

COMPUTATIONAL CHEMISTRY LAB MANUAL

USING SPARTAN TO INVESTIGATE THE MOLECULAR
PROPERTIES OF ATMOSPHERICALLY RELEVANT
GREENHOUSE GASES

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1 Introduction

The present document will guide you through the set up and actual computation process. Computations will be carried out using the SPARTAN suite of codes in its Microsoft Windows release Spartan ES 1.0.2.

Please note that throughout the present document the word “click” refers to the use of the mouse. Left or right click will mean that you are supposed to press down the left or right button on your mouse, respectively. Additionally, technical terminology that strictly refers to the graphical interface you are using will be reported within quotation marks or in a different font.

The first portion of this document is dedicated to guiding you through the process of building the molecule you have been asked to simulate. The model molecule that will be used in this example is CO₂. Carbon dioxide is a linear molecule with a central carbon atom and two oxygen atoms each double bonded to C.

Two sections on the actual computation will follow. The first of these details optimizing the geometry of and calculating vibrational frequencies. A further section guides calculating the distribution of charges and visualizing the electron density. Finally, the last two sections will guide you to connect the results you have obtained with the IR activity of your molecule. A technical appendix closes the document.

We will practice the entire procedure together on CO₂, and then you will repeat the whole process individually for H₂O, N₂O, and O₃.

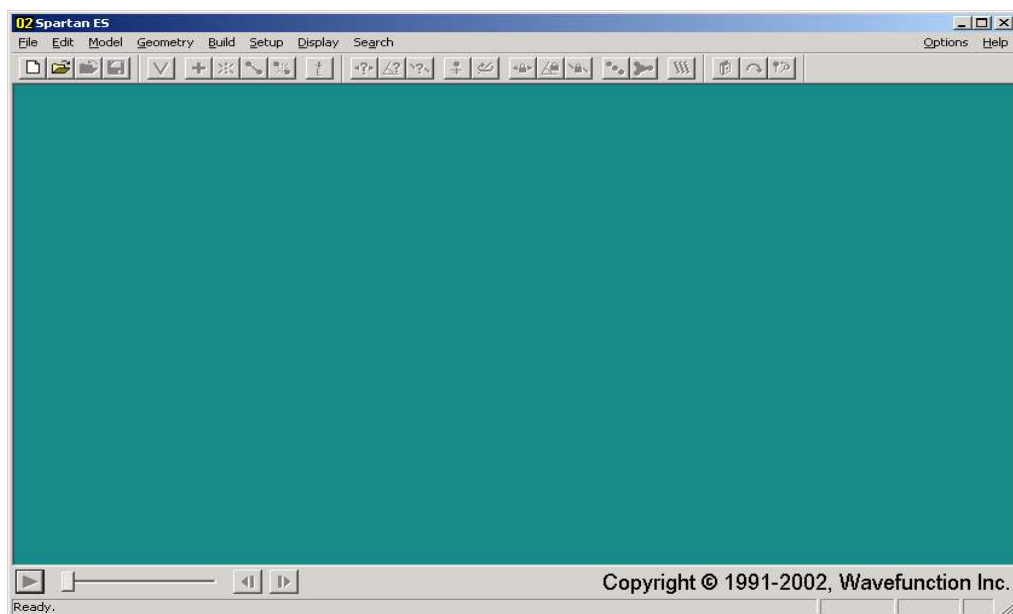
Here are the steps you will have to follow to build your molecule (exemplified with CO₂).

2 Building the molecule

1. log on the machine using the username and password that you will be given
2. left double click on the icon **Apps** on your desktop, a window corresponding to the App(lication)s folder will appear
3. left double click on the **02SpartanES** icon

2 BUILDING THE MOLECULE

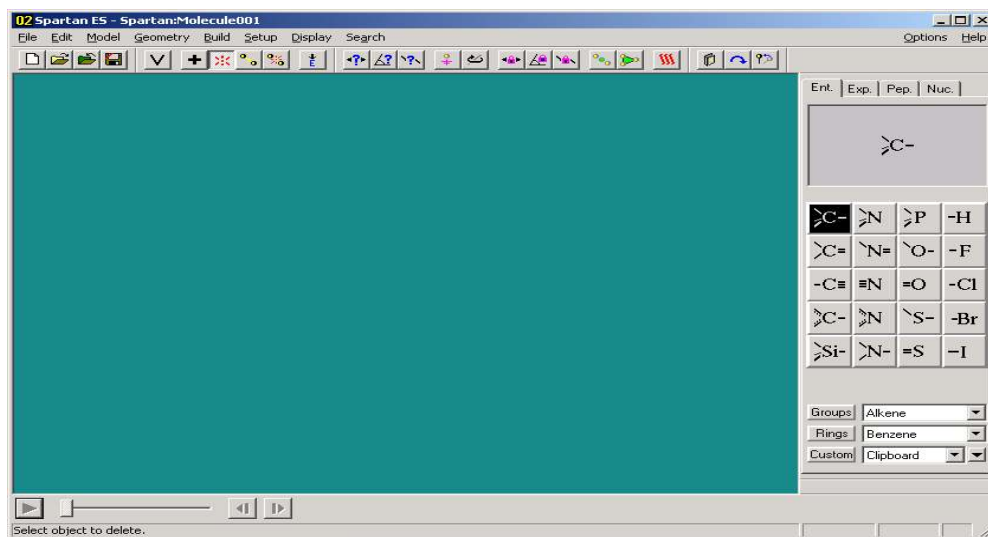
4. the following window will appear:



5. to build your molecule click with the left mouse button on File from the menu bar,

- click on New from the menu which will appear,

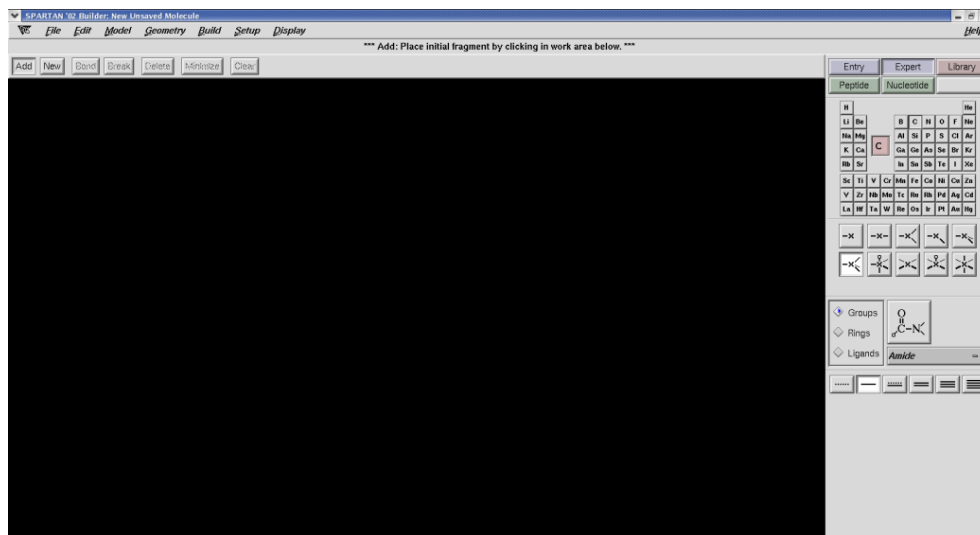
6. the “entry builder screen” depicted below will appear:



2 BUILDING THE MOLECULE

7. The “entry builder screen” is divided into two portions (beneath the File, Edit, Model, etc. menu bar):

- (a) the “work area” (solid color portion on the left of the window);
 - at the top of the “work area” is the toolbar. You can point your mouse (without clicking) on its different icons to visualize their functions as a small “post-it”-like yellow note appears close to where you are pointing the cursor.
- (b) the “model kit” (on the right).
 - at the top of the “model kit” are the Ent. (Entry), Exp. (Expert), etc. bookmarks. By default the Ent. bookmark is selected. The Ent. portion of the “model kit” contains a certain number of atomic fragments and, in some cases, their possible states of hybridizations.
 - Left click on the Exp. bookmark, the “model kit” will change similarly to what shown in the figure below:



8. to build the CO_2 molecule left click on the C atom on the periodic table displayed in the “model kit” (with the Exp. bookmark selected).

9. Left click on the appropriate button below the periodic table displayed in the “model kit” representing the kind of valence configuration you desire to have for your atom (in the present case left click on the --- button).

10. Left click on the “work area” (solid color portion on the left of the window) to place the selected atom.
11. Left click on the “model kit” to select the next atomic fragment to add to the unfilled valences of your original atomic choice.
 - NOTE: Any unfilled valences will automatically be converted to hydrogen atoms upon exiting.

In the present case the next atom is oxygen and the valence configuration is given by the `--` button.

12. On the “work space” left click (one at a time) on the empty valences of the atomic fragment displayed (C) to add the newly selected fragments (O).
13. Left click on the **Minimize** icon on the toolbar on top of the “work area” (or on **Minimize** in the **Build** pull down menu).
14. You have built your molecule!!! Now left click on **File** from the upper menu bar and select **Save As**; choose **SaveHere** as the destination directory.
15. a window will appear with the cursor blinking in the appropriate location: enter the name with which you desire to call your molecule (CO2, for example). And left click on **Save As** button.

Remember to add your name to the title of your job (i.e., CO2_myname)
--

2.1 About changing representation & rotating/translating the molecule

Now that we have built the structure let's familiarize with the different, possible representations of the molecule on your screen:

1. Left click on the **Model** button on the menu bar and select from the pull down menu, which will appear, the graphical representation of the molecule you prefer, for example: **Wire**, **Ball and Wire**, etc. (you can try several to see how do they differ from one another).

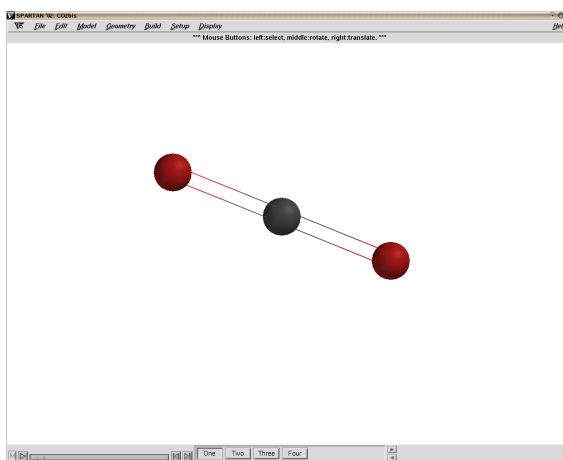
3 GEOMETRY OPTIMIZATION & VIBRATIONAL ANALYSIS

2. The model (shown below) of the molecule can be manipulated: rotated, translated and zoomed.

rotate: drag the mouse while clicking on the left mouse button;

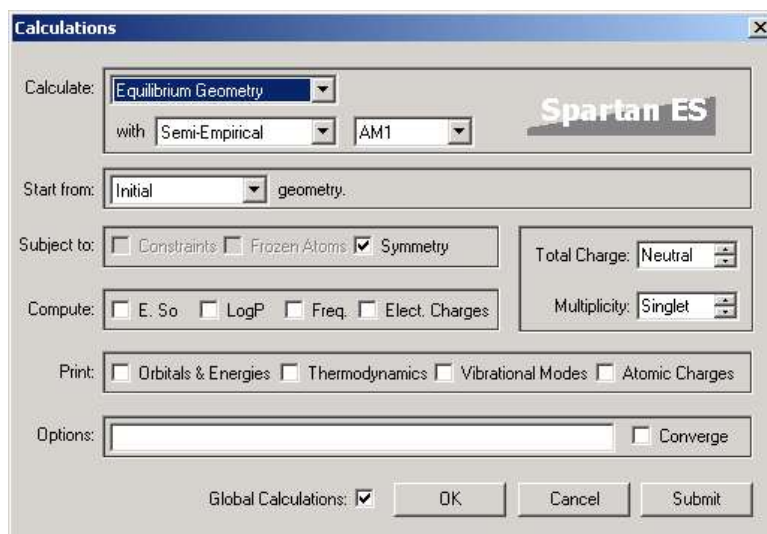
translate: drag the mouse while pressing its right button;

zoom: drag the mouse while pressing its right button and holding down the Shift key on the keyboard.



3 Geometry Optimization & Vibrational analysis

1. To start the actual computation (i.e., the minimization of the conformer you have recently generated) left click on the **Setup** button of the menu bar. And select (left click) **Calculations** from the pull down menu that has appeared under the **Setup** button.
2. A pop up window will appear as in the figure below:



The different fields on the Calculations window are explained below:

- **Calculate:** should be set to **Equilibrium Geometry** meaning that the geometry you have just sketched out is optimized along the energy hypersurface of the molecule until a minimum of such surface is found.

suggestion for discussion: would such a minimum necessarily represent the equilibrium structure?

- **with:** You can choose from the following models: **Molecular Mechanics**, **Semi-Empirical**, **Hartree-Fock**

Each combination of model keywords (such as **Semi-empirical** and either **AM1** or **PM3**, or **Hartree-Fock** and **3-21G(*)**) refers to a particular model chemistry intended to use for the computation.

We will be using the **Hartree-Fock** model.

- **Basis Set:** If you have selected under the **Model** section the **Hartree-Fock** theory you will be able to choose from the following basis sets¹: **STO-3G**, **3-21G(*)**, **6-31G***, **6-31G****, **6-31+G***, **6-311G***, **6-311+G****.

Note: In the **Basis set** pull down menu the basis are generally ordered from smaller to larger. In choosing a basis set the following consideration should be kept in mind. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the location

of the electrons in space. At the same time larger basis sets drastically augment the computation efforts: the larger the basis the better the accuracy, the smaller the basis set the faster the computation. Therefore a practical choice between accuracy and computational feasibility has to be made (this is especially true for molecular systems larger than CO₂). For a very brief explanation of the basis sets nomenclature, see Appendix A.

Choose the 6-31G* basis set for all of your calculations.

- **Start From:** ... **geometry** Make sure that **Initial** is selected.
- **Compute:** Check the **Frequencies** and **Electrostatic Charges** boxes.
- **Total Charge:** Here you have to enter the total charge of the system. Make sure that **Neutral** is selected.
- **Multiplicity:** In short, the multiplicity is the number of unpaired spins + 1. Make sure that **Singlet** is selected if your molecule is a closed shell one.
- **Print:** Select all.
- Remember to check the **Converge** box.

3. Left click on **Submit** button to start the computation.

3.1 Determining the geometrical parameters (bond lengths & bond angles)

You may have noticed that in performing the optimization the bond lengths (and angles where applicable) have changed. To visualize the geometrical information regarding the molecule you have just optimized, use the options in the **Geometry** pull down menu: To visualize the geometrical info regarding the molecule you have just optimized select from the pull down menu of the **Geometry** button of the menu bar the following:

Measure Distance then left click on the first atom of the couple of which you want to know the relative distance (the selected atom will change color), hence left click on the second atom (this too will change color), a number, corresponding to the distance in Angstrom, will appear on the bottom right of the “work area” (alternatively, if the two atoms are bonded try left clicking on the bond).

Measure Angle works similarly: to measure an angle you will click on three atoms.

Annotate the computed values for all bond lengths and angles in the appropriate locations in the chart on your worksheet.

3.1.1 Comparing computed bond distances and angles with experimental values

1. As it was shown above collect the bond distances (and angles).
2. Now open your web browser and go to <http://www.hbcponline.com/> which is the on-line version of the *CRC Handbook of Chemistry and Physics* on the left column of the webpage is the Table of Contents. Click on **Section 9: Molecular Structure and Spectroscopy**, and then “Structure of Free Molecules in the Gas Phase”. Find the experimentally measured bond lengths and angles of the molecules you are working with (note: CO₂ is listed under “carbon dioxide” in part 2 of the table of experimental data), and enter them in the appropriate locations on your worksheet.
3. How do your computed results compare with the experimental values?

3.2 Retrieving the computed vibrational frequencies

On the Spartan main window click on **Display** on the menu bar and choose **Vibrations**. A window will pop up with the list of frequencies. Record the frequencies in the appropriate table in your worksheet.

3.2.1 Comparing the frequencies calculated at the different level of theory with experimental data

1. Open a web browser and go to <http://webbook.nist.gov/chemistry/form-ser.html>
2. Enter the formula of your molecule and select “Vibrational & electronic energy levels” from **Other Data**.

Annotate the experimental values of the frequencies for the most abundant isotopomer (e.g., ¹²C¹⁶O₂) in the appropriate locations in the chart on your worksheet.

4 Charge distribution

To visualize the charge distribution from the **Model** button on the menu bar select **Configure** from the pull down menu and check the **Electrostatic charge** box. The partial charges will appear close to the atoms on your display.

A useful way to depict the charge distribution of your molecule is via electrostatic potential surfaces.

4.1 Computing surface representations of electronic properties

The different types of surfaces include HOMO, LUMO, Electron Density, and Potential. For an explanation of the different kinds of surfaces, please refer to Appendix B.

You will calculate an electrostatic potential surface.

1. Left click on **Setup** button of the menu bar and select **Surfaces**. A window will appear. Click on the **Add** button.
2. To compute the electron density: set the **Surface:** field to **Density**, then set the **Property:** field to **Potential**, you can leave the **Resolution** at medium. Left click on **OK**.
3. Left click on **Setup** button of the menu bar and select **Submit**. A window will appear informing you that the computation has been submitted. Left click on **OK**.
4. A window will appear when the computation is completed (left click on its **OK** button).

4.2 Retrieving the results of the surface calculation

1. Left click on the **Display** button on the menu bar.
2. From the pull down menu that will appear select **Surfaces**.

3. A window will appear: check on the box on the left of the surface you have computed and the electronic density will appear on the main window. You can manipulate the molecule (rotate, translate, zoom).
4. To visualize the molecule (and the labels indicating the partial charges) under the electron density surface you can change the surface texture property from solid to mesh or transparent by clicking on the solid surface displayed and selecting **Properties** from the menu **Display**, and choosing the desired **Style**.

Remove the surface deselecting the box on the window **Surfaces**.

5 Sketching the dipoles

Using the partial molecular charges computed as explained above (*i.e.*, from the **Model** button on the menu bar select **Configure** from the pull down menu and check the Electrostatic charge box), draw a diagram of the molecule along with the bond dipoles you predict from the charges.

Compare your sketched dipole with the dipole computed from Spartan, which can be visualized as follows:

- select **Display** menu and select **Properties**.
- the **Molecule Properties** window will appear.
- check the **Dipole** box.
- the dipole vector will appear.

Note: to better see the vector representing the dipole of the molecule, it is advisable to switch to the **Ball and Wire** molecular representation, this can be done by choosing the **Model** menu and selecting **Ball and Wire**.

6 Which normal modes are IR active?

1. Now you will animate the vibrational modes whose frequencies you recorded previously on your worksheet. Click on **Display** on the menu bar and choose

7 DO THE FREQUENCIES OF THE IR ACTIVE MODES OVERLAP WITH EARTH'S BLACKBODY SPECTRUM?

Vibrations, a window will pop up with the list of frequencies, check, one at a time, the boxes on the left of the frequency value. The picture of the molecule on your screen will undergo the vibration corresponding to the frequency you have checked.

2. Identify which of the normal modes change the electrical dipole of the molecule (i.e., are IR active).

7 Do the frequencies of the IR active modes overlap with Earth's blackbody spectrum?

In order for a molecule to be a potent greenhouse gas, it must have IR active vibrational modes, and those modes should have frequencies that overlap with Earth's blackbody radiation spectrum (reproduced from Baird and Cann's *Environmental Chemistry* textbook in Appendix C; note that the spectrum is plotted as a function of wavelength in μm). In this last part of the exercise, you will determine which modes in each of the molecules considered meet these criteria:

- For each IR active mode in each molecule, convert the *experimentally measured* frequencies you looked up in the NIST database from cm^{-1} to μm . To do this, take the reciprocal of the frequency in cm^{-1} to get the wavelength in cm, and then multiply by 10^4 (the number of μm per cm). Record the values on your worksheet.
- Indicate on your worksheet whether or not the wavelengths corresponding to the vibrational frequencies of the IR active modes overlap with Earth's theoretical blackbody spectrum (Appendix C). You may consider any modes occurring at wavelengths less than $7 \mu\text{m}$ as not overlapping significantly with Earth's blackbody spectrum.

<p>Now repeat this whole procedure for H_2O, N_2O, and O_3.</p>
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8 Appendix A – Basis Sets

Typically, the quantum calculations for molecules are performed as LCAO MO, i.e. Linear Combination of Atomic Orbitals - Molecular Orbitals. This means that molecular orbitals are formed as a linear combination of atomic orbitals (AO). Early, the Slater Type Orbitals (STOs) were used as basis functions due to their similarity to atomic orbitals of the hydrogen atom. Gaussian-type orbitals (GTO) can be used to describe the radial part of the wave function in order to simplify the computational task. When a linear combination of N GTOs is used to approximate the actual shape of the STO the resulting basis set is known as STO-NG (as STO-3G described above).

The number of basis function used to describe a single STO (also known as zeta) has been a measure for the goodness of the set. So that single zeta means one basis function per STO, double zeta means two basis function per STO, etc. Because valence electrons tend to be more involved in bond making a different number of basis functions are assigned to core and valence orbitals in split valence basis sets, with typically more basis functions per valence orbitals.

The basis sets from 3-21G(*) to 6-311G** are Pople's basis sets. Symbols like n-ijG or n-ijkG can be encoded as: n - number of GTOs for the inner shells; ij or ijk - number of GTOs for basis functions in the valence shell. The ij notations describes sets of valence double zeta quality and ijk sets of valence triple zeta quality. The + symbol indicates that diffuse gaussian functions (i.e., GTO that decay slowly with distance from the nucleus) have been used for the heavy atoms; whereas the * or ** symbols indicate that polarization functions (i.e., functions having higher values of L , the angular momentum, than those present in occupied atomic orbitals for the corresponding atom) have been added respectively to the heavy atoms and to the hydrogens and the heavy atoms.

Finally the cc-pVTZ basis set consist in a correlation-consistent (cc) polarized (p) valence triple zeta basis set of Dunning (where V denotes split valence kind of basis set and TZ stands for triple zeta, so that VTZ means that one basis function is used for the inner orbitals and three for the valence orbitals).

9 Appendix B – Molecular Property Surfaces

(Electron) Density is a map of the surface that displays the molecule's size and shape by displaying the surrounding electron cloud. The electron cloud is determined by selecting a probability that an electron would be found within a given volume (often 90% probability is used) and drawing a surface there. This surface then describes the volume with a 90% probability of finding the molecule's electrons within that space.

The electron density at isosurface values provides indication of overall molecular size.

HOMO is an abbreviation for highest occupied molecular orbital; the HOMO is the molecular orbital of highest energy that is occupied by an electron. This surface will show the spatial area where it is most likely to find the electrons in that orbital.

LUMO is short for lowest unoccupied molecular orbital; the LUMO is the molecular orbital of lowest energy that does not contain an electron. This surface will show the spatial area where it would be most likely to find an electron in that orbital if one were there.

- Selection of two of the entries, “HOMO-” and “LUMO+”, results in display of box alongside of the entry. This contains a number providing a decrement value from the HOMO and increment value from the LUMO, and so allows specification of any molecular orbital. This value may be changed.

Potential (Map) refers to an electrostatic potential map. The potential is developed by determining the electrostatic force on a positive point-charge at all points at a given distance surrounding the molecule. Points where the point-charge would experience an attraction (negative charge) are displayed in red, and areas where the point-charge would be repelled by a positive charge are displayed in blue.

10 Appendix C – Earth's Blackbody Spectra

