WebMO – UV-Vis Spectra using TDDFT (Practical Exercise 4)

We will use WebMO for the following exercises
https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi
For this set of exercises, we will use the QChem program rather than GAMESS or Gaussian.

1. Optimize the geometry of formaldehyde (H_2CO, which has a planar ground state) using B3LYP and the 6-31G(d) basis set.
    a. Examine the MOs. Out of orbitals 1-10, which orbitals are the σ orbitals? π orbitals? Nonbonding orbitals? $\sigma*$ orbitals? $\pi*$ orbitals?
    b. Next, use this geometry to perform an excited state calculation. To do this, we will use the "New Job Using This Geometry" button under the geometry. Hit the right arrow. Then, select QChem again. Choose the type of calculation to be "Excited States and UV-Vis" (the other parameters should stay the same as your geometry optimization; you will need to change the excited state method from CIS to B3LYP in order to run a TDDFT calculation with the B3LYP functional).
    c. In the job output, look at the "Excited States" section. This section initially provides the wavelengths of the transitions. To view these in terms of energy (eV), select the Excitation Units to be eV, and then hit the button next to the selection. What is the energy of the first singlet excited state (also called S_1)? Will it have any intensity? What is the energy of the first excited state with intensity above 0.1? In addition, plot the UV-Vis spectrum by clicking on the magnifying glass on the appropriate row. (Note: You can also do this in terms of wavelength, but if so, you want to choose the Peak Width to be 10.)
2. Next, we will consider the simplest conjugated hydrocarbon, 1,3-butadiene (C_4H_6). For this exercise, we will also use B3LYP and the 6-31G(d) basis set.
    a. Optimize the geometry. (Depending on the initial geometry, you may find that you need to use the restart button to restart your job runs. This is a little round yellow button that appears next to failed jobs. It is possible that you may need to restart the calculation several times until it completes the optimization.)
    b. Calculate the excited states of this molecule. (Follow the procedure in question 1.) What is the S_1 energy for this molecule? What is the energy for the first state with a non-zero intensity?