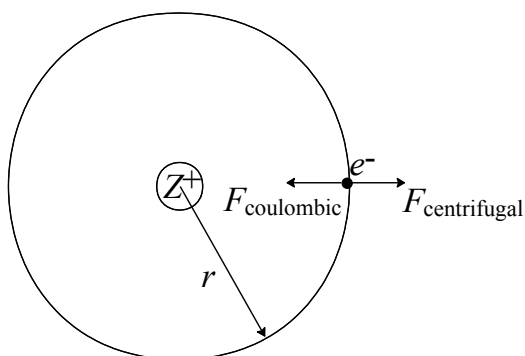


### Derivation of Bohr's Equations for the One-electron Atom

Bohr set about to devise a model that would explain the observed line spectra of one-electron atoms, such as H, He<sup>+</sup>, Li<sup>2+</sup>. The model Bohr used was based on Rutherford's conclusion from his gold foil experiments that the negative electrons in an atom are a great distance away from the positive charge in the nucleus. Bohr began with a classical mechanical approach, which assumes that the electron in a one-electron atom is moving in a circular orbit with a radius,  $r$ , from the nucleus.



The movement of an electron in its orbit would create a centrifugal force, which gives it a tendency to fly away from the nucleus. This force is given by

$$F_{\text{centrifugal}} = -mv^2/r$$

where  $m$  is the mass of the electron, and  $v$  is its velocity. In order to have a stable atom, it was assumed that this centrifugal force was exactly matched by an opposing centripetal force, drawing the electron inward through the coulombic attraction between the electron's negative charge and the positive charge in the nucleus. This coulombic force of attraction is given by

$$F_{\text{coulombic}} = -Ze^2/r^2$$

Equating these two forces, we have

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad (1)$$

We can rearrange equation (1), solving for  $r$ , to obtain the following expression:

$$r = \frac{mv^2r^2}{Ze^2} \quad (2)$$

If we multiply the right side of equation (2) by  $m/m$ , this becomes

$$r = \frac{m^2 v^2 r^2}{mZe^2} = \frac{(mvr)^2}{mZe^2} \quad (3)$$

Written in this way, the numerator is the electron's angular momentum squared,  $(mvr)^2$ . At this point, Bohr made an assumption that departs radically from concepts of classical mechanics. Bohr's assumption, called the *quantum hypothesis*, asserts that the angular momentum,  $mvr$ , can only take on certain values, which are whole-number multiples of  $h/2\pi$ ; i.e.,

$$mvr = nh/2\pi \quad n = 1, 2, 3, \dots$$

where  $h$  is Planck's constant. Substituting  $nh/2\pi$  for  $mvr$  in equation (3) we obtain the Bohr expression for the radius:

$$r = \frac{n^2 h^2}{4\pi^2 mZe^2} \quad (4)$$

For the hydrogen atom ( $Z = 1$ ), the smallest radius, given the symbol  $a_0$ , is obtained from equation (4) when  $n = 1$ :

$$a_0 = \frac{h^2}{4\pi^2 me^2} = 0.529 \text{ \AA} \quad (5)$$

This is called the Bohr radius. Using the definition of  $a_0$  in equation (5), we can rewrite equation (4) to obtain a more compact form of the radius equation for any one-electron atom:

$$r = \frac{n^2 a_0}{Z} \quad (6)$$

Since  $a_0$  is a constant, equation (6) predicts that the radius increases in direct proportion to the square of the quantum number,  $n^2$ , and decreases in inverse proportion to the atomic number,  $Z$ . Thus, the sizes of the orbits in hydrogen are predicted to be  $a_0$ ,  $4a_0$ ,  $9a_0$ ,  $16a_0$ ,  $25a_0$ , etc. Furthermore, the orbits in  $\text{He}^+$  ( $Z = 2$ ) for any value of  $n$  are predicted to be half as large as the comparable orbits in H.

Although the radius equation is an interesting result, the more important equation concerned the energy of the electron, because this correctly predicted the line spectra of one-electron atoms. The derivation of the energy equation starts with the assumption that the electron in its orbit has both kinetic and potential energy,  $E = K + U$ . The kinetic energy, which arises from electron motion, is  $K = \frac{1}{2}mv^2$ . The potential energy, which arises from the coulombic attraction between the negative charge of the electron and the positive charge in the nucleus, is given by  $U = -Ze^2/r$ . Thus,

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} \quad (7)$$

We have seen that in Bohr's model the coulombic force is assumed to be equal and opposite to the centrifugal force [equation (1)]. We can rearrange equation (1) to obtain an expression for  $mv^2$ :

$$mv^2 = \frac{Ze^2}{r} \quad (8)$$

Substituting this into the first term in equation (7) we obtain

$$E = \left(\frac{1}{2}\right)\frac{Ze^2}{r} - \frac{Ze^2}{r} = \left(-\frac{1}{2}\right)\frac{Ze^2}{r} = -\frac{Ze^2}{2r} \quad (9)$$

The negative sign in equation (9) indicates a favorable energy of attraction, which must be overcome to remove the electron to an infinite distance from the nucleus. We can eliminate  $r$  from equation (9) by substituting equation (4):

$$E = \frac{-2\pi^2mZ^2e^4}{n^2h^2} \quad (10)$$

If we gather all the constants to define a single constant,  $B$ , equation (10) can be written most simply as

$$E = -\frac{BZ^2}{n^2} \quad (11)$$

As equation (11) shows, the energy becomes more favorable (negative) in direct proportion to the square of the nuclear charge, and less favorable (less negative) in inverse proportion to the square of the quantum number.

For the one-electron atom (H, He<sup>+</sup>, Li<sup>2+</sup>, etc.), the lowest energy occurs when  $n = 1$ . This energy state is called the *ground state*. If the atom receives sufficient energy, as in a gas discharge tube, its electron may jump to a higher orbit ( $n > 1$ ) with corresponding higher energy. This represents an *excited state*. The only way the atom can assume a lower-energy state is through emission of energy in the form of electromagnetic radiation. The energy of this radiation is equal to the energy difference between the high state and the lower state:

$$E_{\text{light}} = |E_{\text{final}} - E_{\text{initial}}| = |E_{\text{low}} - E_{\text{high}}|$$

In terms of the Bohr energy equation [equation (11)], the energy of the emitted light should be

$$E_{\text{light}} = \left| \frac{-BZ^2}{n_{\text{low}}^2} - \frac{-BZ^2}{n_{\text{high}}^2} \right| = BZ^2 \left[ \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right] \quad (12)$$

We assume that  $n_{\text{high}}$  is always at least one integer value greater than  $n_{\text{low}}$ ; i.e.  $n_{\text{high}} > n_{\text{low}}$ . The lower state,  $n_{\text{low}}$ , may be either the ground state ( $n = 1$ ) or any other excited state with a lower value of  $n$  than the original state,  $n_{\text{high}}$ . Since the energy of electromagnetic radiation is conventionally not given a sense of sign, equation (12) has been formulated here in terms of absolute value.

From Planck we know that  $E = hv$ , so if we divide through equation (12) by  $h$  we can write an expression for the frequencies of the emitted light:

$$\nu = \frac{BZ^2}{h} \left[ \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right] \quad (13)$$

For hydrogen ( $Z = 1$ ), the constants outside the brace equal the Rydberg constant in units of hertz ( $\text{Hz} = \text{s}^{-1}$ ); i.e.,  $BZ^2/h = \mathfrak{R}$ . This general equation predicts the frequencies of the Balmer series, if the low state is  $n_{\text{low}} = 2$ :

$$\nu = \frac{BZ^2}{h} \left[ \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right] = \mathfrak{R} \left[ \frac{1}{4} - \frac{1}{n^2} \right] \quad n = 3, 4, 5, \dots \quad (14)$$

Equation (14) is equivalent to the equation Balmer deduced empirically. It represents the frequencies for the series of transitions from various excited states to the same lower state for which  $n_{\text{low}} = 2$ .

Substituting other values of  $n_{\text{low}}$  in equation (13) gives frequencies that predict other series of line spectra for hydrogen, which had not been observed at the time Balmer did his experiments. Balmer's elucidation of the series for which  $n_{\text{low}} = 2$  was simply a result that visible light was the most readily observed kind of electromagnetic radiation with the spectroscopes available in the late nineteenth century. Other series predicted by equation (13) fall either in the ultraviolet or infrared regions, which are more difficult to observe experimentally. With better instrumentation and the impetus of the Bohr equation, the following line-spectra were subsequently discovered, in addition to the Balmer series:

$n_{\text{low}}$	Region	Series Name
1	ultraviolet	Lyman
2	visible	Balmer
3	infrared	Paschen
4	infrared	Brackett
5	infrared	Pfund

The ability to predict the frequencies of these series gave credibility to the Bohr model. However, all attempts to extend this approach to multi-electron atoms failed. More significantly, its “particle-only” view of the atom and its exact predictions for the location and momentum of the electron were contrary to the subsequent understandings of wave-particle duality and the Heisenberg uncertainty principle. By the 1930's, most physicists (including Bohr) had abandoned this model in favor of the wave mechanical approach formulated by Irwin Schrödinger.