Appendix 1

The electronic structure of ferrocene by semiempirical PM3 calculations with Spartan 2.0.[1]

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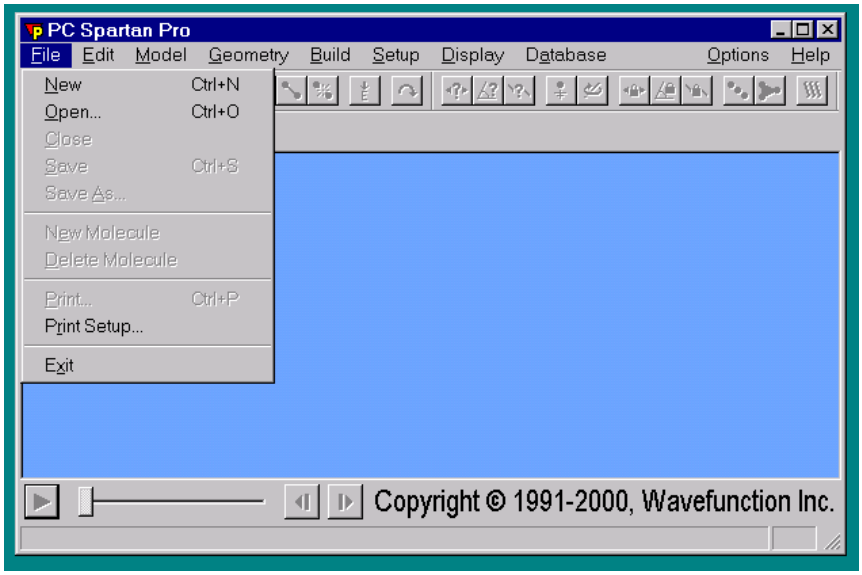
To start **Spartan 2.0** installed on the Dell Dimension 8400, *click* on the **WF2.0** button. The electronic structure computation comprises two steps:

- building the ferrocene molecule
- the PM3 semiempirical computation

A. Build the ferrocene:

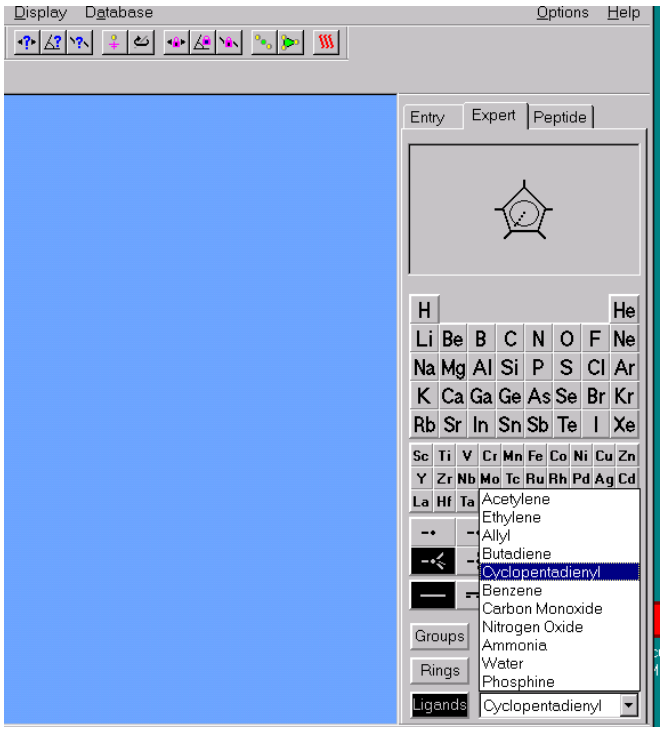
1. Click on the **File** and then on New button.



Screenshot courtesy of Wavefunction, Inc. Used with permission.

[1] **Spartan 2.0** is a product of Wavefunction, Inc., 18401 Von Kartman Ave, Suite 370, Irvine, CA 92612.

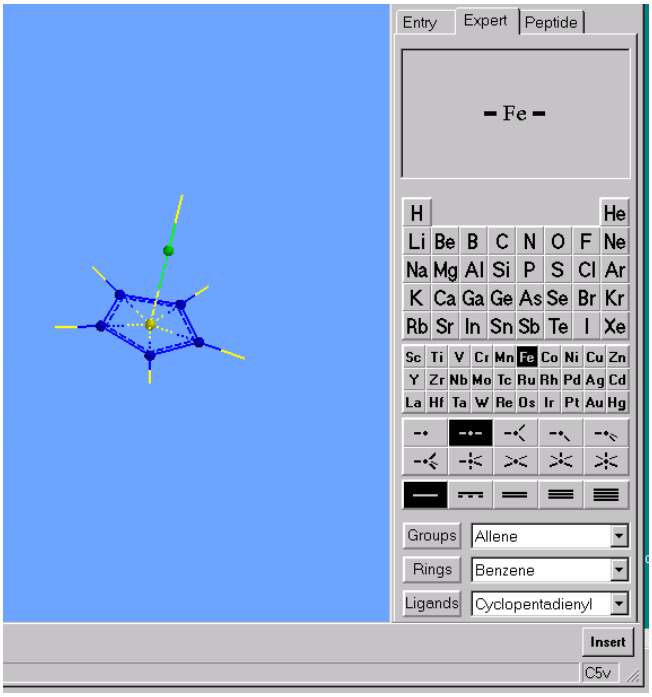
2. The **Builder** window pops-up. Click on the **Exp.** mode tab. Click on the on **Ligands** and choose **Cyclopentadienyl**.



Screenshot courtesy of Wavefunction, Inc. Used with permission.

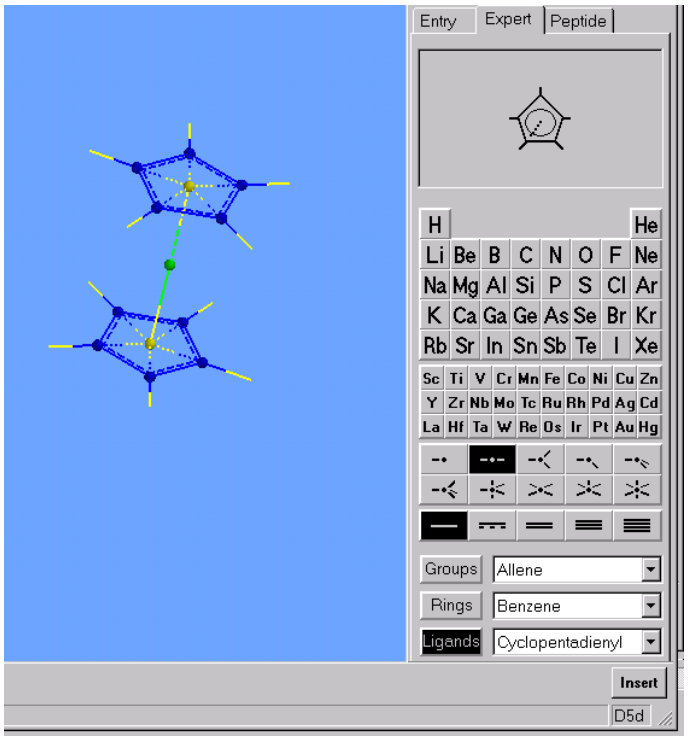
3. Click anywhere in the Spartan window. The **Cyclopentadienyl** ligand is displayed. Rotate the fragment by keeping depressed the left button and moving the mouse.

4. Click on **Fe** from the Periodic Table that is displayed and then on the -.- sign. Click on **Cyclopentadienyl** free valence stick that originates from the center of the ring.



Screenshot courtesy of Wavefunction, Inc. Used with permission.

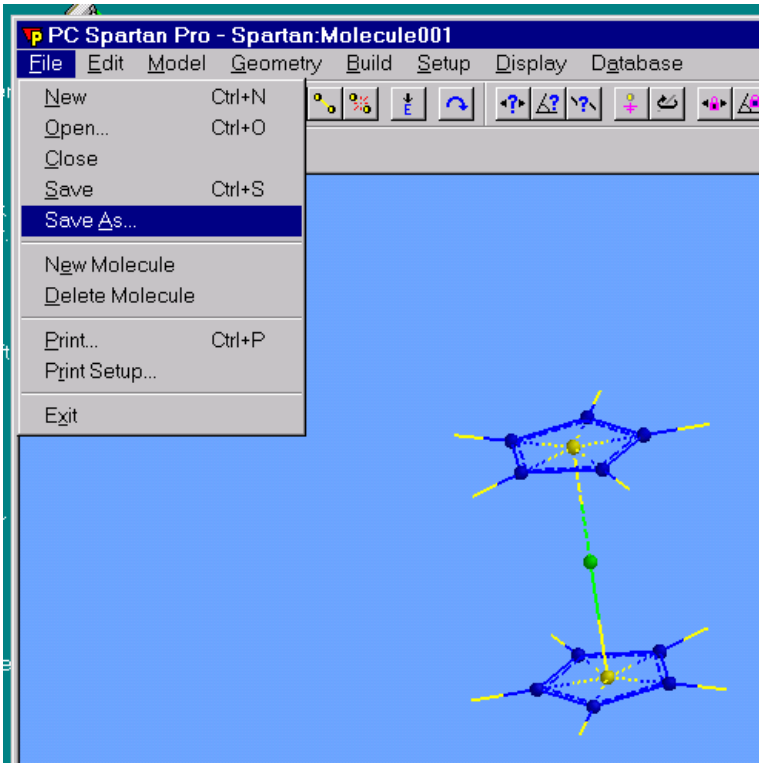
5. Go to step 3 and add a new **Cyclopentadienyl** fragment on the Fe free valence. A D_{5d} ferrocene structure results (see the left lower box from the next picture).



Screenshot courtesy of Wavefunction, Inc. Used with permission.

6. **Save as…** the structure in the C:\5.311 directory.

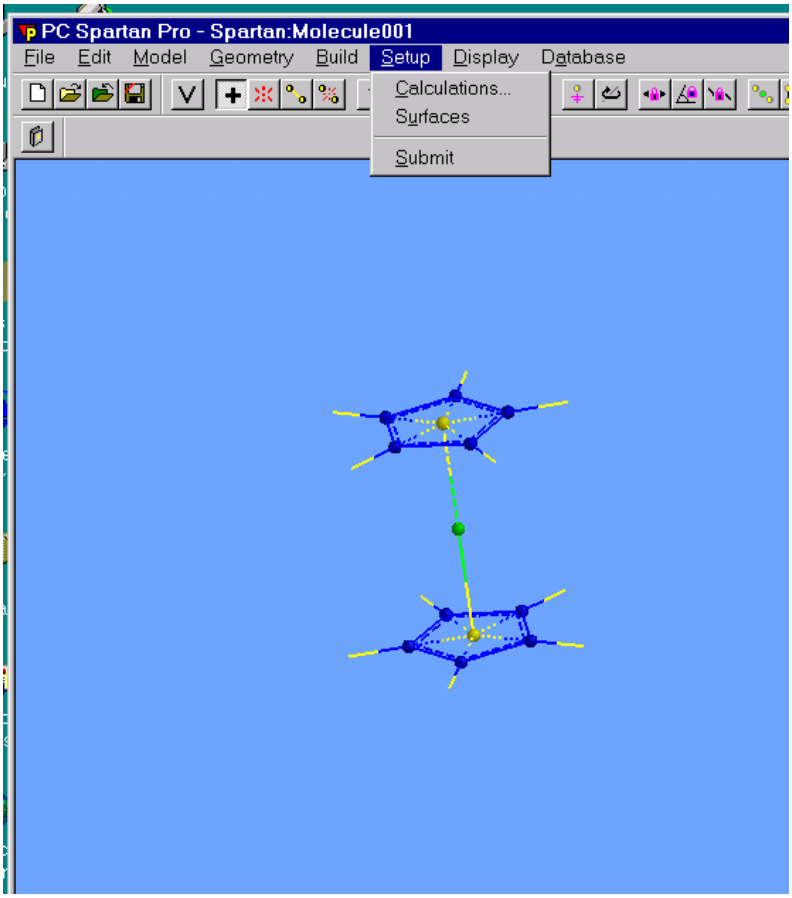
7. You can select the type of model you wish to view from the choices in the Model menu. Rotate the molecule by holding down the left mouse button and moving the mouse.



Screenshot courtesy of Wavefunction, Inc. Used with permission.

B. Calculations.

1. Go to **Setup** click on **Calculation.**

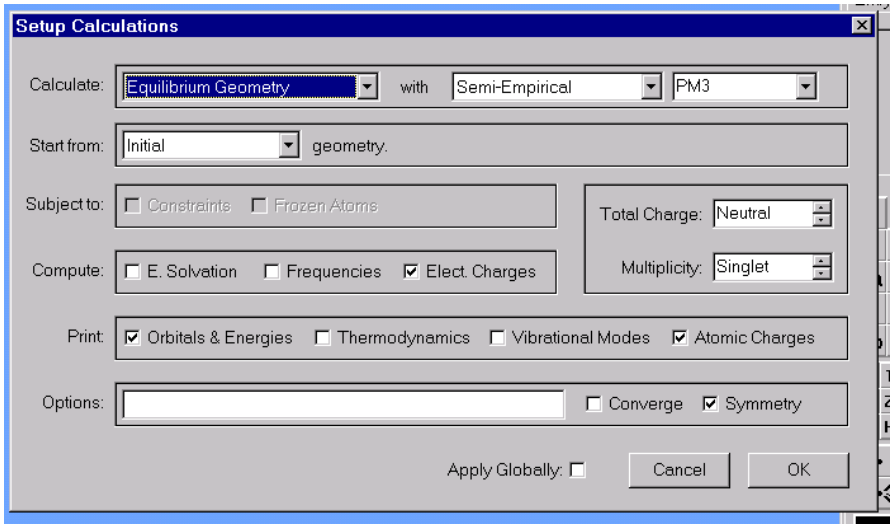


Screenshot courtesy of Wavefunction, Inc. Used with permission.

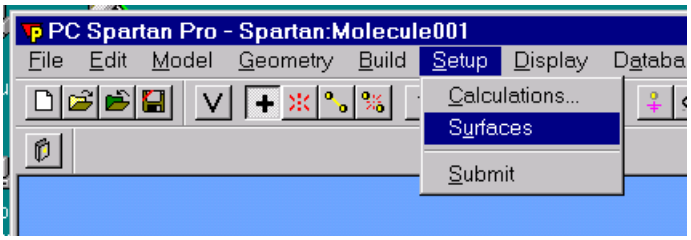
2. Start the PM3 setup by clicking setup, then calculations. Fill in all the pertinent input:

   Calculation: **Equilibrium geometry** (e.g. optimization)
   With: Semiempirical PM3
   Start from: initial geometry
   Total Charge: neutral; **Multiplicity**: **Singlet**
   Print (in the output file): **Orbital energy**
   Check **Symmetry** box. This means that during the minimization the symmetry is kept.
   Click on **SUBMIT**.

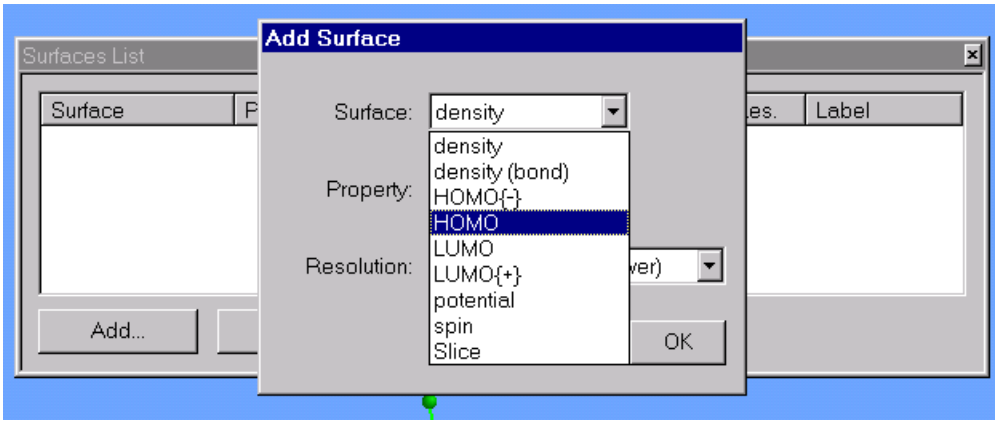
   You will need to wait about a minute.



3. Before (or after) submitting PM3, add the surfaces **HOMO**[2] - **HOMO-8**. Click on **Setup** and then on **Surfaces**:



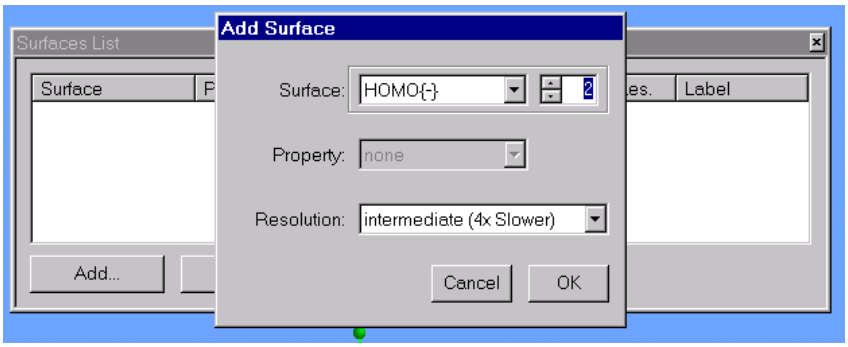
4. The **Surface List** appears. Click on **Add…** and then on **Surface**. Choose **HOMO**, click **OK**.



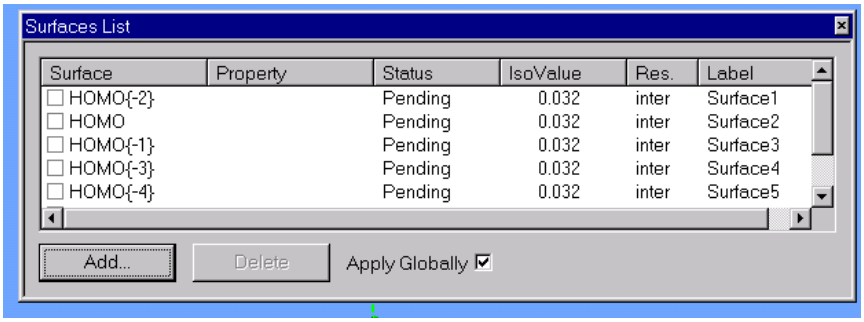
5. Then add **HOMO-1** (in the picture is **HOMO{-1}**). To add **HOMO-2**, click first on **HOMO{-1}** and then increase to 2 in the small window. And click **OK**.

Screenshots courtesy of Wavefunction, Inc. Used with permission.

[2] HOMO: **H**ighest **O**ccupied **M**olecular **O**rbital. HOMO-1 is the next below HOMO….

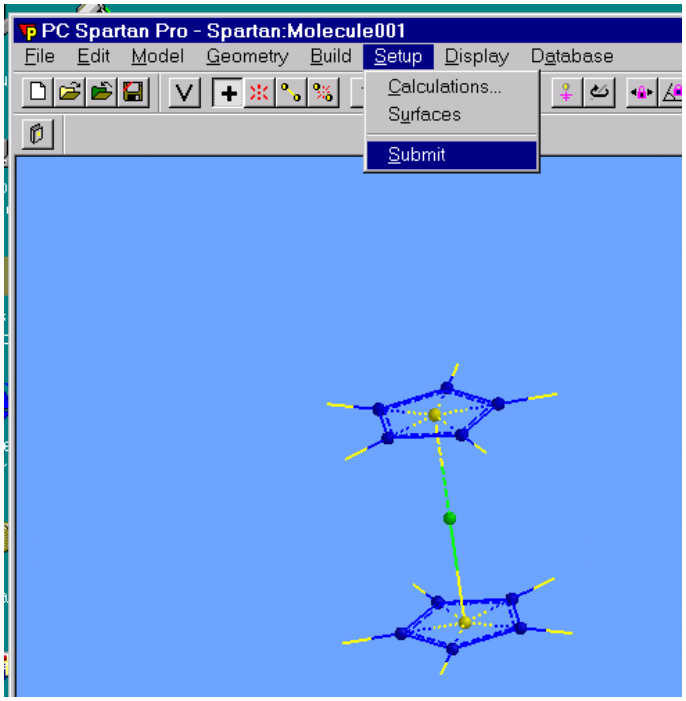


Do it as as many times as to end with **HOMO-8**.



Close the **Surface List** window.

6. **Submit** the job by clicking Setup, then Submit.



Screenshots courtesy of Wavefunction, Inc. Used with permission.

7. The execution starts right away and the following window appears. Click on **OK**.

8. approximately one minute, the following window will appear. Click **OK**. The molecule on the screen will be adjusted to the newly calculated geometry.

9. Save the output file on a floppy disk that you can buy from the stockroom. With this file step 11 may be completed at home.

10. To display the calculated molecular orbital surfaces, click **Output**, then **Surfaces**. Check the surface you want to be displayed on the screen. To see another surface check only the box next to surface. Do not leave check signs on the previous examined surfaced.

11. To examine the Output, click Display, then Output. Examine the HOMO[3] throught HOMO-8 wave functions. Answer the questions from the experiments.

Screenshots courtesy of Wavefunction, Inc. Used with permission.

[3] In order to find out in the output which orbital is HOMO, take the total number of electrons and divide by 2.