2.7: Derivation of the Rydberg Equation from Bohr's Model

Bohr postulated that electrons existed in orbits or states that had discrete energies. We therefore want to calculate the energy of these states and then take the differences in these energies to obtain the energy that is released as light when an electron makes a transition from one state to a lower energy one.

Because the proton is so much more massive than the electron, we can consider the proton to be fixed and the electron to be rotating around it. For the general case, two particles rotate about their center of mass, and this rotation can be described as the rotation of a single particle with a reduced mass.

To explain the hydrogen luminescence spectrum, we write the energy, E, of an orbit or state of the hydrogen atom as the sum of the kinetic energy, T, and potential energy, V, of the rotating electron. The potential energy is just the Coulomb energy for two particles with charges q_1 and q_2.

$$E = T + V \tag{2.7.1}$$

$$T = \frac{1}{2} m_e v^2 \tag{2.7.2}$$

and

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{(Ze)(-e)}{4\pi\epsilon_0 r} = \frac{-Ze^2}{4\pi\epsilon_0 r} \tag{2.7.3}$$

In general the charge on an atomic nucleus is Ze, where Z is the number of protons in the nucleus. The charge on a single proton is simply the fundamental constant for the unit charge, e, and the charge on an electron is $-e$. The factor $4\pi\varepsilon_0$ is due to the use of SI units, and ε is the permittivity of free space ($8.85419 \times 10^{-12} C^2 N^{-1} m^{-2}$).

Even though $Z = 1$ for the hydrogen atom, Z is retained in Equation 2.7.3 and subsequent equations so the results apply to any one-electron ion as well (e.g., He^+, Li^{2+}, etc.).

> **Example 2.7.1**
>
> Show that 1 $C^2 N^{-1} m^{-2}$ is equivalent to 1 F/m.

By invoking the **Virial Theorem** for electrostatic forces, we can determine the radii of the orbit and the energy of the rotating electron, derive the Rydberg equation, and calculate a value for the Rydberg constant. This theorem says that the total energy of the system is equal to half of its potential energy and also equal to the negative of its kinetic energy.

$$E = \frac{V}{2} = -T \tag{2.7.4}$$

The Virial Theorem has fundamental importance in both classical mechanics and quantum mechanics. It has many applications in chemistry beyond its use here. The word virial comes from the Latin word for force, vires, and the Virial Theorem results from an analysis of the forces acting on a system of charged particles. A proof of the validity of this theorem for the hydrogen atom is available.

The Virial Theorem makes it possible to obtain the total energy from the potential energy if we have the radius, r, of the orbit in Equation 2.7.3. We can obtain the radius of the orbit by first expressing the kinetic energy T in terms of the angular momentum M,

$$T = \frac{M^2}{2m_e r^2} \tag{2.7.5}$$

where $M = m_e v r$.

Using the Virial Theorem, Equation 2.7.4, to equate the expressions for $V/2$ and $-T$ (Equations 2.7.3 and 2.7.5), introducing Bohr's proposal that angular momentum M is quantized, $M = nhbar$, and solving for r gives

$$r_n = \frac{\pi\epsilon_0 \hbar^2 n^2}{m_e Z e^2} \tag{2.7.6}$$

Notice in equation 2.7.6 how the quantization of angular momentum results in the quantization of the radii of the orbits. The smallest radius, for the orbit with $n = 1$, is called the Bohr radius and is denoted by a_0.

$$a_0 = 52.92\, pm = 0.5292\, \text{Å} \tag{2.7.7}$$

Substituting Equations 2.7.3 and 2.7.6 into Equation $2-15$ for the total energy gives

$$E_n = \frac{-m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2} \tag{2.7.8}$$

which shows that the energy of the electron also is quantized. Equation 2.7.8 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level.

Example 2.7.2

Calculate the potential energy, the kinetic energy, and the total energy for hydrogen when r = 52.92 pm.

Example 2.7.3

Sketch an energy level diagram for the hydrogen atom. Label each energy level with the quantum number n and the radius of the corresponding orbit.

Example 2.7.4

Calculate a value for the Bohr radius using Equation 2.7.6 to check that this equation is consistent with the value 52.9 pm. What would the radius be for n = 1 in the Li^{2+} ion.

Example 2.7.5

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. To which family of curves does this plot belong? States of hydrogen atoms with n = 200 have been prepared. What is the diameter of the atoms in these states? Identify something else this size.

To explain the hydrogen atom luminescence spectrum, Bohr said that light of frequency vif is produced when an electron goes from an orbit with n = i ("i" represents "initial") to a lower energy orbit with n = f ("f" represents "final"), with i > f. In other words, the energy of the photon is equal to the difference in energies of the two orbits or hydrogen atom states associated with the transition.

$$E_{photon} = h\nu_{if} = E_i - E_f = \Delta E_{if} = \frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{1}{f^2} - \frac{1}{i^2}\right) \tag{2.7.9}$$

Using $\nu_{if} = c\bar{\nu}_{if}$ converts Equation (2.20) from frequency to wave number units,

$$\bar{\nu}_{if} = \frac{me^4}{8\epsilon_0^2 h^3}\left(\frac{1}{f^2} - \frac{1}{i^2}\right) \tag{2.7.10}$$

When we identify R_H with the ratio of constants on the right hand side of Equation (2-21), we obtain the Rydberg equation with the Rydberg constant as in Equation (2-22).

$$R_H = \frac{me^4}{8\epsilon_0^2 h^3} \tag{2.7.11}$$

Evaluating R_H from the fundamental constants in this formula gives a value within 0.5% of that obtained experimentally from the hydrogen atom spectrum.

Example 2.7.6

Calculate the energy of a photon that is produced when an electron in a hydrogen atom goes from an orbit with n = 4 to and orbit with n = 1. What happens to the energy of the photon as the initial value of n approaches infinity?
