The experiments described in these materials are potentially hazardous and require a high level of safety training, special facilities and equipment, and supervision by appropriate individuals. You bear the sole responsibility, liability, and risk for the implementation of such safety procedures and measures. MIT shall have no responsibility, liability, or risk for the content or implementation of any of the material presented. Leaal Notice

## Appendix 1

# The electronic structure of ferrocene by semiempirical PM3 calculations with Spartan 2.0.<sup>1</sup>

### Mírcea D. Gheorghíu

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.

| <b>PC Spartan</b><br>File Edit Mo             | <b>Pro</b><br>Idel Geometry | · Build Setup | Display          | Database    | <br>Options H | □×<br>Help |
|---|-----------------------------|---------------|------------------|-------------|---------------|------------|
| <u>N</u> ew<br><u>O</u> pen<br>Close          | Ctrl+N<br>Ctrl+O            | <u>\</u> ##A  | 49- <u>68</u> 19 | -<br>-<br>- |               | <i>III</i> |
| <u>S</u> ave<br>Save <u>A</u> s               | Ctrl+S                      |               |                  |             |               |            |
| N <u>e</u> w Molecula<br><u>D</u> elete Molec | :<br>.le                    |               |                  |             |               |            |
| <u>P</u> rint<br>P <u>r</u> int Setup         | Ctrl+P                      |               |                  |             |               |            |
| E <u>x</u> it                                 |                             |               |                  |             |               |            |
|   |                             |               |                  |             |               |            |
|   |                             |               | right © 1        | 991-2000, \ | Navefunction  | Inc.       |
|   |                             |               |                  |             |               |            |

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<sup>&</sup>lt;sup>1</sup> 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**.

| <u>D</u> isplay D <u>a</u> tabase | <u>O</u> ptions <u>H</u> elp  |
|-----------------------------------|---|
|                                   |   |
|                                   | Entry Expert Peptide  |
|                                   | ☆   |
|                                   | H He  |
|                                   | LIBEBCNOFNE<br>No Mar Al Si D. S. Cl. Ar  |
|                                   | K Ca Ga Ge As Se Br Kr  |
|                                   | Rb Sr In Sn Sb Te I Xe  |
|                                   | Sc Ti V Cr Mn Fe Co Ni Cu Zn<br>Y Zr Nb Mo Tc Ru Rh Pd Ag Cd<br>La Hf Ta Acetylene<br>Ethylene<br>Allyl<br>Butadiene<br>Benzene<br>Carbon Monoxide<br>Nitrogen Oxide<br>Ammonia<br>Water<br>Phosphine |
|                                   | Ligands 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.

| Entry Expert Peptide  |
|---|
| H He<br>Li Be B C N O F Ne<br>Na Mg Al Si P S Cl Ar<br>K Ca Ga Ge As Se Br Kr<br>Rb Sr In Sn Sb Te I Xe<br>Sc Ti V Cr Mn Tc Co Ni Cu Zn<br>Y Zr Nb Mo Tc Ru Rh Pd Ag Cd<br>La Hf Ta W Re Os Ir Pt Au Hg<br> |
| Insert  |

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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).

| Entry Expert Peptide   |
|--|
| H He<br>Li Be B C N O F Ne<br>Na Mg Al Si P S Cl Ar<br>K Ca Ga Ge As Se Br Kr<br>Rb Sr In Sn Sb Te I Xe<br>Sc Ti V Cr Mn Fe Co Ni Cu Zn<br>Y Zr Nb Mo Tc Ru Rh Pd Ag Cd<br>La Hf Ta W Re Ds Ir Pt Au Hg<br><br><br>Groups Allene<br>Rings Benzene<br>Igenos Cyclopentadienyl |
| Insert D5d   |

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**.

| PC Spartan Pro - Spartan:Molecul                               | e001   |                   |
|--|--|-------------------|
| <u>File E</u> dit <u>M</u> odel <u>G</u> eometry <u>B</u> uild | <u>S</u> etup <u>D</u> isplay  | D <u>a</u> tabase |
|  | Calculations   | 2 @ • A 15 %      |
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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.

| Setup Calc  | ulations  |
|-------------|---|
| Calculate:  | Equilibrium Geometry with Semi-Empirical PM3                                  |
| Start from: | Initial geometry.   |
| Subject to: | Constraints Frozen Atoms Total Charge: Neutral                                |
| Compute:    | E. Solvation Frequencies F Elect Charges                                      |
| Print       | ☑ Orbitals & Energies 	☐ Thermodynamics 	☐ Vibrational Modes ☑ Atomic Charges |
| Options:    | Converge 🔽 Symmetry   |
|             | Apply Globally: 🗖 Cancel OK   |

3. Before (or after) submitting PM3, add the surfaces HOMO<sup>2</sup> - HOMO-8. Click on Setup and then on Surfaces:

| PC Spartan Pro - Spartan:Molecul                                       | e001                                      |                 |                 |
|--|---|-----------------|-----------------|
| <u>F</u> ile <u>E</u> dit <u>M</u> odel <u>G</u> eometry <u>B</u> uild | <u>S</u> etup                             | <u>D</u> isplay | D <u>a</u> taba |
|  | <u>C</u> alculations<br>S <u>u</u> rfaces |                 | <u></u>         |
|  | <u>S</u> ubrr                             | nit             |                 |
|  |   |                 |                 |

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

| Surfaces List | Add Surface |  |      | ×         |
|---------------|-------------|--|------|-----------|
| Surface P     | Surface:    | density 💌  |      | es. Label |
|               | Property:   | density<br>density (bond)<br>HOMO <del>{-}</del><br>HOMO |      |           |
|               | Resolution: | LUMO<br>LUMO{+} ver                                      | r) 💌 |           |
| Add           |             | spin<br>Slice  | ок   |           |
|               |             | •  |      |           |

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**.

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<sup>&</sup>lt;sup>2</sup> HOMO: Highest Occupied Molecular Orbital. HOMO-1 is the next below HOMO....

| Surfaces List | Add Surface |                          | ×          |
|---------------|-------------|--------------------------|------------|
| Surface P     | Surface:    | HOMO{-}                  | .es. Label |
|               | Property:   | none                     |            |
|               | Resolution: | intermediate (4x Slower) |            |
| Add           |             | Cancel OK                |            |

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

| Surfaces List |          |                  |          |       |          |         |
|---------------|----------|------------------|----------|-------|----------|---------|
| Surface       | Property | Status           | IsoValue | Res.  | Label    | <b></b> |
| □ HOMO{-2}    |          | Pending          | 0.032    | inter | Surface1 |         |
| □ НОМО        |          | Pending          | 0.032    | inter | Surface2 |         |
| □ HOMO{-1}    |          | Pending          | 0.032    | inter | Surface3 |         |
| □ HOMO{-3}    |          | Pending          | 0.032    | inter | Surface4 |         |
| □ HOMO{-4}    |          | Pending          | 0.032    | inter | Surface5 | -       |
| •             |          |                  |          |       |          | ۱       |
| Add           | Delete   | Apply Globally 🗹 |          |       |          |         |

Close the Surface List window.

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



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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<sup>3</sup> throught HOMO-8 wave functions. Answer the questions from the experiments.

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 $<sup>^{3}</sup>$  In order to find out in the output which orbital is HOMO, take the total number of electrons and divide by 2.