

# PHY140Y

## 19 Beginnings of Quantum Mechanics

### 19.1 Overview

- Atomic Spectra
- Balmer and Lyman Lines
- Bohr Model of the Atom

### 19.2 Atomic Spectra

It was noted already in the late 1800's that atomic gases interact with light. In particular, if one excited a diffuse gas by either heating it or by passing a current through it, one found that a given gas gave off specific frequencies of light. This “emission spectra” was characteristic of the type of gas. In the case of a current, we understand the interaction of the electrons flowing through the gas and the atoms of the gas to excite the atoms causing them to give off light.

A second form of spectra can be observed if one simply shines a light through a diffuse gas. In this case, the atoms preferentially interact with light of given frequencies, causing this light to be scattered in essentially all directions. The other light passes through the gas without any interaction. The result is that the spectrum of the light passing through the gas shows absorption lines, where it appears that specific frequencies have been removed from light by passing through the gas. The absorption lines in this spectra are exactly at the same frequency as the emitted light seen in emission spectra. The two are this the one and the same phenomenon.

An understanding of this interaction of matter and light was considered to be one of the challenges in the late 1800's by physicists and chemists trying to understand the structure of matter and the nature of light.

### 19.3 Balmer and Lyman Lines

The earliest studies of these emission spectra showed that the frequencies emitted by the gas had some pattern. In 1884, Johann Balmer showed that the first four lines of the emission spectra of hydrogen obeyed the rule

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad (1)$$

where  $n = 3, 4, 5$  and  $6$ , and the Rydberg constant  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ . These sets of lines have been named the “Balmer series” in recognition of his initial observation. However, he was unable to explain the reason for this pattern. Shortly after this, additional sets of lines were discovered

outside of the visible spectrum. The Lyman series were a set of lines observed in the ultraviolet spectrum, and satisfied a similar equation

$$\frac{1}{\lambda} = R_H \left( 1 - \frac{1}{n^2} \right), \quad (2)$$

while additional lines were observed in the infrared (the Paschen series is the next one to be discovered). The general pattern was that the wavelength of an emission line satisfied

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad (3)$$

where  $n_1 = 1, 2, 3, \dots$  and  $n_2 = n_1 + 1, n_1 + 2, \dots$

## 19.4 Bohr Model of the Atom

These observations motivated Niels Bohr in 1913 to develop a new theory of the atom. At this time, the nucleus had already been discovered by Lord Rutherford in 1909, and so it was thought that the electrons in an atom were in some sort of orbit around the positively-charged nucleus. He also knew that he had to introduce a principle that required the electron in an atom to have specific energy states. To this end, he suggested that the angular momentum of an electron orbiting the nucleus of an atom had to be quantized. We will focus on the example of the hydrogen atom, which has a nucleus consisting of only one proton.

In particular, he proposed that this angular momentum take on the values

$$L = n\hbar, \quad (4)$$

where  $n = 1, 2, \dots$ , and  $\hbar \equiv h/(2\pi) = 1.03 \times 10^{-34}$  J s. Then he just used classical mechanics. For a circular orbit, we know that the electrostatic force acting on the electron

$$F = \frac{kq_1q_2}{r^2} = \frac{m_e v^2}{r}, \quad (5)$$

where  $q_1$  and  $q_2$  are the electric charges of the electron and nucleus,  $r$  is the radius of the orbit,  $m_e$  is the mass of the electron and  $v$  is its orbital speed.<sup>1</sup> The kinetic energy of the electron is therefore

$$K = \frac{1}{2} m_e v^2 \quad (6)$$

$$= \frac{ke^2}{2r}, \quad (7)$$

where we have now assumed that the electron carries one negative unit of elementary charge  $e = 1.60 \times 10^{-19}$  C and the nucleus carries one unit of positive charge. Since the total energy

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<sup>1</sup>We have assumed that we can ignore the motion of the nucleus, which is not so unreasonable given the mass of the nucleus is so much larger than the mass of the electron.

of the electron,  $E$ , is given by the sum of the electrostatic potential energy and the kinetic energy, we find that

$$E = K + U = \frac{ke^2}{2r} - \frac{ke^2}{r} \quad (8)$$

$$= -\frac{ke^2}{2r} \quad (9)$$

$$\Rightarrow r = \frac{-ke^2}{2E}. \quad (10)$$

Since the total energy is equal to the negative of the kinetic energy, we have

$$-E = K = \frac{1}{2}m_e v^2 \quad (11)$$

$$\Rightarrow v = \sqrt{\frac{-2E}{m_e}}. \quad (12)$$

If we now introduce Bohr's quantization condition, we find

$$L = m_e v r = n\hbar \quad (13)$$

$$\Rightarrow m_e \sqrt{\frac{-2E}{m_e}} \left( \frac{-ke^2}{2E} \right) = n\hbar \quad (14)$$

$$E = - \left( \frac{m_e k^2 e^4}{2\hbar^2} \right) \frac{1}{n^2}. \quad (15)$$

This predicts that the atom has an infinite number of possible energy states, given by Eq. 15. It also predicts that the electron should be orbiting the nucleus at a fixed radius that depends on the energy level. For the  $n = 1$  state, which is now seen as the lowest energy state of the Bohr atom, we find that the orbital radius is

$$r_1 \equiv a_0 = \frac{-ke^2}{2E} \quad (16)$$

$$= \frac{\hbar^2}{ke^2 m_e} = 5.29 \times 10^{-11} \text{ m}. \quad (17)$$