### 3.4.2 Bohr's Atomic Model

Many theorists tried to develop models that could explain the experimental findings. However, most of these models could describe some results but not all of them in a consistent way without any contradictions. After many efforts *Nils Bohr* (1885–1962) (Fig. 3.41) starting from Rutherford's atomic model finally developed in 1913 the famous planetary model of the atoms [3.3, 4, 17], which we will now discuss for atomic systems with only one electron (H atom, $He^+$ ion, $Li^{++}$ ion, etc.).

In Bohr's atomic model 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 $\mu = (m_e m_N)/(m_e + m_N) \approx m_e$ in the Coulomb potential $E_{pot}(r)$ 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

$$\frac{\mu v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}, \tag{3.81}$$

which determines the radius

$$r = \frac{Ze^2}{4\pi\varepsilon_0 \mu v^2} \tag{3.82}$$

of the circular path of the electron. As long as there are no further restrictions for the kinetic energy $(\mu/2)v^2$ any radius $r$ is possible, according to (3.82).

If, however, the electron is described by its matter wave, $\lambda_{dB} = h/(\mu v)$ a stationary state of the atom

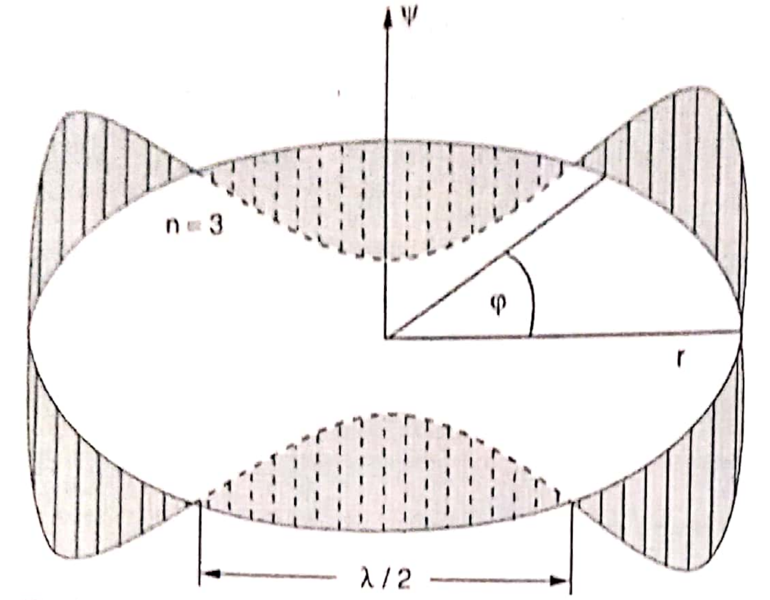


**Fig. 3.42.** Standing de Broglie matter wave illustrating the quantum condition for the angular momentum in Bohr's model

must be described by a standing wave along the circle (Fig. 3.42) since the electron should not leave the atom. This gives the quantum condition:

$$2\pi r = n\lambda_{\mathrm{dB}} \quad (n = 1, 2, 3, \ldots)\,, \tag{3.83}$$

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

$$v = n\frac{h}{2\pi\mu r} \tag{3.84}$$

between velocity and radius is obtained. Inserting this into (3.82) yields the possible radii for the electron circles:

$$r_n = \frac{n^2h^2\varepsilon_0}{\pi\mu Z e^2} = \frac{n^2}{Z}a_0\,, \tag{3.85}$$

where

$$a_0 = \frac{\varepsilon_0 h^2}{\pi\mu e^2} = 5.2917\times10^{-11}\,\mathrm{m} \approx 0.5\,\text{Å}$$

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

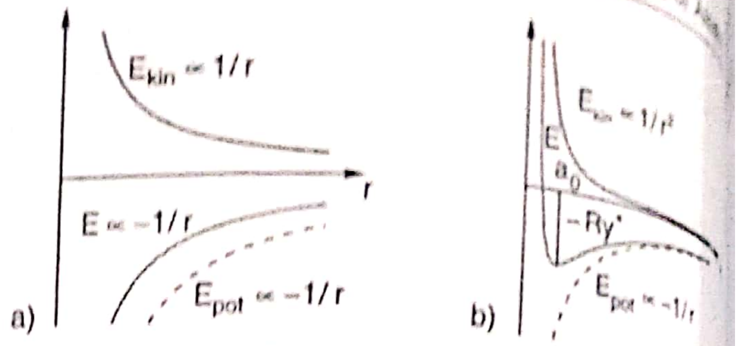


**Fig. 3.43a,b.** Radial dependence of kinetic, potential, and […] energy of the electron in the Coulomb field of the nucle[…] (**a**) Classical model (**b**) Quantum mechanical model

The kinetic energy $E_{\mathrm{kin}}$ of the atom in the center of mass system is obtained from (3.81) as

$$E_{\mathrm{kin}} = \frac{\mu}{2}v^2 = \frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{1}{2}E_{\mathrm{pot}} \tag{3.86}$$

and equals $-1/2$ times its potential energy. The total energy (Fig. 3.43)

$$E = E_{\mathrm{kin}} + E_{\mathrm{pot}} = +\frac{1}{2}E_{\mathrm{pot}} = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{3.87}$$

is negative and approaches zero for $r \to \infty$. Inserting (3.85) for $r$ yields for the possible energy values $E_n$ of an electron moving in the Coulomb potential of the nucleus:

$$E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 h^2 n^2} = -Ry^*\frac{Z^2}{n^2} \tag{3.88}$$

with the Rydberg constant

$$Ry^* = hcRy = \frac{\mu e^4}{8\varepsilon_0^2 h^2} \tag{3.89}$$

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* $n = 1, 2, 3, \ldots$ (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.

**Note:**

1. The exact value of the Rydberg constant $Ry$ depends, according to (3.89), on the reduced

### 5.1.2 Solution of the Radial Equation

With the product-ansatz

$$\psi(r, \vartheta, \varphi) = R(r) Y_l^m(\vartheta, \varphi)$$

for the wave function $\Psi(r, \vartheta, \varphi)$ in Sect. 4.3.2 we had already obtained (4.65) for the radial part $R(r)$, which converts for $m \to \mu$ and $C_2 = l(l+1)$ into

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2\mu}{\hbar^2}\left(E - E_{\mathrm{pot}}(r)\right)R(r) = \frac{l(l+1)}{r^2}R(r) \,. \tag{5.9}$$

The integer $l$ describes, according to (4.89), the integer quantum number of the orbital angular momentum of the particle with respect to the origin $r = 0$ in our relative coordinate system, where the nucleus is at rest at $r = 0$.

Differentiation of the first term and introducing the Coulomb-potential for $E_{pot}(r)$ yields

$$\frac{\mathrm{d}^2 R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \left[\frac{2\mu}{\hbar^2}\left(E + \frac{Ze}{4\pi\varepsilon_0 r}\right) - \frac{l(l+1)}{r^2}\right]R = 0 \,. \tag{5.10}$$

In the limit $r \to \infty$ all terms with $1/r$ and $1/r^2$ approach zero and (5.10) becomes for this limiting case:

$$\frac{\mathrm{d}^2 R(r)}{\mathrm{d}r^2} = -\frac{2\mu}{\hbar^2}ER(r) \,. \tag{5.11}$$

The solutions of this equation describe the asymptotic behavior of the radial wave function $R(r)$. The probability of finding the electron in a spherical shell with volume $4\pi r^2\,\mathrm{d}r$ around the nucleus between the radii $r$ and $r + \mathrm{d}r$ is given by $4\pi|R|^2 r^2\,\mathrm{d}r$. The absolute square of the function $R$ therefore gives the probability of finding the electron within the unit volume of the spherical shell.

Introducing $W(r) = r \cdot R(r)$ into (5.10) and neglecting all terms with $1/r$ and $1/r^2$ yields, with $k = \sqrt{2\mu E}/\hbar$, the asymptotic solution

$$W(r \to \infty) = A\,\mathrm{e}^{ikr} + B\,\mathrm{e}^{-ikr} \,. \tag{5.12a}$$

This gives for $R(r) = W(r)/r$

$$R(r) = \frac{A}{r}\mathrm{e}^{ikr} + \frac{B}{r}\mathrm{e}^{-ikr} \,. \tag{5.12b}$$

For $E > 0$ $k$ is real and the first term in (5.12b) represents the spatial part of an outgoing spherical wave

$$\psi(r, t) = \frac{A}{r}\mathrm{e}^{i(kr - \omega t)} \,, \tag{5.12c}$$

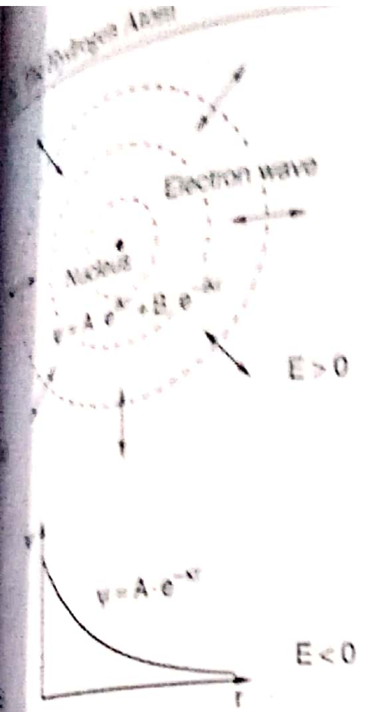


**Fig. 5.2.** (**a**) Ingoing and outgoing spherical waves as solutions to the Schrödinger equation for an electron with $E > 0$ in a spherical potential. (**b**) Experimentally decreasing wave amplitude for $E < 0$

…h describes an electron that can, with a positive …al energy, leave the atom and can reach $r \to \infty$ …Fig. 5.2a). The second term corresponds to an ingoing …erical wave that represents an electron coming from $r = \infty$ and approaching the nucleus (this is called …collision process).

For $E < 0$ we substitute $\kappa = \sqrt{-2\mu E}/\hbar = ik$ and …ain the real asymptotic solutions

$$R(r \to \infty) = A\,e^{-\kappa r} + B\,e^{+\kappa r} . \tag{5.12d}$$

…ce $R(r)$ must be finite for all values of $r$ (otherwise …e function $R(r)$ could not be normalized) it follows …at $B = 0$. We then obtain the asymptotic solution

$$R(r \to \infty) = A\,e^{-\kappa r} .$$

…is is an exponentially decreasing function which has …cayed to $1/e$ for $r = 1/\kappa$.

For the general solution, valid for all values of $r$, we …y the ansatz

$$R(r) = u(r)\,e^{-\kappa r} . \tag{5.12e}$$

…serting this into (5.10) we obtain for $u(r)$ the equation

$$\frac{d^2u}{dr^2} + 2\left(\frac{1}{r} - \kappa\right)\frac{du}{dr} + \left[\frac{2a - 2\kappa}{r} - \frac{l(l+1)}{r^2}\right]u = 0 . \tag{5.13}$$

…here the abbreviation $a$ is

$$a = \frac{\mu Z e^2}{4\pi\varepsilon_0 \hbar^2} .$$

The reciprocal value $r_1 = 1/a = 4\pi\varepsilon_0\hbar^2/(\mu Z e^2)$ gives, according to (3.85), the Bohr radius of the lowest energy level.

We write $u(r)$ as the power series

$$u(r) = \sum_j b_j r^j . \tag{5.14}$$

Inserting this into (5.13) the comparison of the coefficients of equal powers in $r$ yields the recursion formula

$$b_j = 2b_{j-1}\frac{\kappa j - a}{j(j+1) - l(l+1)} . \tag{5.15}$$

Since $R(r)$ must be finite for all values of $r$, the power series can only have a finite number of summands. If the last nonvanishing coefficient in the power series (5.14) is $b_{n-1}$ than $b_j$ becomes zero for $j = n$. This immediately gives, from (5.15), the condition, that only the coefficients $b_j$ with $j < n$ contribute to the series (5.14).We therefore have the condition

$$j < n . \tag{5.16}$$

Since for $j = n \Rightarrow b_j = 0$ we obtain from (5.15)

$$a = n\kappa . \tag{5.17}$$

With $\kappa = +\sqrt{-2\mu E}/\hbar$ this yields the condition for the energy values

$$E_n = -\frac{a^2\hbar^2}{2\mu n^2} = -\frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^2} = -Ry^*\frac{Z^2}{n^2} \tag{5.18}$$

with the Rydberg constant

$$Ry^* = \frac{\mu e^4}{8\varepsilon_0^2 h^2} . \tag{5.18a}$$

Note that this formula is identical to that of Bohr's model in (3.88).

> The quantum mechanical calculation of one-electron systems gives the same energy values as Bohr's atomic model.

**Note:**

1. From the derivation of (5.18) it can be recognized that the discrete eigenvalues $E_n$ of possible energies stem from the restraint $\psi(r \to \infty) \to 0$, which