

**Problem VI.S . . . exciting quanta**

10 points; průměr 5,93; řešilo 29 studentů

The lowest-lying excited singlet state of beta-carotene has an energy 1.8 eV, which is higher than the ground state energy. However, the transition between this state and the ground state is prohibited, so the molecule does not absorb photons at this energy. On the other hand, the transition to the second lowest-lying singlet state with energy 2.4 eV is allowed and responsible for the bright orange color of the molecule. The lowest-lying triplet level is at 0.9 eV energy. Draw a Jablonski diagram and use it to explain why beta-carotene does not fluoresce even though it significantly absorbs visible light. (3 pts)

*Bonus:* Why is it so important for life on earth that oxygen is a triplet in the ground state? (+1 pts)

Try to calculate the approximate limit on the number of orbitals in the active space with the CASSCF method. Consider that you have as many electrons as orbitals in the active space (which corresponds to the fact that half of them in HF will be occupied) and that the most of today's supercomputers have at most 1 TB of RAM for computing, in which you need to fit a Hamiltonian. (3 pts)

For lithographic manufactured modern semiconductor chips, so-called excimer lasers are used to glow with the spectrum far into UV region. They are based on so-called excimers, which are molecules that are stable only in the excited state, while in the ground state, they decay. As a result, the molecule decays after the photon is emitted, ensuring that a larger fraction of the molecules are in the higher state than in the lower state. That is the necessary condition for the laser to work. Try using Psi4 for the helium dimer ( $\text{He}_2^*$ ) to calculate and plot the dissociation curves of the ground and lowest-lying excited states. ( $\text{He}_2^*$  is not yet used for lasers, but for example  $\text{Ar}_2^*$  or  $\text{Kr}_2^*$  are.) At what wavelength would the laser work? Compare it with the experimental wavelength 66 nm. (4 pts)

*Note:* In the problem statement on the website, you will find a prepared input file for one geometry. Do not be surprised that it has a total of three states set up. It needs to have those because we have two excited states close to each other. If we were to include only one of them in the calculations for some internuclear distances, this would lead to problems with convergence. Do not worry; the next gift from Mikuláš will not arrive before 5th December.

Jablonski diagram of beta-carotene looks quite similar to the general one shown in the serial. We only adjusted the vertical positions of electron shells to correspond with the ones in the problem statement.

Why is beta-carotene not fluorescent, though? Because the radiative transition to the lowest singlet level is prohibited, the transition from this level to the ground state must also be forbidden. (If this was not the case, we could reach a stage where the heated beta-carotene would be cooling itself by radiating heat to the surroundings while simultaneously not receiving any from the surroundings. Therefore, it could be transferring heat spontaneously to an object warmer than itself, thus, violating the second law of thermodynamics.) The molecule is excited to the  $S_2$  state and, as a result of vibrations, quickly relaxes to the  $S_1$ . The molecule has to stay in this state until the internal conversion occurs because a photon-emitting transition (fluorescence) is prohibited. Thus, it cannot emit a photon from either of the excited states. The transition from the  $S_1$  is prohibited, and the transition from the  $S_2$  state would not be quick enough as the vibrational relaxation occurs much faster. Theoretically, it could also transition to a triplet state, but this transition is conditioned by relativistic effects and hence will be weak for organic molecules since relativity is more prominent in the lower part of the periodic table.

The solution to the bonus is quite simple if we realize one thing. Just like the transitions between different spin states of a single molecule are forbidden, reactions where spin changes will be slower. As was discussed in part four of this series, most organic molecules and common products of oxidation reactions are singlets in the ground state, so triplet oxygen “has no one” to give its spin. We can also think of it as oxygen “forcing” a triplet transition structure with a higher energy when reacting with organic molecules. That increases the activation energy of the whole reaction. In any case, if oxygen in its ground state was a singlet, it would be so reactive that life, as we know it in an oxygen atmosphere, would not be possible because all organic molecules would burn up rather quickly.

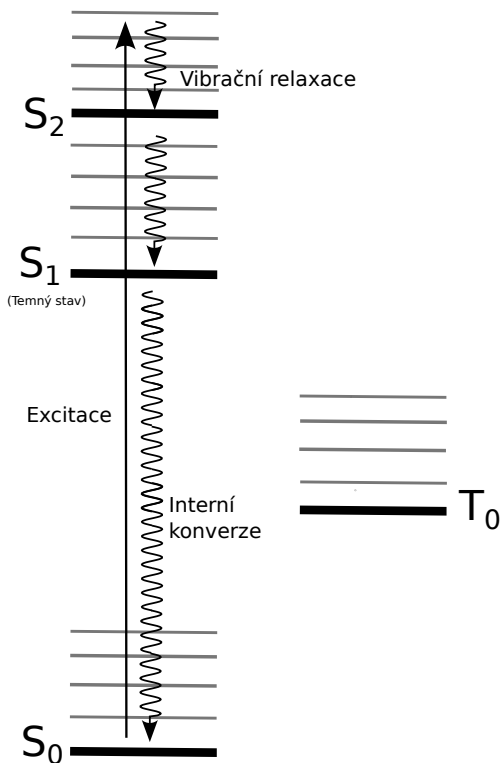


Fig. 1: Jablonski diagram of beta-carotene.

There is still a possibility that oxygen molecules in living organisms excite into a singlet state, which then damages the cell. Therefore, it is problematic to go out in the sun while taking certain drugs (antibiotics) or St. John’s wort, as these substances facilitate the excitation of oxygen into a singlet state. Plants, which have a greater tendency to form singlet oxygen due to photosynthesis, have beta-carotene and other similar molecules in their leaves, which are able to deexcite this oxygen before it can cause any harm.

In the third problem, we should not be fooled by the question about the limiting number of orbitals. The limiting factor for us is primarily the number of configurations, i.e., the possibilities

of how to fit electrons into a given number of orbitals. For instance, for two orbitals and two electrons in an active space, we have six ways to arrange the electrons - four of which are shown in the text of the series. The other two have either of the orbitals occupied twice. In practice, we would limit it to the configurations with the correct spin value. In this case, we would have three singlet configurations and three spin projections for one triplet configuration. For our estimation, however, we will not be concerned with this. Instead, we will take the total number of ways of arranging  $N$  electrons into  $N$  orbitals. The number of all those configurations is  $\binom{2N}{N}$  because we have  $2N$  boxes,  $N$  for an electron with spin up and  $N$  for an electron with spin down.

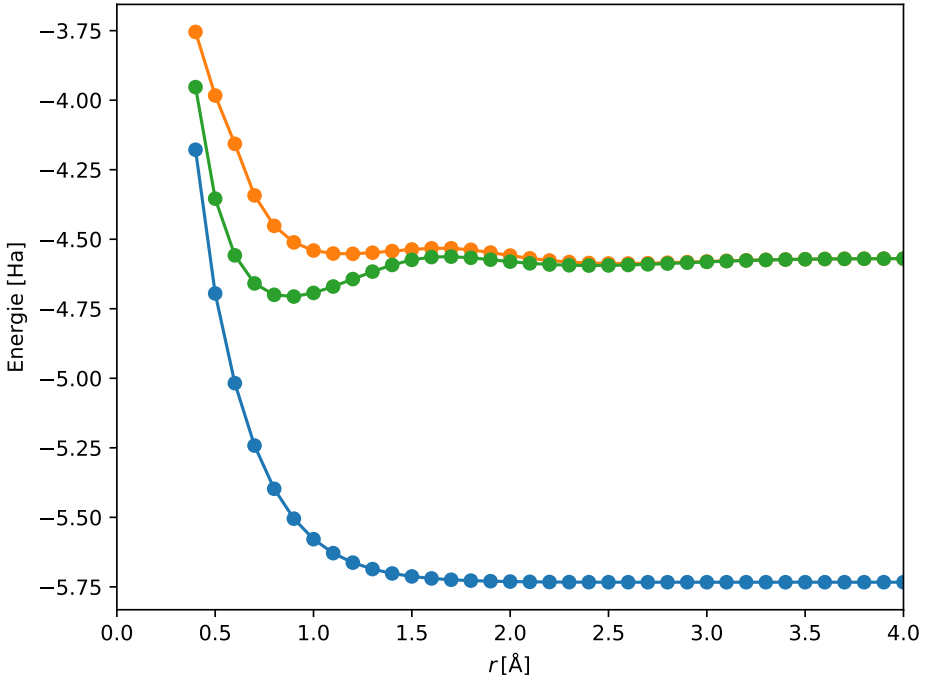


Fig. 2: Potential curves of the ground and two excited states of the helium dimer.

We can reduce this number by considering only configurations with the same number of electrons with different spins. The number of those configurations is lower and can be found by independently placing  $N/2$  electrons with spin up and spin down in a set of  $N$  orbitals. That corresponds to  $\binom{N}{N/2}^2$  configurations. Therefore, we can see that the number of configurations is growing with the number of orbitals rather quickly, so we can expect that the limiting number of orbitals will not be that high.

In any case, if we use Stirling's approximation of the factorial for both estimates, we get an upper estimate, according to which the number of configurations grows as  $2^{2N}$ , which would

correspond to a state where the configuration is not even bound to have the right number of electrons. (Each of the  $2N$  boxes can be either occupied or empty.)

The Hamiltonian matrix will contain  $X^2$  values, where  $X$  is the number of configurations. Because of the representation of decimals in the computer, each value will take up 8 bytes of space. If we have a RAM size of 1 TB, then after dividing by 8 B and taking a square root, we get a limit of about 370 000 configurations.

If we start from the formula  $2^{2N}$ , we will get  $\log_2(370000) \doteq 18.5$ , which gives us a limit on the order of something over 9 orbitals. If we take the formula  $\binom{N}{N/2}^2$ , then for  $N = 10$ , we get a lower number, less than 64 000 configurations, and for  $N = 12$ , we have 850 000 of them. Hence, with this estimate, we have a limit between 11 and 12 orbitals.

Let us add that in practice, when strongly optimizing by selecting only those configurations with the correct spin state and while taking advantage of the fact that a great part of the values in the matrix of the Hamiltonian is zeroes, then this bound can be pushed to just over 16 orbitals. For larger active spaces, we must use a method that selects only the most significant configurations for the problem description.

We can easily solve the last task using the prepared input, in which we only modify the inter-nuclear distance. When we plot the graph of the energies of all three states, we get the following figure:

In the figure, we can clearly see that the lowest (ground) state is not subject to a minimum single function constraint, while the first excited state has a minimum in which the excited molecule remains before de-excitation to the ground state and emission of the ultraviolet photon. To find the energy of this photon, we need to look at the graph to determine where is the minimum of the excited state. Although it would be ideal to search for the optimal geometry of the excited state, we will settle for choosing the structure with the lowest energy out of those plotted with the dissociation curves. A simple glance at the graph will tell us that the structure with an internuclear distance of  $0.9 \text{ \AA}$  has the lowest energy. If we go through the output of the calculation with this internuclear distance, we will get the following lines:

```
==> Energetics <==

SCF energy = -5.495165873340969
Total MCSCF energy = -4.907437749031700

==> MCSCF root 0 information <==

MCSCF Root 0 energy = -5.504811925243551

Active Space Natural occupation numbers:

A 1.996503 A 1.994097 A 0.005637
A 0.003764
```

We might be confused by the **Total MCSCF energy** line on the output. That is the “averaged” energy across all states, which is useless for our purpose. We have to look at the energy of the individual states, which are listed below on the output.

We will get the ground state energy from the line

```
MCSCF Root 0 energy = -5.504811925243551.
```

A little bit lower, we can find the energy of the excited state

$$\text{MCSCF Root 1 energy} = -4.706122682516050.$$

We will get the energy of transition from the difference between these two energies, i.e., approximately 0.8 Ha or 21.7 eV. That corresponds to radiation with a wavelength of 57 nm, which falls into extreme ultraviolet light. It is actually bordering with the X-ray region. When comparing it to the experimental value of 66 nm, we find out that our result is close.

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