Bohr's Theory of the Hydrogen Atom

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1 Constants

- $ke = 8.91 * 10^9$ Nm$^2/C^2$
- $h = 6.63 * 10^-34$ Js
- $\hbar = h/2\pi = 1.05 * 10^-34$ Js
- $Bohr'sRadius = 5.3 * 10^-19$

2 Derivation

Bohr suggested that the planetary model could be saved if one new assumption were made: certain "special states of motion" of the electron, corresponding to different orbital radii, would not result in radiation, and could therefore persist indefinitely without the electron falling into the nucleus. Specifically, Bohr postulated that the angular momentum of the electron, mvr (the mass and angular velocity of the electron and in an orbit of radius r) is restricted to values that are integral multiples of h/2. The radius of one of these allowed Bohr orbits is given by:

$$nh/2\pi mv \tag{1}$$

in which h is Planck's constant, m is the mass of the electron, v is the orbital velocity, and n can have only the integer values 1, 2, 3, etc. The most revolutionary aspect of this assumption was its use of the variable integer n; this was the first application of the concept of the quantum number to matter. The larger the value of n, the larger the radius of the electron orbit, and the greater the potential energy of the electron. As the electron moves to orbits of increasing radius, it does so in opposition to the restoring force due to the positive nucleus, and its potential energy is thereby raised. This is entirely analogous to the increase in potential energy that occurs when any mechanical system moves against a restoring force— as, for example, when a rubber band is stretched or a weight is lifted.

Thus what Bohr was saying, in effect, is that the atom can exist only in certain discrete energy states: the energy of the atom is quantized. Bohr noted that this quantization nicely explained the observed emission spectrum of the hydrogen atom. The electron is normally in its smallest allowed orbit, corresponding to n = 1; upon excitation in an electrical discharge or by ultraviolet light, the atom absorbs energy and the electron gets promoted to higher quantum levels. These higher excited states of the atom are unstable, so after a very short time (around 10—9 sec) the electron falls into lower orbits and finally into the innermost one, which corresponds to the atom's ground state. The energy lost on each jump is given off as a photon, and the frequency of this light provides a direct experimental measurement of the difference in the energies of the two states, according to the Planck-Einstein relationship

$e = hv$

3 Calculation

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:

$$Fcentrifugal = \frac{-mv^2}{r} \tag{2}$$

$$Fcoulombic = -Ze2/r2 \tag{3}$$

$$mv^2/r = Ze^2/r^2 \tag{4}$$

$$r = mv^2r^2/Ze^2 \tag{5}$$

$$r = m^2v^2r^2/Mze^2 = (mvr)^2/mZe^2 \tag{6}$$

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; i.e.,

$$mvr = nh2\pi \tag{7}$$

When n=1,2,3

Substituting $nh/2\pi$ for mvr in equation (7)

$$r = n^2h^2/4\pi^2mZe^2 \tag{8}$$

For the hydrogen atom (Z = 1), the smallest radius, given the symbol ao, is obtained from equation (8) when n = 1:

$$ao = h^2/4\pi^2me^2 \tag{9}$$

This is called the Bohr radius.We can rewrite equation (9) to obtain a more compact form of the radius equation for any one-electron atom

$$r = \frac{n^2ao}{z} \tag{10}$$

Since ao is a constant, equation (6) predicts that the radius increases in direct proportion to the square of the quantum number, n2, and decreases in inverse proportion to the atomic number, Z. Thus, the sizes of the orbits in hydrogen are predicted to be ao, 4ao, 9ao, 16ao, 25ao, etc. Furthermore, the orbits in 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 = 12mv2. 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 = –Ze2/r. Thus,

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} \tag{11}$$

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 mv2:

$$mv^2 = \frac{Ze^2}{r} \tag{12}$$

Substituting this into the first term in equation (11) we obtain

$$E = \frac{-2\pi mv^2}{n^2h^2} \tag{13}$$

If we gather all the constants to define a single constant, B, equation (13) can be written most simply as

$$E = \frac{-BZ^2}{n^2} \tag{14}$$

4 Spectral Series

- n=1 Lyman Series
- n=2 Balmer Series
- n=3 Paschen Series

For the one-electron atom (H, He+, Li2+, 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

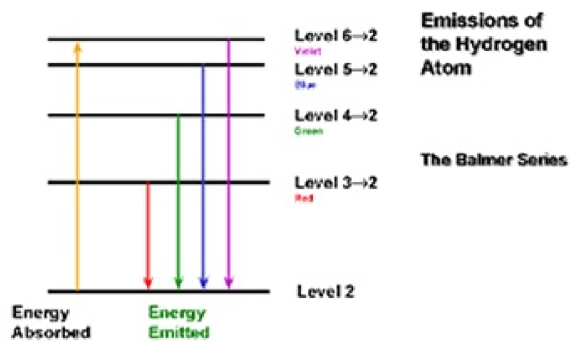

Figure 1: The Balmer Series

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:

$$Elight = |Efinal - Einitial| = |Elow - Ehigh| \tag{15}$$

In terms of the Bohr energy equation [equation (15)], the energy of the emitted light should be:

$$Elight = \frac{-BZ^2}{n^2low} - \frac{-BZ^2}{n^2high} \tag{16}$$

From Planck we know that E = h, so if we divide through equation (16) by h we can write an expression for the frequencies of the emitted light:

$$v = \frac{BZ^2}{h}[\frac{1}{n^2low} - \frac{1}{n^2high}] \tag{17}$$

For hydrogen (Z = 1), the constants outside the brace equal the Rydberg constant in units of hertz (Hz = s-1) ; i.e., BZ2/h = U. This general equation predicts the frequencies of the Balmer series, if the low state is nlow = 2 For hydrogen (Z = 1), the constants outside the brace equal the Rydberg constant in units of hertz (Hz = s-1) ; i.e., BZ2/h = U. This general equation predicts the frequencies of the Balmer series, if the low state is nlow = 2 Substituting other values of nlow in equation (17) gives frequencies that predict other series of line spectra for hydrogen

5 Bibliography

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