

Problem I.S ... search for quanta

10 points; (chybí statistiky)

Find the Rydberg constant's value and determine which hydrogen spectral lines belong to the visible spectrum. These lines are the only ones Rydberg could use to discover his formula, as neither UV nor IR spectra could yet be measured. What color are they, and which transitions in the Bohr model do they correspond to? (3pts)

Calculate de Broglie wavelength of your body. How does this value compare to the size of an atom or atomic nucleus? (3pts)

Assume you have a cuvette with 10 ml of fluorescein water solution. Then, you point an argon laser at the cuvette. The laser is characterized by a wavelength of 488 nm and a power of 10 W. At the same time, the fluorescein molecule fluoresces at a wavelength of 521 nm with a quantum yield (proportion of absorbed photons that are emitted back) of 95 %. If the initial temperature of the cuvette is 20 °C, how long will it take for its contents to start boiling? Assume that the cuvette is perfectly thermally insulated, the laser beam is fully absorbed in it, and the amount of fluorescein is negligible in terms of heat capacity. (4pts)

A gift from Mikuláš.

If we look in the appropriate physics table (or in the deep end of the internet – it doesn't matter), we can find at least two different “Rydberg” constants. One, most commonly denoted R_∞ , is indeed a fundamental constant of 10973731m^{-1} . But this value would only be valid if we had a truly stationary nucleus unaffected by the motion of the electron. In a real hydrogen atom, of course, it does affect it a little, just as the Moon and Earth orbit around a shared center of gravity. However, this can be included analytically (similar to how we introduce reduced mass in the motion of space bodies) and we obtain the Rydberg constant for hydrogen R_H . The value is very similar though, $1.09678 \cdot 10^7 \text{m}^{-1}$. But for deuterium, for example, it would be different. Since the values differ on the fourth valid digit, it doesn't matter which one we use in our example.

We begin by looking at transitions from the ground state, i.e., for $n_1 = 1$ in the Rydberg formula. If we choose $n_2 = 2$, then substitution gives us a wavelength value of about 122 nm, which is already hard ultraviolet radiation, which is already vacuum ultraviolet radiation – the name comes from the fact that it is strongly absorbed in air, so we need a vacuum apparatus to work with it. The transitions to higher levels will have even more energy, so there's no point in calculating their wavelengths because they will be even further away from visible light.

If we move from the first excited state of hydrogen to the closest higher one ($n_1 = 2, n_2 = 3$), we obtain the wavelength 656 nm, i.e., already in the visible part of the spectrum. Specifically, it's in the red region, near the shift to orange. Let's try the other possible values of n_2 . For $n_2 = 4$ we have a wavelength of about 486 nm and the corresponding line has a color that is probably best described as cyan. The transition to $n_2 = 5$ corresponds to a wavelength of 434 nm (notice how the spectral lines densify!) and the line is blue. The next one with $n_2 = 6$ has 410 nm and is violet. The next line has a wavelength of 397 nm, which falls outside the region traditionally thought of as visible light, which extends to about 400 nm. In reality, this distinction between visible and UV light is blurred, and often 390 nm or 380 nm is given as the cutoff, which would add another 1 to 3 lines, but the fact remains that in the real world, the decreasing sensitivity of the eye to near-UV wavelengths combines with the fact that the intensity of emission of these higher excitations decreases, and in practice the line at 410 nm is already almost imperceptible.

If we consider transitions from $n_1 = 3$ to higher levels, then for the closest higher level $n_2 = 4$ we get a wavelength of 1875 nm, which is already in the infrared region. Even if we

consider arbitrarily high levels, in the limit for $n_2 \rightarrow \infty$ we are at wavelength 821 nm, which is still in the infrared region. Even for excitations from higher values of n_1 we will not get out of the infrared region.

For clarity, we will summarize the results in a table, together with the labeling used in astronomy.

Line	Transition	Wavelength	Color
H $_{\alpha}$	2 \rightarrow 3	656 nm	Red
H $_{\beta}$	2 \rightarrow 4	486 nm	Cyan
H $_{\gamma}$	2 \rightarrow 5	434 nm	Blue
H $_{\delta}$	2 \rightarrow 6	410 nm	Violet

You have surely noticed that the spectral lines for excitation from a particular n_1 level fall in some single region of the electromagnetic spectrum. We are talking about the so-called spectral line series, which are usually named after the person who discovered them. The exception is just the series for $n_1 = 2$, whose origin is in the visible spectrum, which is called the Balmer series. We already mentioned this in the first text of the series, by the way.

For $n_1 = 1$ we speak of a Lyman series that is entirely in the ultraviolet region of the spectrum. For the lines with excitations from $n_1 = 3$ we speak of the Paschen series, which in turn is in the infrared region. These two series were observed between 1906 and 1914, so it fits quite well with the historical timeline described in the series. The other two series (Brackett's, Pfund's) were observed in 1922 and 1924. The next series was not experimentally observed until 1953, roughly thirty years later. Scientists have also long been confused by the spectral lines of He $^+$ in the spectra of stars. These come out in such a way that half of the lines in the visible spectrum overlap with the hydrogen ones, while the other half comes out exactly in between. For a long time, hydrogen lines were thought to be "half-integer" lines before Niels Bohr correctly assigned them to the He $^+$ ion.

At the same time, it is worth mentioning that each series contains an infinite number of lines that include excitations at all higher electron levels up to the limit for $n_2 = \infty$, which corresponds to a complete detachment of the electron from the atom. So, we are actually lucky that the spectral lines of the Balmer series escape into the UV region, otherwise this sample solution would have infinite length.

Before finding your de Broglie wavelength, we must realize that the problem is (on purpose) incompletely specified because the de Broglie wavelength depends on our momentum. So, we choose a walking speed of 5 km/h and a mass of 60 kg. This will give us momentum from the formula $p = mv$ of about 80 kg·m/s (let's not worry too much about rounding, it's more of an order of magnitude estimate anyway). Now, we need to plug in the formula from the series $\lambda = h/p$. The value of Planck's constant is approximately $6.6 \cdot 10^{-34}$ kg·m 2 /s, which gives a de Broglie wavelength of about $8 \cdot 10^{-36}$ m. This is completely negligible compared to the size of the atom $\sim 10^{-10}$ m and the size of the atomic nucleus $\sim 10^{-15}$ m. It is even less than the Planck distance $1.6 \cdot 10^{-35}$ m, which is considered in modern theoretical physics to be the smallest distance that makes sense in terms of the laws of physics.

But what does that mean? If we look at classical optics, the wave properties of light manifest themselves (as diffraction or interference) on scales comparable to the wavelength (grating size, film thickness). So, if we move on our macroscopic scales, the wave characters are "desynchronized" and no interference is observed. This is technically called decoherence. Because of this, quantum phenomena do not manifest in everyday life, just as the light of a light bulb does not

interfere on a fine net. In this way, Planck's constant h determines the scale on which quantum effects appear. If its value were on the order of 1 J·s, our life would be quantum.

Finally, it should be mentioned that, like momentum, the de Broglie wavelength depends on the choice of reference frame. However, this does not preclude formulating quantum theory so that it is independent of the choice of reference frame.

To solve the fluorescein problem, it is useful to first understand what is happening in the cuvette. The laser light is absorbed, and each photon of radiation excites one fluorescein molecule to a higher excited state. The excited states of a molecule can be visualized using a simple model. The electrons cannot move freely in the atoms of the molecule but have their allowed paths similar to the orbits of the Bohr model. These orbits are not around the nucleus of a single atom, instead, the electrons orbit the entire molecule. The excited state is when an electron jumps to any higher orbit (we will see later that it is not such a silly idea). From there, it gradually “falls” to the second lowest state. In this case, it does not radiate the excess energy as a photon but transfers it to the surrounding water molecules in the form of kinetic energy during mutual collisions (we macroscopic creatures call this kinetic energy heat). Of course, this molecule could also emit a photon, but the transfer of energy to the surrounding molecules is much faster in this case, so for practical purposes, we can ignore the photon emission. From the second lowest state, the molecule then transitions to the lowest (ground) state. It can do this in two ways: either it jumps to the ground state and emits a single photon of wavelength 521 nm, which happens in 95% cases. In the other cases, it continues to transfer energy to the surrounding water molecules, so nothing is emitted (we're talking about a non-radiative transition).

Now that we've got the physics of the problem clear (although simplistically, since we don't distinguish the states of the molecule caused by the vibration of the nuclei from those caused by the motion of the electrons), we can calculate how much of the laser power is actually used. Clearly, in the 5% cases where the photon is absorbed and no photon is emitted back, all the laser energy is used to heat the solution. In the other case, we have to calculate the fraction of energy that causes heating. “Efficiency” of fluorescent heating will be given by

$$\eta_{\text{F1}} = \frac{E_{\text{La}} - E_{\text{F1}}}{E_{\text{La}}},$$

where the energy of the photon coming from the laser is denoted as E_{La} and the photon emitted by the fluorescence as E_{F1} . If we substitute the energy of the photon $h\nu = hc/\lambda$ and simplify, we obtain the equation

$$\eta_{\text{F1}} = 1 - \frac{\lambda_{\text{La}}}{\lambda_{\text{F1}}}.$$

From this, we get the total efficiency

$$\eta = 0.05 + 0.95\eta_{\text{F1}}.$$

By substitution, we find that this efficiency is about 11%.

Now that we know the efficiency, we can easily calculate the heating time

$$t = \frac{mc_{\text{H}_2\text{O}}\Delta T}{\eta P}.$$

Substituting in the previous expression gives a result of just over 3000 s, or about 50 min.

Mikuláš Matoušek
mikulas@fykos.org

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