Appendix 1

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

This appendix describes the use of Gaussian 98W software for running Density Functional Theory (DFT) calculations of hyperfine coupling constants (the isotropic Fermi contact couplings) for alkyl substituted semibenzoquinones. This appendix describes the building of the semibenzoquinones molecules for the Gaussian 98W input file, the running of the calculation, and reading of the output file.

1. Building Alkyl Semibenzoquinone Structures

The Gaussian 98W DFT calculation requires an initial structure that is contained in Cartesian coordinates in an input file. The structure can be built interactively with the GaussView, which saves the input file. To start GaussView installed on the Dell Precision 330 (Room 4-472) under Windows NT, *click* on Shortcut to gview.


In GaussView, there are three windows design to assist you in building the geometry for the input file: (i) **GaussView 2.1**, (ii) **Builder** and (iii) **View1** (see Fig.1).
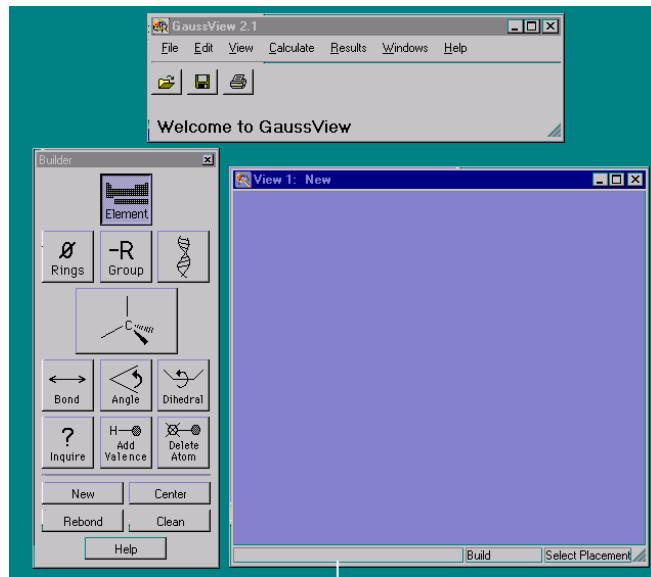
First, let us build the semi-benzoquinone:

1. Click on the **∅ Rings** button in the **Builder** window and the larger fragment button directly beneath it. The **Select Ring Fragment** screen will appear. Select the benzene ring.
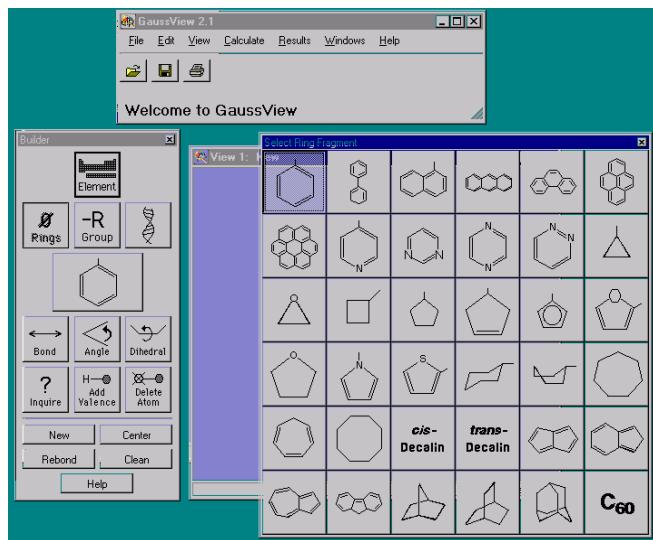

2. Put the mouse arrow on the **View1** surface and right-click. If necessary, drag the ring to center using **Shift-Left** button.
3. Click **View** (**GaussView 2.1**) and click **Labels**. All atoms become numbered (see below).
4. Add the oxygen atoms. Double click on the **Element** button (**Builder**). **Select Element** table will pop-up. Click on "**O**". 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.
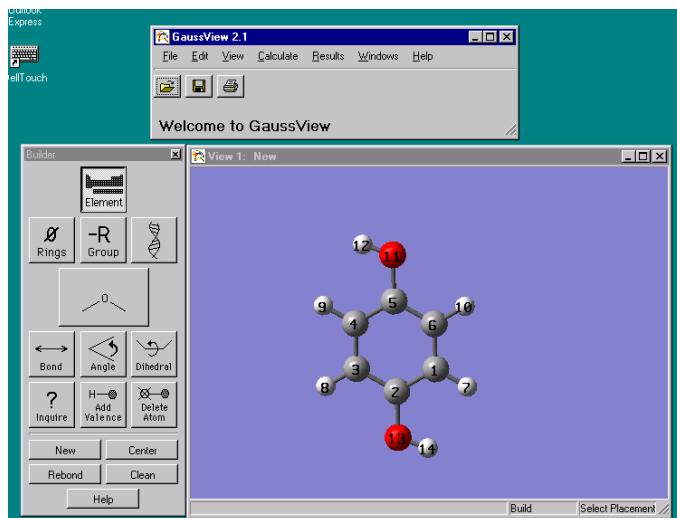
5. Click on **Delete Atom** button (**Builder**) and delete the two hydrogen atoms attached to the **OH** groups.
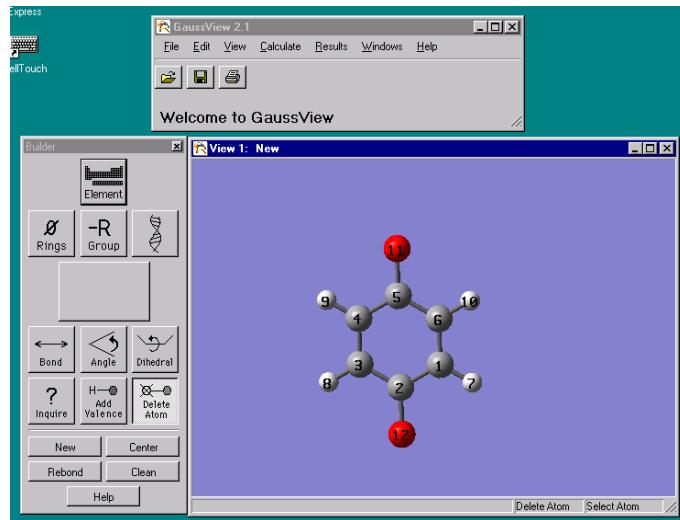
6. Cick on **File** (**GaussView 2.1**), than on **Save….** Save the file in **d:/GaussView/5.33** directory.
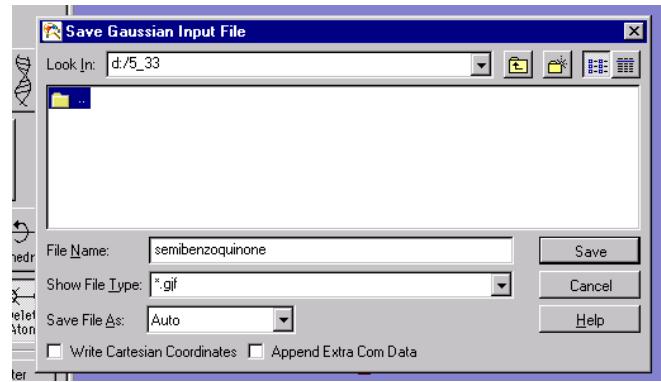
2. Calculation of Spin-Density of Alkylsemiquinones by DFT

Now you have created the starting structure for the calculation. Now enter the setup to set the calculation parameters and define the level of theory used.

1. Click on **Calculate** (**GaussView 2.1**), then on Gaussian. **Gaussian Calculation Setup** window will appear.
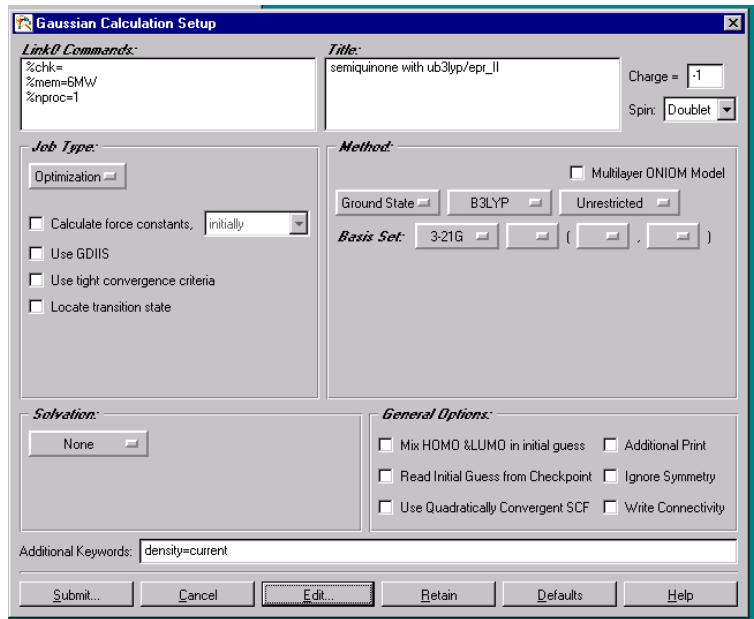
2. In **Title** window type the a **Name for your job**.
3. Change **Charge** to **–1** and **Spin** to **doublet**.
4. The **Job type** is **optimization**.
5. In **Method** choose unrestricte**d B3LYP**. Leave the **Basis Se**t as 3-21G. It will be edited latter to **epr-II** (this latter basis set is not an option available from this window).
6. **Solvation** should be **None**.
7. In **General Options** leave all boxes unchecked.
8. In **Additional**, add the keywords **density=current**.
9. 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.
10. A notepad file will pop-up. Now is time for the final editing:

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11. Type a "T" after the pound sign to make **#T** instead of **#** (**T** is keyword for terse printing).
12. 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 (α electrons and β 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[1] 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.

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

The calculation will start immediately. To complete the run, it takes ca. 30 minutes for semibenzoquinone, XX minutes for methyl- semibenzoquinone and XX minutes for t-butyl-semibenzoquinone. Budget your time wisely. Sign up for calculation as early as possible.

3. 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-

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[1] Barone, V. in *Recent Advances in Density Functional Methods, Part I,* Chong, D. P., Ed., World Scientific Publ. Co.: Singapore, 1966.

benzoquinone output file. The couplings are found in column 5 in values of Gauss. Here, because all hydrogens are equivalent (group D_{2h}), the coupling constant value is equal at –2.39 Gauss. Also information regarding the optimized geometry of the anion radical is also available.
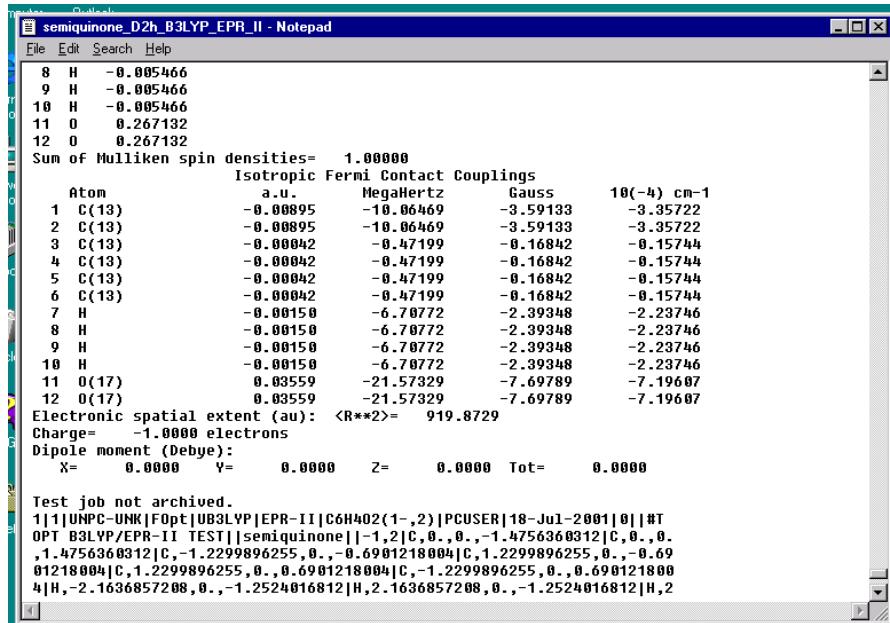


```
semiquinone_D2h_B3LYP_EPR_II - Notepad
File  Edit  Search  Help
   8  H    -0.005466
   9  H    -0.005466
  10  H    -0.005466
  11  O     0.267132
  12  O     0.267132
Sum of Mulliken spin densities=   1.00000
                        Isotropic Fermi Contact Couplings
     Atom              a.u.        MegaHertz        Gauss      10(-4) cm-1
   1  C(13)          -0.00895      -10.06469      -3.59133      -3.35722
   2  C(13)          -0.00895      -10.06469      -3.59133      -3.35722
   3  C(13)          -0.00042       -0.47199      -0.16842      -0.15744
   4  C(13)          -0.00042       -0.47199      -0.16842      -0.15744
   5  C(13)          -0.00042       -0.47199      -0.16842      -0.15744
   6  C(13)          -0.00042       -0.47199      -0.16842      -0.15744
   7  H              -0.00150       -6.70772      -2.39348      -2.23746
   8  H              -0.00150       -6.70772      -2.39348      -2.23746
   9  H              -0.00150       -6.70772      -2.39348      -2.23746
  10  H              -0.00150       -6.70772      -2.39348      -2.23746
  11  O(17)           0.03559      -21.57329      -7.69789      -7.19607
  12  O(17)           0.03559      -21.57329      -7.69789      -7.19607
Electronic spatial extent (au):  <R**2>=   919.8729
Charge=     -1.0000 electrons
Dipole moment (Debye):
    X=      0.0000   Y=      0.0000   Z=      0.0000  Tot=      0.0000

Test job not archived.
1|1|UNPC-UNK|FOpt|UB3LYP|EPR-II|C6H4O2(1-,2)|PCUSER|18-Jul-2001|0||#T
OPT B3LYP/EPR-II TEST||semiquinone||-1,2|C,0.,0.,-1.4756360312|C,0.,0.
,1.4756360312|C,-1.2299896255,0.,-0.6901218004|C,1.2299896255,0.,-0.69
01218004|C,1.2299896255,0.,0.6901218004|C,-1.2299896255,0.,0.690121800
4|H,-2.1636857208,0.,-1.2524016812|H,2.1636857208,0.,-1.2524016812|H,2
```

All calculations in **Gaussian98W** end with a proverb. Here is a superb sample:
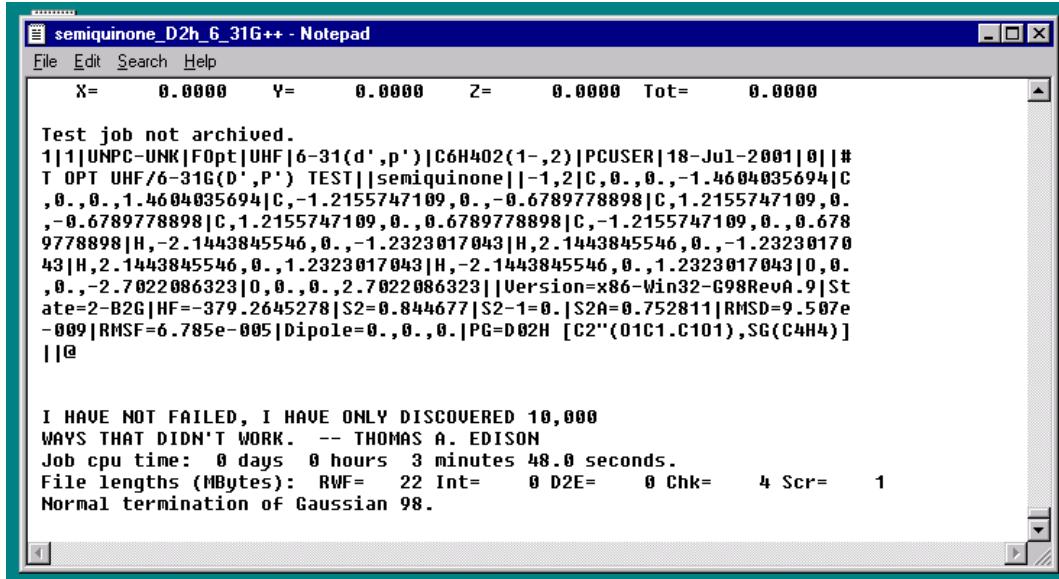

```
semiquinone_D2h_6_31G++ - Notepad
File  Edit  Search  Help
    X=      0.0000   Y=      0.0000   Z=      0.0000  Tot=      0.0000

Test job not archived.
1|1|UNPC-UNK|FOpt|UHF|6-31(d',p')|C6H4O2(1-,2)|PCUSER|18-Jul-2001|0||#
T OPT UHF/6-31G(D',P') TEST||semiquinone||-1,2|C,0.,0.,-1.4604035694|C
,0.,0.,1.4604035694|C,-1.2155747109,0.,-0.6789778898|C,1.2155747109,0.
,-0.6789778898|C,1.2155747109,0.,0.6789778898|C,-1.2155747109,0.,0.678
9778898|H,-2.1443845546,0.,-1.2323017043|H,2.1443845546,0.,-1.23230170
43|H,2.1443845546,0.,1.2323017043|H,-2.1443845546,0.,1.2323017043|O,0.
,0.,-2.7022086323|O,0.,0.,2.7022086323||Version=x86-Win32-G98RevA.9|St
ate=2-B2G|HF=-379.2645278|S2=0.844677|S2-1=0.|S2A=0.752811|RMSD=9.507e
-009|RMSF=6.785e-005|Dipole=0.,0.,0.|PG=D02H [C2"(O1C1.C1O1),SG(C4H4)]
||@


I HAVE NOT FAILED, I HAVE ONLY DISCOVERED 10,000
WAYS THAT DIDN'T WORK.  -- THOMAS A. EDISON
Job cpu time:  0 days  0 hours  3 minutes 48.0 seconds.
File lengths (MBytes):  RWF=   22 Int=     0 D2E=     0 Chk=     4 Scr=     1
Normal termination of Gaussian 98.
```

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.

R = H, Me, t-Bu
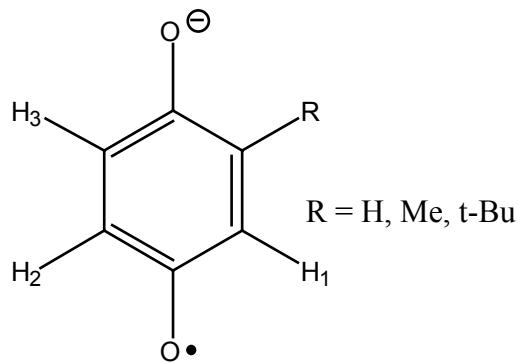
Benzosemiquinone R is the substituent	DTF: B3LYP/EPR-II	Your data
R=H H$_2$		
R=Me H$_2$ H$_3$ H$_4$ average CH$_3$		

Benzosemiquinone R is the substituent	DTF: B3LYP/EPR-II	Your data
R= isopropyl H_2 H_3 H_4 CH average CH_3		