

## Appendix 1b

### Gaussian 03W on Dell XPS

#### Density Functional Theory Calculation of Isotropic Fermi Contact Couplings of Alkyl Semibenzoquinones

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This appendix describes the use of Gaussian 03W Density Functional Theory (DFT) software to calculate hyperfine coupling constants (the isotropic Fermi contact couplings) for semi-1,4-benzoquinone, methyl-, ethyl-, *i*-propyl- and *t*-butyl semibenzoquinones.

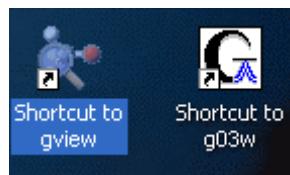
Content:

1. Building benzosemiquinone structures.
2. Calculation of spin-density of semiquinones by DFT.
3. Single input file for multiple jobs.
4. The output file.

#### 1. Building Benzosemiquinone Structures

The **Gaussian 03W** DFT calculation requires an initial structure that is contained in cartesian coordinates (in Å) or in an input file. The structure can be built interactively with the **GaussView**.

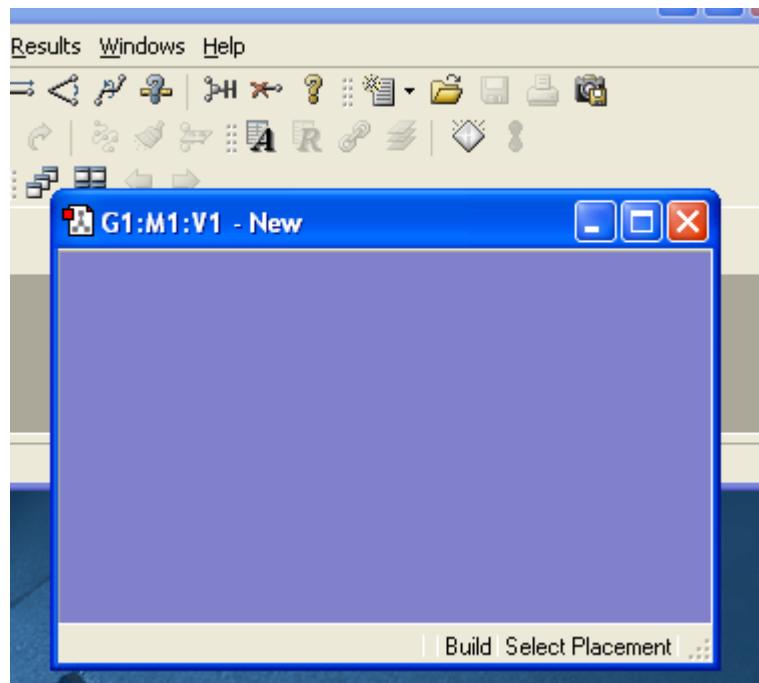
To start **GaussView** installed on the Dell XPS (Room 4-460) under Windows XP, *click on Shortcut to gview*.



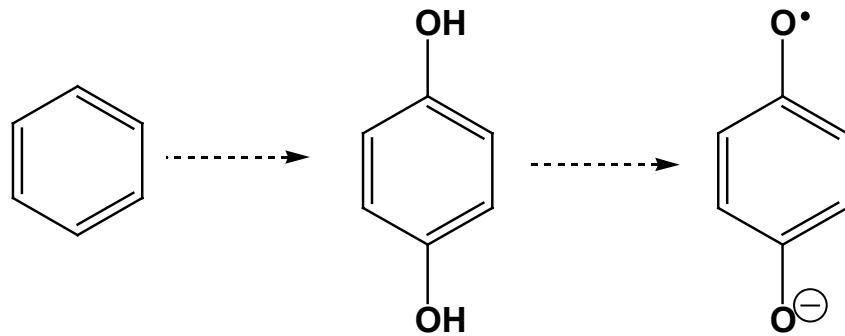
In **GaussView**, there are several windows designed to assist you in building the geometry for the input file. For example, the main **GaussView** (see Fig.1) control panel that contains the menu bar, a large variety of toolbars and the **Current Fragment** window.



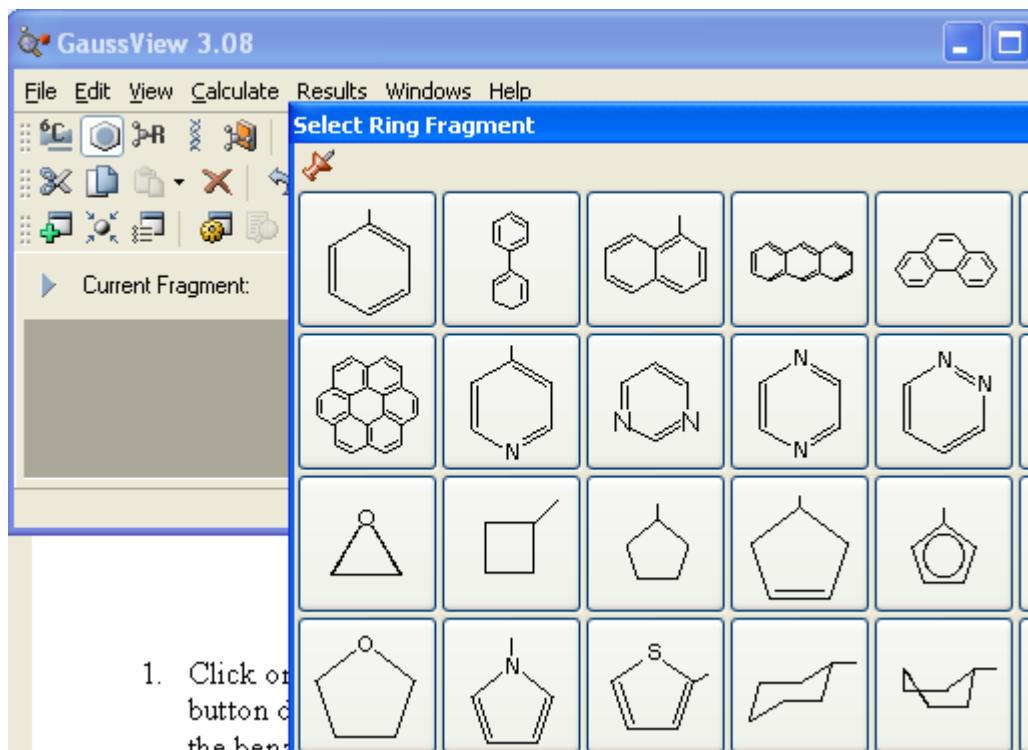
The active **ViewWindow**, in our case **G1:M1:V1**, will immediately contain the benzosemiquinone:



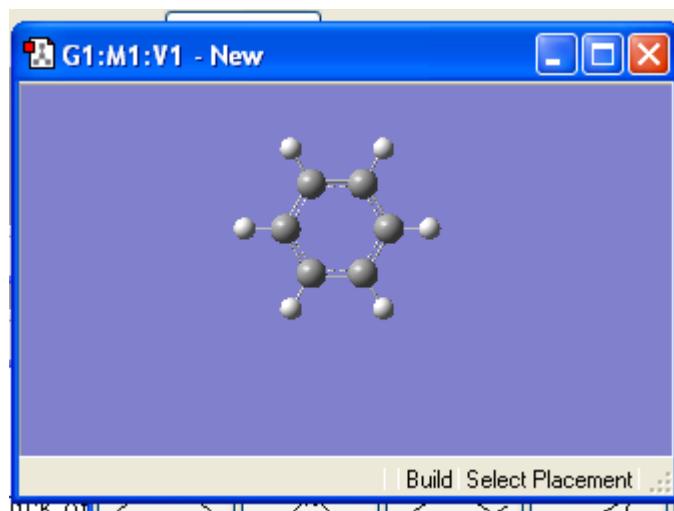
Basically to build the semi-1,4-benzoquinone, you have to start from benzene, add two OH groups, and then strip off the hydrogens. The charge and the spin will be inputted later.



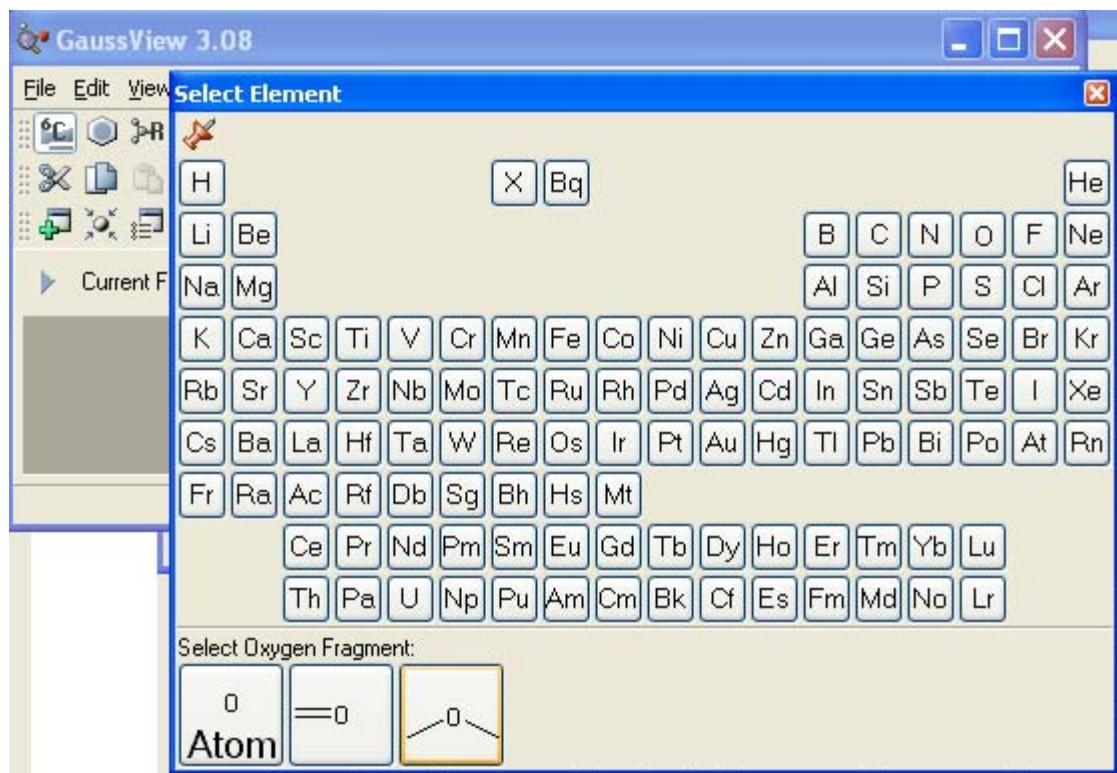
1. Click on the **icon with a benzene ring on it**. The **Select Ring Fragment** appears.



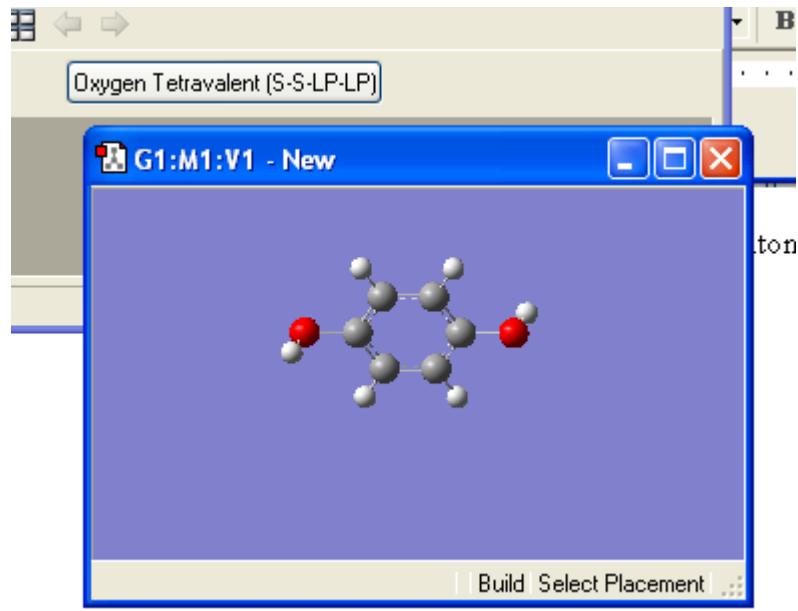
2. Next click anywhere in the **G1:M1:V1** window. The benzene ring is displayed.



3. Add the oxygen atoms. Double click on the **“C”** button. Click on “**O**” than select at the bottom of the periodic Table the sp<sup>3</sup> bivalent “oxygen” fragment (S-S-LP-LP).



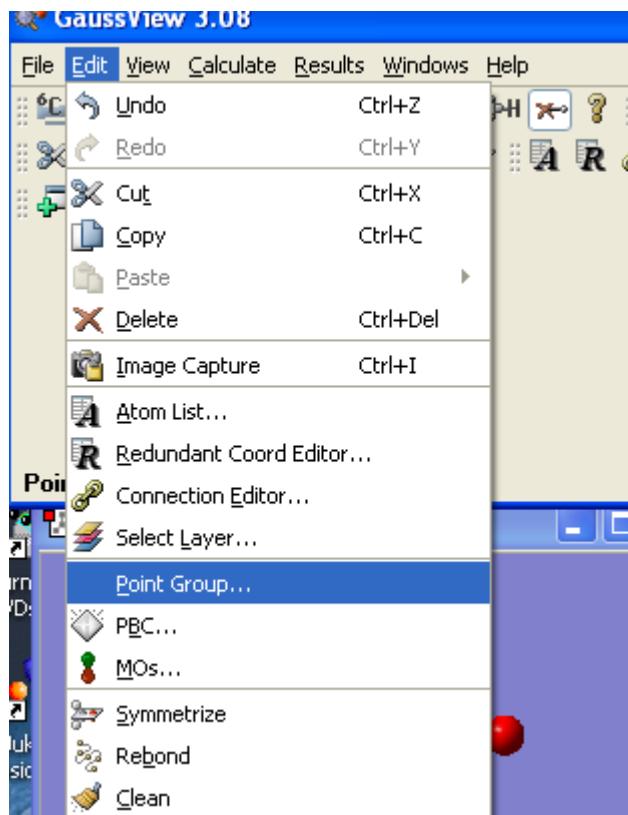
4. Click on any hydrogen from the benzene ring, an **OH** will be inserted. Click on the hydrogen from the *para* position. A second **OH** will be attached.



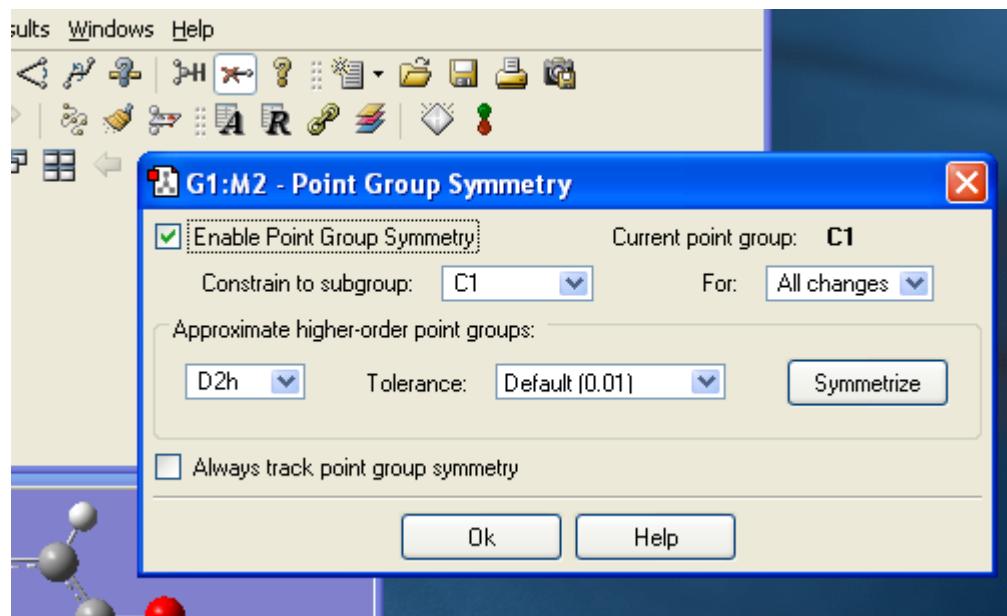
5. Click on **Delete Atom** button (**left to the ? button**) and delete the two hydrogen atoms attached to the **OH** groups.



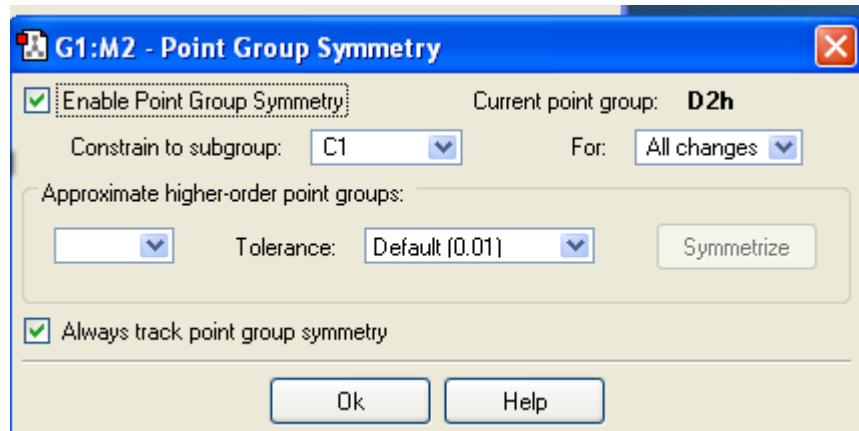
6. The benzosemiquinone built so far is not necessarily symmetrized  $D_{2h}$ . Under **Edit** click on the **Point Group....**



For example, the **G1:M2 Point Group Symmetry** window appears. Check the box **Enable Point Group Symmetry**. From this window you will learn that your molecule



has C1 symmetry, however you can convert this geometry to D<sub>2h</sub> by clicking **Symmetrize**. If you do so you will get a D<sub>2h</sub> benzosemiquinone.

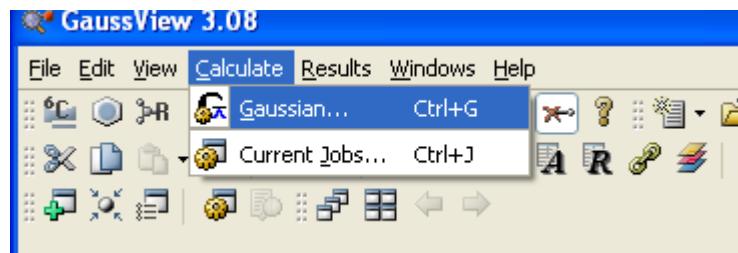


Click **OK**. The current point group is now D<sub>2h</sub>. Now you are ready to start the calculation.

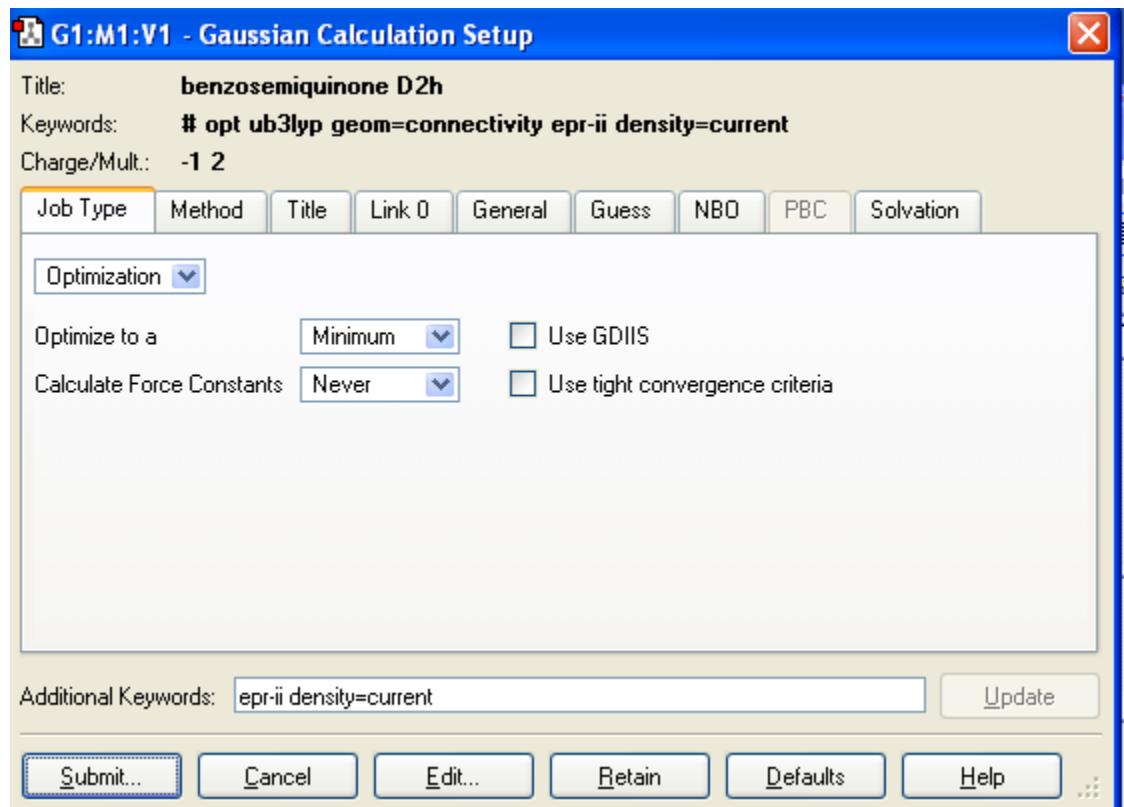
## **2. Calculation of Spin-Density of Alkylsemiquinones by DFT**

At this stage, you have to enter the setup to set the calculation parameters and define the level of theory used.

1. Click on **Calculate (GaussView 3.08)**, then on **Gaussian**....



2. **Gaussian Calculation Setup** window will appear.



- The **Job Type** is **optimization**
- In **Method** choose **ground state, DFT..., Unrestricted, B3LYP**. Leave the **Basis Set** as **3-21G**. It will be edited latter to **epr-II** (this latter basis set is not an option available from this window). Change **Charge** to **-1** and **Spin** to **doublet**.
- In **Title** window type the a **Name for your job**.
- **Solvation** should be **None**.
- In **Additional keywords**, add the keywords **density=current**.
- Now we want to make extra changes to the input file, which is being written with these parameters. Click on **edit...** button. Save the file in **d:/5.33** directory.
- A notepad file will pop-up. Now is time for the final editing:

```

%chk=semiquinone-mg.chk
%mem=6MW
%nproc=1
#T opt ub3lyp/epr_II geom=connectivity density=current

benzosemiquinone D2h

-1 2
C
C 1 B1
C 2 B2 1 A1
C 3 B3 2 A2 1
C 4 B4 3 A3 2
C 1 B5 2 A4 3
H 1 B6 6 A5 5
H 2 B7 1 A6 6
H 4 B8 3 A7 2
H 5 B9 4 A8 3
O 3 B10 2 A9 1
O 6 B11 1 A10 2

```

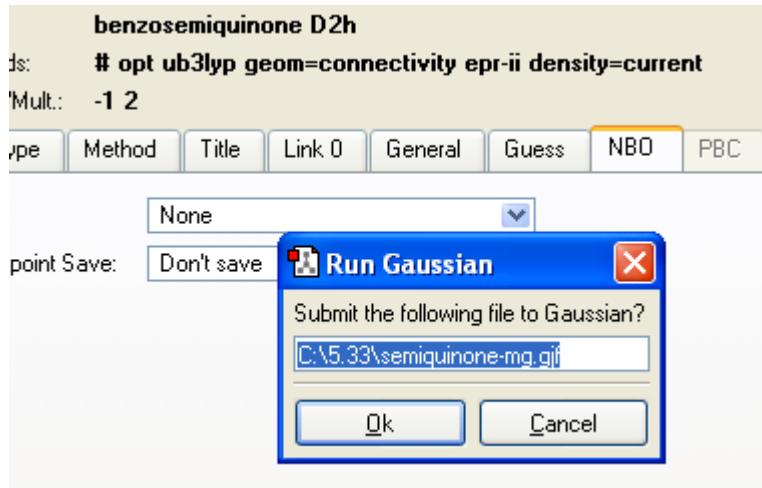
3. Type a “T” after the pound sign to make **#T** instead of **#** (**T** is keyword for terse printing).
4. Replace **ub3lyp/3-21g** (or any other basis set) with **ub3lyp/epr-II**.

For the time being, please ignore the first three lines. For the time being, the first significant is the fourth line, the so-called route line, which begins with the keyword “**#**”. Here “**T**” is keyword for terse output printing. The keyword “**opt**” requests optimization of the geometry of molecule. Electronic structure of the radicals (open shell system) are calculated in the unrestricted model ( $\alpha$  electrons and  $\beta$  electrons are handled separately). The keyword “**u**” prepending the method keyword, requests open shell calculation. The method of calculation, density functional theory, is “**b3lyp**” that stands for Bethe-style-3 parameter DFT using the Lee-Yang-Parr correlation functional. The keyword for the basis set used in the calculation is “**epr-II**”. This basis set was designed by Barone<sup>1</sup> and are optimize for the computation of the **hyperfine coupling constants** by DFT methods. Other keywords will be available consulting the main reference that will be on the computer Table.

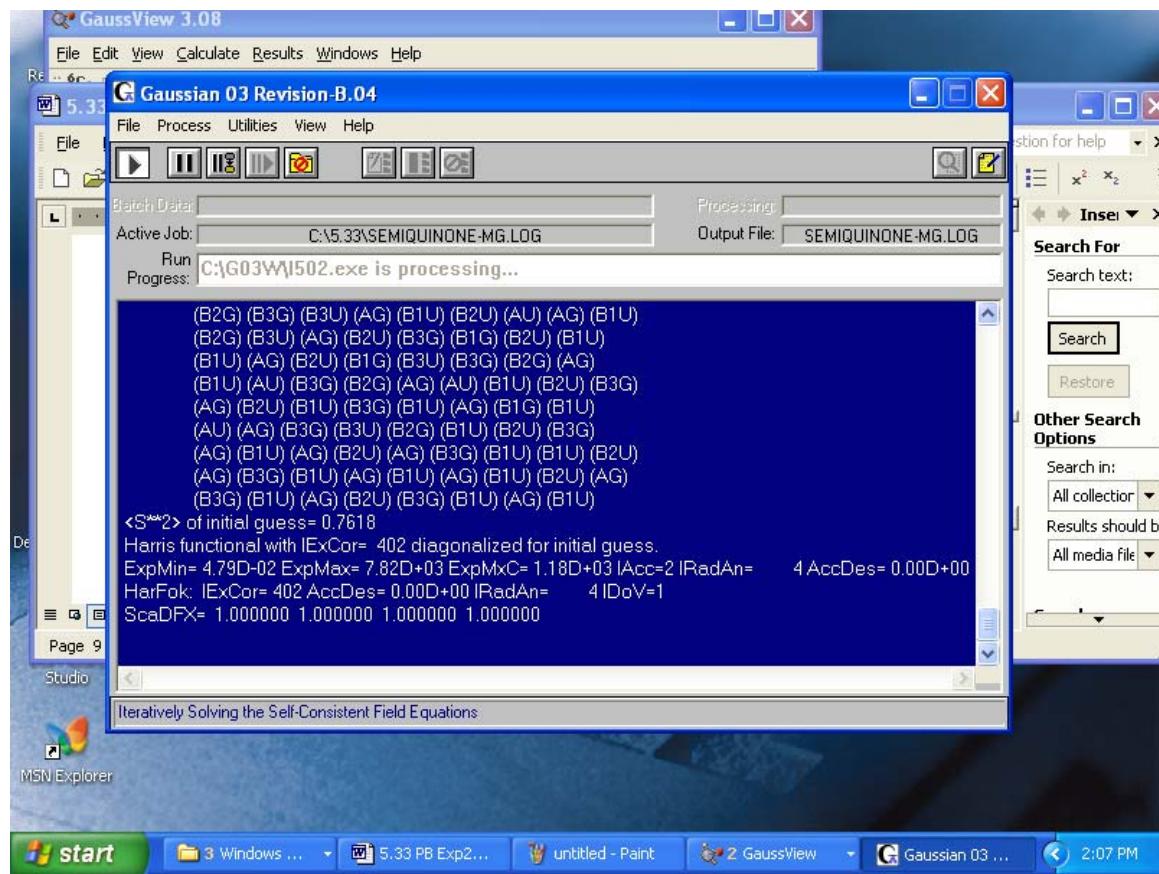
---

<sup>1</sup> Barone, V. in *Recent Advances in Density Functional Methods, Part I*, Chong, D. P., Ed., World Scientific Publ. Co.: Singapore, 1996.

5. Save the file (**File**) and **Exit**.
6. The **RunGaussian** window appear. Click on **Okay** button.



The calculation will start immediately. Details regarding the actual processing is displayed in the **GaussView 3.08** window.



To complete the run strating from the builder geometry, it takes ca. 10 minutes for benzosemiquinone D<sub>2h</sub>, ca. 2 hours for methylbenzosemiquinone, ca. 5.5 hours for

ethylbenzosemiquinone, ca 9 hours for the *i*-propylbenzosemiquinone and ca 15 hours for t-butylsemibenzoquinone. Budget your time wisely. Sign up for calculation as early as possible.

You can run a multiple job file. See the next discussion (**Single input file for multiple jobs**).

### **3. Single Input File for Multiple Jobs.**

The input file to submit, for example, three calculations is displayed next **in blue** (on the web site) Berlin Sans FB fonts to differ from the regular text. Suggestions:

1. Start with the benzosemiquinone file (perhaps saved under a different name).
2. Build methylbenzosemiquinone. Save the input file.
3. Leave a line after the last information regarding the benzosemiquinone. Type in (correctly) the link line, the check file name, and the route line.
4. Leave a line as space.
5. Open the file with the second molecule. Copy and paste the title, charge, multiplicity and the geometric information concerning the second molecule in the multi jobs input file.
6. For the third (next molecule) go to step 1 through step 5.
7. If the new molecule is the last input, add the NoSave command (see the example below).
8. Leave to empty lines at the end.

```
%chk=semiquinone.chk
%mem=6MW
%nproc=1
#T opt ub3lyp geom=connectivity epr-ii density=current
```

benzosemiquinone D2h

-1 2  
insert the geometry of benzosemiquinone

```
--link1--
%chk=semiquinone.chk
#T opt ub3lyp geom=connectivity epr-ii density=current
```

methyl benzosemiquinone

-1 2  
insert the geometry of methylbenzosemiquinone

```
--link1--
%chk=semiquinone.chk
```

```
%NoSave
# opt ub3lyp geom=connectivity epr-ii density=current
```

### t-butyl benzosemiquinone

-1 2

insert the geometry of t-butylbenzosemiquinone

## 4. The Output File

The output (or LOG) file for the b3lyp/epr-II calculation will provide you with the isotropic Fermi contact couplings. This file should be saved with the same name as your input file with a .LOG extension. In the figure below is an example of the semi-benzoquinone output file. The couplings are found in column 5 in values of Gauss. Here, because all hydrogens are equivalent (group D<sub>2h</sub>), the coupling constant value is equal at -2.39 Gauss. Also information regarding the optimized geometry of the anion radical is also available.

```
Symmetry B2U KE= 4.491250422785D+01
Symmetry B3U KE= 5.846213836252D+00
                                         Isotropic Fermi Contact Couplings
      Atom          a.u.      MegaHertz      Gauss      10(-4) cm-1
      1  C(13)      -0.00042      -0.47178      -0.16834      -0.15737
      2  C(13)      -0.00042      -0.47178      -0.16834      -0.15737
      3  C(13)      -0.00895     -10.05990      -3.58962      -3.35562
      4  C(13)      -0.00042      -0.47178      -0.16834      -0.15737
      5  C(13)      -0.00042      -0.47178      -0.16834      -0.15737
      6  C(13)      -0.00895     -10.05990      -3.58962      -3.35562
      7  H(1)       -0.00150      -6.70870      -2.39383      -2.23778
      8  H(1)       -0.00150      -6.70870      -2.39383      -2.23778
      9  H(1)       -0.00150      -6.70870      -2.39383      -2.23778
     10 H(1)       -0.00150      -6.70870      -2.39383      -2.23778
     11 O(17)       0.03557     -21.56538      -7.69506      -7.19344
     12 O(17)       0.03557     -21.56538      -7.69506      -7.19344
```

All calculations in **Gaussian03W** end with a proverb. Here is a superb sample:

```

12 o(17) Baa -0.5756 41.651 14.862 13.893 0.0000 0.0000 1.0000
          Bbb -0.5669 41.018 14.636 13.682 0.0000 1.0000 0.0000
          Bcc 1.1425 -82.669 -29.498 -27.575 1.0000 0.0000 0.0000

```

```

1|1|UNPC-UNK|FOpt|UB3LYP|EPR-II|C6H4O2(1-,2)|PCUSER|16-Sep-2003|0||# O
PT UB3LYP GEOM=CONNECTIVITY EPR-II DENSITY=CURRENT||benzosemiquinone D
2h||-1,2|C,-1.2300173355,0.,-0.6900845267|C,-1.2300173355,0.,0.6900845
267|C,0.,0.,1.4758944703|C,1.2300173355,0.,0.6900845267|C,1.2300173355
,0.,-0.6900845267|C,0.,0.,-1.4758944703|H,-2.1641832335,0.,-1.25162165
22|H,-2.1641832335,0.,1.2516216522|H,2.1641832335,0.,1.2516216522|H,2.
1641832335,0.,-1.2516216522|O,0.,0.,2.7469855669|O,0.,0.,-2.7469855669
||Version=x86-Win32-G03RevB.04|State=2-B2G|HF=-381.5936519|S2=0.761767
|S2-1=0.|S2A=0.750042|RMSD=6.115e-009|RMSF=1.179e-004|Dipole=0.,0.,0.|PG=D02H [C2"(O1C1.C1O1),SG(C4H4)]||@
```

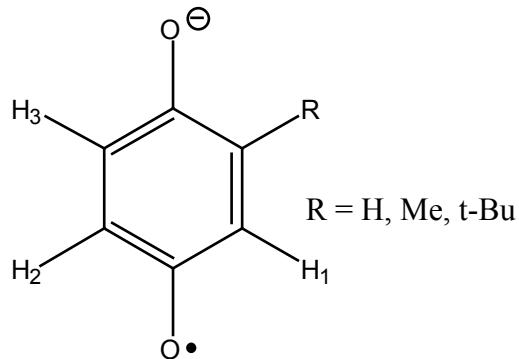
```

IT IS A SIMPLE TASK TO MAKE THINGS COMPLEX,
BUT A COMPLEX TASK TO MAKE THEM SIMPLE.
Job cpu time: 0 days 0 hours 9 minutes 52.0 seconds.
File lengths (MBytes): RWF=      44 Int=      0 D2E=      0 Chk=      9 Scr=      1
Normal termination of Gaussian 03 at Tue Sep 16 14:10:17 2003.

```

**If you have any problems, do not hesitate to talk to TAs and Dr. Mircea Gheorghiu.**

Table. The calculated hyperfine coupling constant,  $a_H$ , (in gauss), according to equation 10 and your data.



Benzosemiquinone R is the substituent	DTF: B3LYP/EPR-II	Your data
R=H  H <sub>2</sub>		

Benzosemiquinone R is the substituent	DTF: B3LYP/EPR-II	Your data
R=Me  H <sub>2</sub>  H <sub>3</sub>  H <sub>4</sub>  average CH <sub>3</sub>		
R= isopropyl  H <sub>2</sub>  H <sub>3</sub>  H <sub>4</sub>  CH  average CH <sub>3</sub>		