

Problem II.S ... calculating with quanta 10 points; průměr 7,44; řešilo 61 studentů

1. Find a beta-carotene molecule and calculate what color should it have or rather what wavelength it absorbs. Use a simple model of an infinite potential well in which π electrons from double bonds are “trapped” (i.e., two electrons for each double bond). The absorption then corresponds to such a transition that an electron jumps from the highest occupied level to the first unoccupied level.

Compare the calculated value with the experimental one. Why doesn't the value obtained by our model come out the way we would expect? (5b)

2. Let's try to improve our model. When studying some substances, especially metals or semiconductors, we introduce the effective mass of the electron. Instead of describing the environment in which the electrons move in a complex way, we pretend that the electrons are lighter or heavier than in reality. What mass would they need to have to give us the correct experimental value? Give the result in multiples of the electron's mass. (2b)
3. If we produce microscopic spheres (nanoparticles) of cadmium selenide /CdSe) with a size of 2.34 nm, they will glow bright green when irradiated by UV light with a wavelength of 536 nm. When enlarged to a size of 2.52 nm, the wavelength of the emitted light shifts to the yellow region with a wavelength of 570 nm. What would the size of spheres need to be to make them emit orange with a wavelength of 590 nm? (3b)

Hint CdSe is a semiconductor, so it has a fully occupied electron band, then a (narrow!) forbidden band, and finally an empty conduction band. Thus, we must consider that the emitted photon corresponds to a jump from the conduction band (where such states are as in the infinite potential well) to the occupied band. Therefore, all the energies of the emitted photons will be shifted by an unknown constant value corresponding to the width of the forbidden band.

Finally, a bonus for those who would be disappointed if they didn't integrate – the 1s orbital of the hydrogen atom has a spherically symmetric wave function with radial progression $\psi(r) = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}}$, where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ is the Bohr radius. Since the orbitals as functions of three spatial variables would be hard to plot, we prefer to show the region where the electron is most likely to occur. What is the radius of the sphere centered on the nucleus in which the electron will occur with a probability of 95%? (+2b)

An early Mikuláš's package.

If we look at the formula for the energy of the levels in an infinite potential well, the only parameters that are not fundamental constants are the mass of the particle and the width of the well. Since we are working with electrons, we have the mass of the particle given, and now we need to determine the size of the well. Since in hydrocarbons, the bonds are not in a straight line, but zigzag, the question arises as to how we should calculate the distance and whether the electrons also run straight or zigzag. However, since we already have such a rough approximation, we do not have to worry too much about precision. (I thought of the “accuracy to millimeters” formulation, but that is not ideal in this context.) Therefore, as a first approximation, we will choose the average bond length in beta-carotene, i.e., 140 pm, and multiply it by the number of bonds. There are 21 of them, 11 double bonds and 10 single bonds in between. (Because of conjugation, we can not distribute them like this straight away, which is what we are calculating here!) It gives us a well's length of 2.94 nm. If we plug these values into the formula for the energy of the levels, we get $E_n = n^2 \cdot (6.97 \cdot 10^{-20} \text{ J})$. We have 11 double bonds, which correspond to 22 electrons. Therefore, in the ground state, the levels will be up to $n = 11$ occupied by 2 electrons. We get the lowest excited state when we excite

one electron from the $n = 11$ level to the $n = 12$ level. Then, the absorbed energy is $\Delta E = (12^2 - 11^2) \cdot (6.97 \cdot 10^{-21} \text{ J}) = 1.6 \cdot 10^{-19} \text{ J}$, which is the energy of a photon with a wavelength of approximately 1240 nm. This wavelength lies in the near-infrared region and is far from the actual wavelength of about 450 nm. (This is the value of the absorption maximum, but otherwise, beta-carotene absorbs from circa 500 nm (green) to the violet region over the entire interval. Therefore, only yellow and red light remain, which makes the beta-carotene appear orange.) Let us consider the variant that the electrons move “straight”. We can approximate it by using the fact that the angle between adjacent bonds is 120° . Thus, we will multiply the length of the carotene by $\sqrt{3}/2$, which is the ratio of the length of the two sides of the hexagon and the corresponding “chord”. It will result in the wavelength being $3/4$ of the original one, or about 930 nm, which is slightly more accurate but not in the visible spectrum yet.

Why is that? After all, our approximation is quite rough. For one thing, the electrons in beta-carotene are not entirely free. They are affected by the electrostatic potential of the nuclei despite being shielded by electrons in lower energy levels. For another thing, we completely ignore the electrostatic repulsion between the individual electrons, which has a similar, if not more significant, effect on the final result. The evidence for this is that the state corresponding to the absorption at 450 nm is the second excited state because the transition to the first excited state is so-called forbidden and hardly takes place. (We also call it the dark state.)

If we then look at the characteristics of the wave function of these states, we find out that the state corresponding to absorption does indeed look like one electron is excited to one level (atomic orbital) higher. However, at the same time, the dark state has a complicated electronic structure with a wave function, which is the sum of many different excited states. Thus, in reality, absorption by photons is linked to excitation to the second excited state. However, the excitation characteristics correspond to what we have calculated – to the lowest excitation in our potential well model. This shows that real molecules are often much more complicated than our models.

So if we want to improve our model, we have to utilize the mass of the electron. By looking at the equation for the energy of an infinite potential well, we can see that the transition energy is inversely proportional to the mass, thanks to which is the transition wavelength and the mass of the particle directly proportional to each other. Therefore, we can find a relationship for the effective mass m^* of an electron simply by using the rule of three according to

$$\frac{m^*}{m_e} = \frac{\lambda_{\text{Experiment}}}{\lambda_{\text{Calculation}}}.$$

By substitution, we can find the effective mass m^* we are looking for equals about $0.5m_e$. It may seem absurd that an electron lost over half its mass through interactions. However, in solids (metals and semiconductors), the effective mass of conduction electrons ranges from a fraction to several times the original mass.

From the previous calculation, we can see that calculating the exact values of the spectral lines from a simple model is a bit silly. We can use the fact that we got two values for different sizes from the problem statement for the quantum dots. Looking back on the formula for the energy levels, we see that the energy is inversely proportional to the length of the well squared. This scaling with respect to size will also apply to the 3D well, even though the solution looks slightly different. If we assume that the length of the well corresponds to the diameter of the

nanoparticle, we can write right away the dependence of the transition energy on the diameter d of the nanoparticle as

$$E = \frac{hc}{\lambda} = a + \frac{b}{d^2}, \quad (1)$$

where we introduced two unknown parameters a and b . The equation's form has a physics approach. The parameter a corresponds to the size of the forbidden energy gap given by the nanoparticle's material. In b , we hid all the parameters of our infinite potential well model (except the dependence on the nanoparticle size).

If we now plug the diameters and wavelengths of the two given nanoparticles into this equation, we obtain a system of two equations in the two unknown variables a and b

$$\begin{aligned} \frac{hc}{\lambda_1} &= a + \frac{b}{d_1^2}, \\ \frac{hc}{\lambda_2} &= a + \frac{b}{d_2^2}. \end{aligned}$$

By subtracting the equations from each other, we can express b as

$$b = \frac{\frac{hc}{\lambda_1} - \frac{hc}{\lambda_2}}{\frac{1}{d_1^2} - \frac{1}{d_2^2}}.$$

Then, we can plug this into the first equation to get a

$$a = \frac{hc}{\lambda_1} - \frac{\frac{hc}{\lambda_1} - \frac{hc}{\lambda_2}}{1 - \frac{d_1^2}{d_2^2}} = \frac{\frac{hc}{\lambda_2} - \frac{d_1^2}{d_2^2} \frac{hc}{\lambda_1}}{1 - \frac{d_1^2}{d_2^2}}.$$

Substituting the given values, we get parameters $a = 1.31 \text{ eV}$, $b = 5.48 \text{ eV} \cdot \text{nm}^{-1} \text{m}^{-2}$. If we now express the diameter of the sphere from its original equation (1)

$$d_3 = \sqrt{\frac{b}{\frac{hc}{\lambda_3} - a}},$$

by substitution we find the diameter $d_3 = 2.63 \text{ nm}$. It is also worth noting that the value a roughly corresponds to the size of the forbidden energy gap of CdSe, which equals 1.74 eV .

Bonus

Although the bonus solution is pretty much straightforward, it requires very advanced mathematics. We will integrate the probability density over the sphere's radius in spherical coordinates. Since we have spherical symmetry, we can integrate only over the radial coordinate if we

add a factor corresponding to the surface of a sphere with a given radius. The probability of an electron occurring in a sphere with radius R will be

$$\begin{aligned} P &= \int_0^R \rho(r) 4\pi r^2 dr = \int_0^R |\psi(r)|^2 4\pi r^2 dr = \\ &= \int_0^R \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr = \\ &= 1 - \left(\frac{2R^2}{a_0^2} + \frac{2R}{a_0} + 1 \right) e^{-2R/a_0}, \end{aligned}$$

where we used integration by parts twice to compute the integral. If we set this probability equal to 0.95, as requested, we will get the equation for the unknown value with radius $x = R/a_0$

$$1 - (2x^2 + 2x + 1)e^{-2x} = 0.95$$

We will solve this equation numerically and find that the radius we are looking for is approximately $3.15a_0$, or 167 pm. This is a slightly greater distance than the standard length of covalent bonds involving hydrogen atoms but smaller than the length of hydrogen bonds, which is reasonably expected (covalent bonds are based on overlapping orbitals, whereas hydrogen bonds are not).

Mikuláš Matoušek
mikulas@fykos.org

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