# Physikalische Chemie III für Lehramt

# Übungsblatt 7

(16.06.2023)

### Besprechung 22.06.2023

The following questions are from the book *Modern Physics* by Kenneth S. Krane.

## 1 Line spectra

In 1885, Johann Balmer, a Swiss mathematics teacher, noticed (mostly by trial and error) that the wavelengths of the group of emission lines of hydrogen in the visible region could be calculated very accurately from the formula

$$\lambda = (364.5 \,\mathrm{nm}) \frac{n^2}{n^2 - 4} \qquad (n = 3, 4, 5, \dots). \tag{1}$$

For example, for n = 3, the formula gives  $\lambda = 656.1$  nm, which corresponds exactly to the longest wavelength of the series of hydrogen lines in the visible region. This formula is now known as the *Balmer formula* and the series of lines that it fits is called the *Balmer series*. The wavelength 364.5 nm, corresponding to  $n \to \infty$ , is called the series limit.

It was soon discovered that all of the groupings of lines in the hydrogen spectrum could be fit with a similar formula of the form

$$\lambda = \lambda_{\text{limit}} \frac{n^2}{n^2 - n_0^2} \qquad (n = n_0 + 1, n_0 + 2, n_0 + 3, \dots),$$
(2)

where  $\lambda_{\text{limit}}$  is the wavelength of the appropriate series limit. For the Balmer series,  $n_0 = 2$ . The other series are today known as Lyman  $(n_0 = 1)$ , Paschen  $(n_0 = 3)$ , Brackett  $(n_0 = 4)$ , and Pfund  $(n_0 = 5)$ .

Another interesting property of the hydrogen wavelengths is summarized in the *Ritz combination principle*. If we convert the hydrogen emission wavelengths to frequencies, we find the curious property that certain pairs of frequencies added together give other frequencies that appear in the spectrum.

- **a.** The series limit of the Paschen series  $(n_0 = 3)$  is 820.1 nm. What are the three longest wavelengths of the Paschen series?
- b. Show that the longest wavelength of the Balmer series and the longest *two* wavelengths of the Lyman series satisfy the Ritz combination principle. For the Lyman series,  $\lambda_{\text{limit}} = 91.13 \,\text{nm}$ .

## 2 One-dimensional hydrogen atom

To analyze the hydrogen atom according to quantum mechanics, one must solve the Schrdinger equation for the Coulomb potential energy of the proton and the electron:

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}.$$
(3)

Here  $\epsilon_0$  is the dielectric permittivity of the vacuum, and r is the distance between the proton and the electron.

In class you discussed the solutions to the three-dimensional problem for the hydrogen atom using spherical polar coordinates. In this question you will examine the simpler one-dimensional problem, in which a proton is fixed at the origin (x = 0) and an electron moves along the positive x axis. (This doesn't represent a real atom, but it does show how some properties of electron wave functions in atoms emerge from solving the Schrödinger equation.)

In one dimension, the Schrödinger equation for an electron with potential energy

$$U(x) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{x} \tag{4}$$

would be

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n(x)}{\mathrm{d}x^2} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{x}\psi_n(x) = E_n\psi_n(x),\tag{5}$$

where the subscript n enumerates the different wave functions  $\psi_n$  and their corresponding energies  $E_n$ .

a. Show that the wave function

$$\psi_1(x) = Ax \mathrm{e}^{-\alpha x},\tag{6}$$

where A is the normalization constant, is one possible solution of the Schrödinger equation (5) if the constant  $\alpha$  and the energy  $E_1$  are selected appropriately.

Obtain an expression for  $\alpha$  in terms of the fundamental constants appearing in the Schrödinger equation. Express the energy  $E_1$  in terms of this  $\alpha$  and the other fundamental constants.

**b.** The *Bohr radius*  $a_0$  is defined as

$$a_0 = 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2},\tag{7}$$

where  $m_e$  is the electron mass and e is the elementary charge. How is  $\alpha$  that you obtained in part **a** related to the Bohr radius?

#### **c.** Using the numerical values

$$\epsilon_0 = 8.854 \,\mathrm{F/m}$$
 (Farads per meter)  
 $m_e = 9.109 \times 10^{-31} \,\mathrm{kg}$  (8)  
 $e = 1.602 \times 10^{-19} \,\mathrm{C}$ 

calculate the numerical value of the Bohr radius  $a_0$  in units of nanometers.

**d.** Calculate the numerical value of the energy  $E_1$  that you obtained in part **a**. Express this value in units of eV (electron-volt).