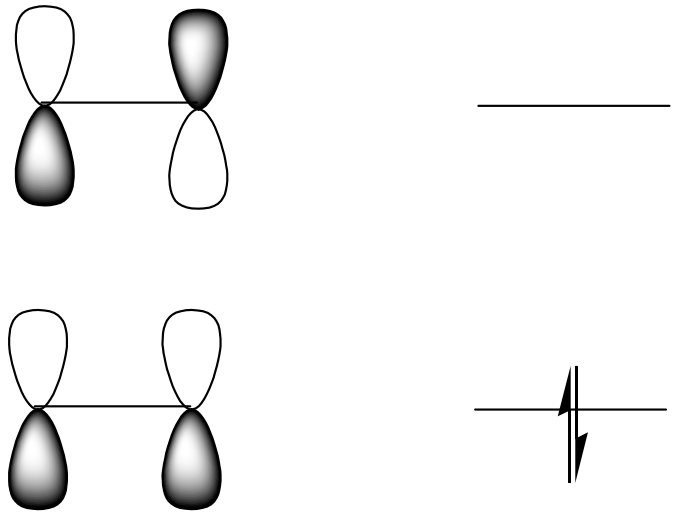
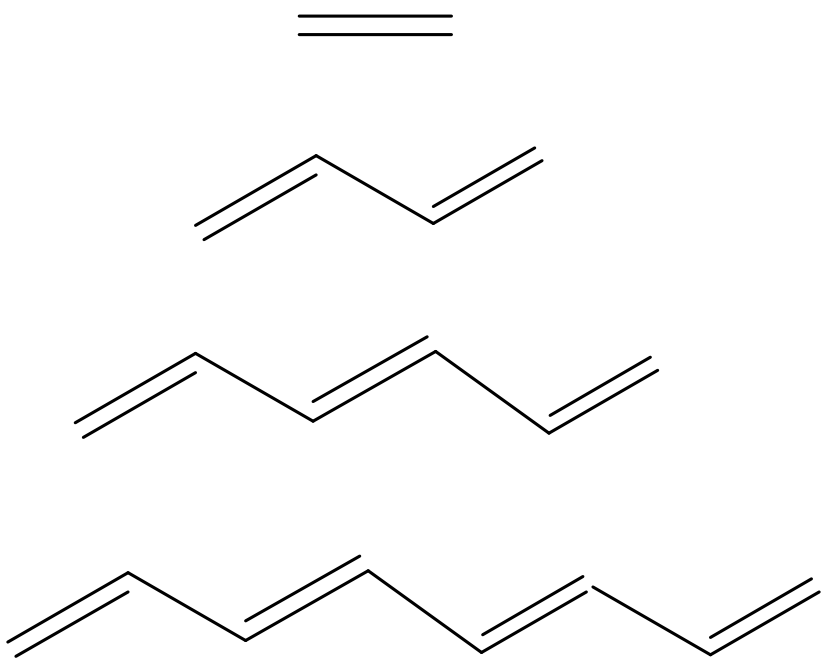
Free electron model for electronic spectra

Before the advent of computers, models such as particle-in-a-box were used for linear polyenes. The idea of such a model is that the electrons from the p-orbitals in a molecule are particles and the molecule is the “box”. For example, we can think of ethylene as a short box with two electrons as shown in the figure. The HOMO and LUMO are shown on the left and the representation of the two lowest electronic states is shown.



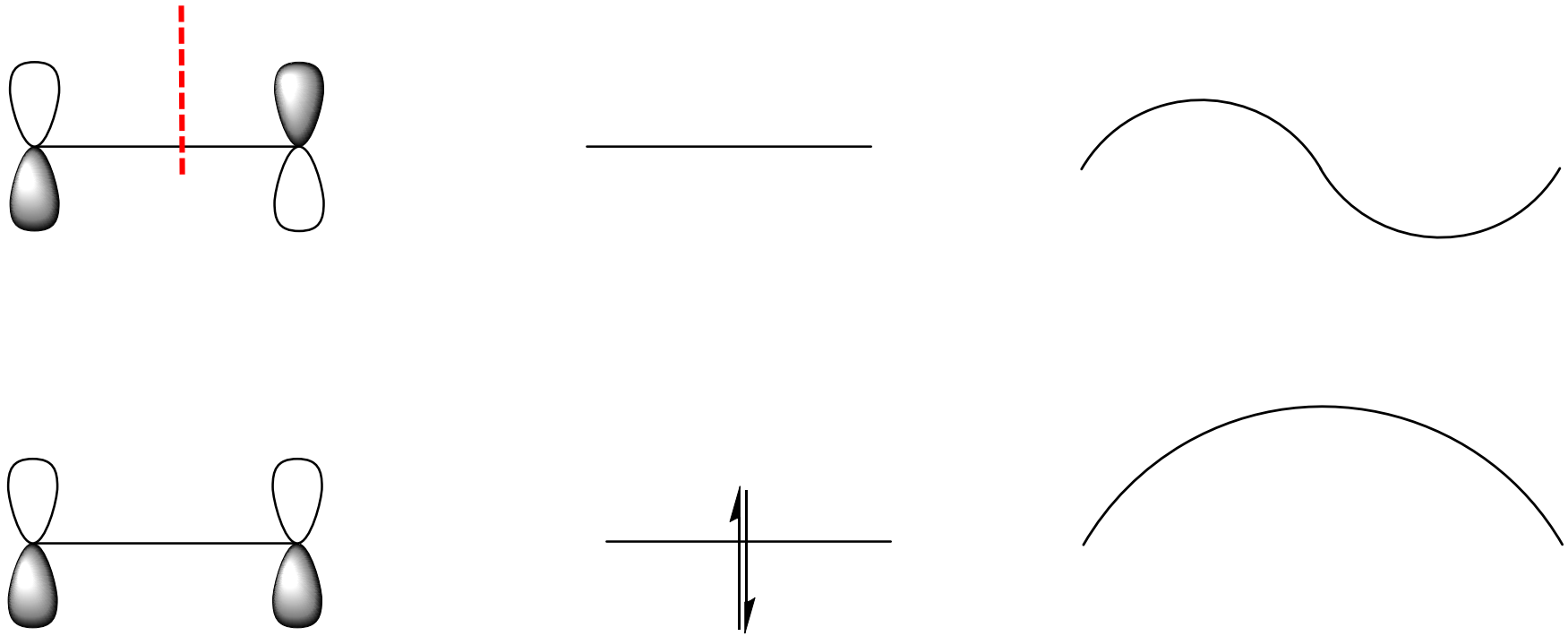
Polyenes



The first four members of the class of polyenes are shown. We can treat the p-system of these molecules using the model with 2, 4, 6 and 8 electrons, respectively. As a general rule the model can be applied to any number of p-orbitals, with the assumption each p-orbital will contribute one electron to the total. Then we populate the levels calculated using the particle-in-a-box and determine the transition between the HOMO and LUMO.

Ethene

In this model the solutions give appropriate energies, but the shape of the wave functions in the particle in a box provide an outline for the wave functions formed by the LCAO-MO approach for polyenes as well.



Butadiene

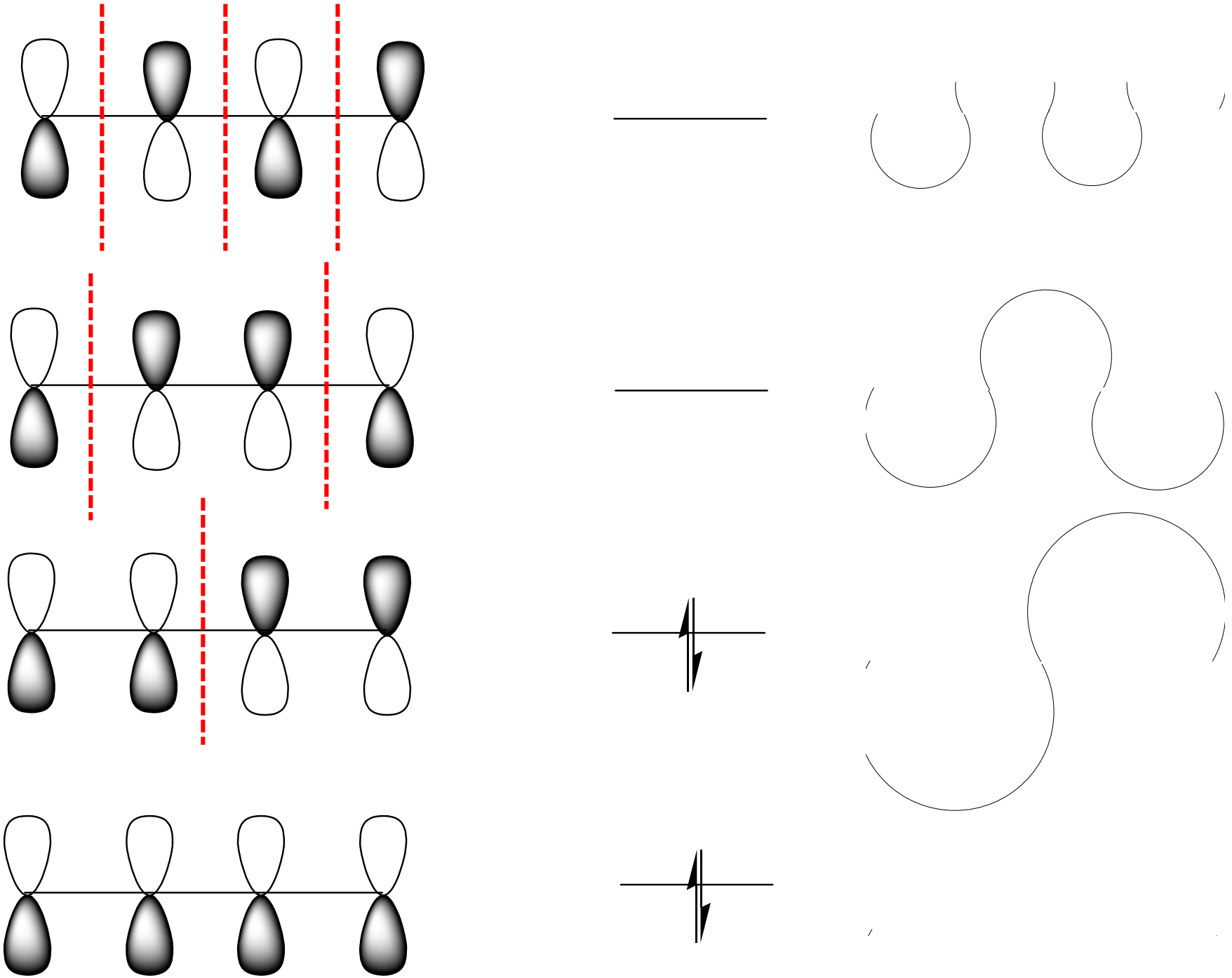
There are four electrons and two occupied π-orbitals.

The transition is from

$\phi_1 + \phi_2 - \phi_3 - \phi_4$

to

$\phi_1 - \phi_2 - \phi_3 + \phi_4$



Hexatriene

There are six electrons and three occupied π-orbitals.