepsilon_0\hbar^2)^2} = -\frac{me^4}{8\varepsilon_0^2 h^2} = -Ry^*\ ,$$

which is consistent with the energy of the lowest state with n = 1 in Bohr's model.

Although the quantum mechanical results for the energy confirms Bohr's result, the explanation of the stability is different.

According to the uncertainty principle, the atom cannot radiate in its lowest state because it has minimum energy. In order to emit a photon, it would have to make a transition to a higher energy state, which contradicts energy conservation. The reason for this energy minimum is the sharp increase of the kinetic energy of the electron with decreasing distance a, due to the uncertainty of its momentum (Fig. 3.43).

In higher energy states the atom can radiate, in accordance with the experimental results.

In Bohr's model the stability is explained by the assumption of standing waves for the electron, where the Poynting vector is zero. ***However, this does not explain why higher energy states, which are also represented by standing waves, do radiate.***