Chapter 5

Example

The helium atom has 2 electronic energy levels: $E_{3p} = 23.1$ eV and $E_{2s} = 20.6$ eV where the ground state is $E = 0$. If an electron makes a transition from 3p to 2s, what is the wavelength of the photon emitted?

$$E_\gamma = E_{3p} - E_{2s} = 2.5 \text{ eV} \tag{1}$$

So

$$\lambda = \frac{hc}{E_\gamma} = \frac{1240 \text{ eV} - \text{nm}}{2.5 \text{ eV}} \approx 500 \text{ nm} \tag{2}$$

This is blue-green light.

Bohr Model of the Hydrogen Atom

In the Bohr model of the atom, the electrons orbit the nucleus like planets around the sun. (Whether the orbits are circular or elliptical doesn't matter much. Bohr worked out both possibilities. We will assume circular orbits for simplicity.) Bohr assumed that only some orbits were allowed.

Let us consider the classical mechanics of an electron orbiting a proton. We assume the proton is fixed in position and has charge $+e$ while the electron has mass m and charge $-e$. The force between the proton and electron is due to Coulomb attraction:

$$F = \frac{ke^2}{r^2} \tag{3}$$

where $k = 1/(4\pi\varepsilon_0) = 8.99 \times 10^9$ N-m^2/C^2. The centripetal acceleration is $a = v^2/r$, so $F = ma$ implies

$$m\frac{v^2}{r} = \frac{ke^2}{r^2} \tag{4}$$

or

$$mv^2 = \frac{ke^2}{r} \tag{5}$$

We have 1 equation and 2 unknowns: v and r. So there is no unique value of v and r, and no quantization of the energy. The kinetic energy is

$$K = \frac{1}{2}mv^2 = \frac{ke^2}{2r} \tag{6}$$

If we compare this to the potential energy

$$U = -\frac{ke^2}{r} \tag{7}$$

where the minus sign means that the proton and electron attract one another. $U = 0$ corresponds to $r = \infty$. So we see that

$$K = -\frac{1}{2}U \tag{8}$$

This is an example of the virial theorem. So the total energy is

$$E = K + U = \frac{1}{2}U = -\frac{1}{2}\frac{ke^2}{r} \tag{9}$$

The fact that the total energy is negative means that the electron is bound to the proton. So as the electron gets farther and farther away, the energy approaches 0. In general, $-\infty < E < 0$.

To get quantized energy levels, Bohr proposed that the electron's orbital angular momentum was quantized. Recall that angular momentum

$$\vec{L} = \vec{r} \times \vec{p} \tag{10}$$

For an orbiting electron, the magnitude of L is

$$L = mvr \tag{11}$$

Bohr proposed that the electron's orbital angular momentum was quantized in integer multiples of

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ J} - \text{s} \tag{12}$$

Note that Planck's constant has units of angular momentum:

$$[h] = \text{energy} \cdot \text{time} = \frac{ML^2}{T^2} \times T = \frac{ML^2}{T} \tag{13}$$

and

$$[\text{angular momentum}] = [mvr] = M \times \frac{L}{T} \times L = \frac{ML^2}{T} \tag{14}$$

Bohr proposed that the electron's orbital angular momentum L was quantized:

$$\begin{aligned} L &= \frac{h}{2\pi},\ 2\frac{h}{2\pi},\ 3\frac{h}{2\pi}, ... \\ &= \hbar,\ 2\hbar,\ 3\hbar, ... \\ &= n\hbar \quad \text{where} \quad n = 1, 2, 3, ... \end{aligned} \tag{15}$$

Techically speaking, the correct theory of quantum mechanics says that the components of L are quantized in integer multiples of $\hbar$.

For circular orbits, $L = mvr$, so we have

$$L = mvr = n\hbar \quad \text{where} \quad n = 1, 2, 3, ... \tag{16}$$

Now we have our second equation. So we have 2 equations (Eqs. (4) and (16)) and 2 unknowns: v and r. Solving Eq. (16) for v, we get

$$v = \frac{n\hbar}{mr} \tag{17}$$

Plugging into Eq. (4), we find

$$m\left(\frac{n\hbar}{mr}\right)^2 = \frac{ke^2}{r} \tag{18}$$

and hence,

$$r = \frac{n^2\hbar^2}{ke^2 m} \tag{19}$$

We can write this as

$$r = n^2 a_B \quad \text{where} \quad n = 1, 2, 3, ... \tag{20}$$

where the Bohr radius a_B is defined as

$$a_B = \frac{\hbar^2}{ke^2 m} = 0.0529 \text{ nm} \tag{21}$$

The Bohr radius is half an angstrom. We see that the radius of the electron orbits in hydrogen are quantized as integer multiples of the Bohr radius. The smallest orbit (n=1) has the radius a_B.

Now that we know the allowed radii of the orbits, we can immediately obtain the energy associated with each orbit:

$$E = -\frac{ke^2}{2r} = -\frac{ke^2}{2a_B}\frac{1}{n^2} \quad \text{where} \quad n = 1, 2, 3, ... \tag{22}$$

We see that the energies are quantized. Each orbit is associated with a particular energy level. Let E_n denote the nth energy level or the nth orbit. When the electron makes a transition from n to n', a photon is emitted (if the electron decreases its energy) or absorbed (if the electron increases its energy). The energy of the photon is given by

$$E_\gamma = E_n - E_{n'} = \frac{ke^2}{2a_B}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \tag{23}$$

which has the same form as the Rydberg formula

$$E_\gamma = hcR\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \tag{24}$$

So Bohr's model predicts the Rydberg formula. Comparing these 2 formulas gives us an expression for the Rydberg constant R

$$R = \frac{ke^2}{2a_B(hc)} = \frac{1.44 \text{ eV} - \text{nm}}{2(0.0529 \text{ nm})(1240 \text{ eV} - \text{nm})} = 0.0110 \text{ nm}^{-1} \tag{25}$$

in perfect agreement with the observed value. The Rydberg or Rydberg energy E_R is defined by

$$E_R = hcR = \frac{ke^2}{2a_B} = \frac{m(ke^2)^2}{2\hbar^2} = 13.6 \text{ eV} \tag{26}$$

This is the binding energy of the electron in the ground state of the hydrogen atom. This is the amount of energy you would have to give to the electron in the lowest orbital in order to liberate it from the proton. In other words, this is the binding energy. In terms of E_R, the quantized energies of the electron in the hydrogen atom are

$$E_n = -\frac{E_R}{n^2} \quad \text{where} \quad n = 1, 2, 3, ... \tag{27}$$

Properties of the Bohr Atom

The lowest energy state of the hydrogen is called the **ground state**. This corresponds to $n = 1$ and

$$E_{n=1} = E_1 = -E_R = -13.6 \text{ eV} \tag{28}$$

In this state, the electron orbit has the smallest radius which is the Bohr radius a_B:

$$r = a_B = 0.0529 \text{ nm} \tag{29}$$

This is the radius of a hydrogen atom in its ground state and gives the order of magnitude of the outer radius of all atoms in their ground states. The allowed energies or the energy levels are

$$E_n = -\frac{E_R}{n^2} \quad \text{where} \quad n = 1, 2, 3, ... \tag{30}$$

The excited states correspond to $n > 1$, i.e., $n =$ 2, 3, ... , e.g.,

$$\begin{aligned} E_2 &= -\frac{E_R}{4} = -3.4 \text{ eV} \\ E_3 &= -\frac{E_R}{9} = -1.5 \text{ eV} \end{aligned}$$

An energy level diagram looks like a ladder with the allowed energies represented as horizontal lines, and the energies increasing as you go up. It's a good way to show transitions between energy levels (see Figure 5.4 in your book). So going from $n = 1$ to $n = 2$ requires a photon with energy equal to 10.2 eV.

When electrons make transitions from excited states (n) down to lower energy states (n'), a photon is emitted according to the formula:

$$E_\gamma = E_n - E_{n'} = E_R \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) \tag{31}$$

$n' = 2$ corresponds to the Balmer series. $n' = 1$ is called the Lyman series, and $n' = 3$ is the Paschen series. The names are from the names of the discoverers.

The radius of the orbit for the nth level is given by

$$r_n = n^2 a_B \tag{32}$$

Note that the radius increases rapidly with n since it goes as n^2.

We assumed circular orbits, but Bohr showed that elliptical orbits give the same energy. Since this picture of orbits isn't really correct, we won't pursue this.

Example: What is the diameter of a hydrogen atom with $n = 100$? Such atoms have been observed in the vacuum. The diameter is

$$d = 2r = 2n^2 a_B = 2 \times 10^4 \times (0.05 \text{ nm}) = 1\ \mu\text{m} \tag{33}$$

Hydrogen-Like Ions

A hydrogen-like ion is any atom that has lost all but one of its electrons, and therefore consists of a single electron orbiting a nucleus with charge $+Ze$. For example, a He^+ ion or a Li^{2+} ion (an electron and a lithium nucleus of charge $+3e$).

The math for hydrogen-like ions is the same as before if we replace e^2 by Ze^2. For example, the magnitude of the force between the electron and the nucleus with charge Ze^2 is

$$F = \frac{Zke^2}{r^2} = \frac{mv^2}{r} \tag{34}$$

The potential energy is

$$U = -\frac{Zke^2}{r} \tag{35}$$

The total energy is

$$E = K + U = \frac{U}{2} = -\frac{Zke^2}{2r} \tag{36}$$

To find the allowed radii of an electron moving in a circular orbit around a charge Ze, we go through the same argument as before:

$$\begin{aligned} L &= mvr = n\hbar \\ v &= \frac{n\hbar}{mr} \\ mv^2 &= \frac{Zke^2}{r} = m\left(\frac{n\hbar}{mr}\right)^2 \end{aligned}$$

Solving for r yields

$$r = n^2 \frac{\hbar^2}{Zke^2 m} = n^2 \frac{a_B}{Z} \tag{37}$$

So

$$r \sim \frac{1}{Z} \tag{38}$$

i.e., the larger the charge Z, the smaller the radius. The bigger charge pulls the electron closer.

Plugging Eq. (37) into Eq. (36) gives

$$\begin{aligned} E_n &= -Z^2 \frac{ke^2}{2a_B} \frac{1}{n^2} \\ &= -Z^2 \frac{E_R}{n^2} \end{aligned} \tag{39}$$

The 2 factors of Z are easy to understand. One comes from the Z in the energy and one comes from the $1/Z$ in the radius.