ABC of DFT: Hands-on session 2

Molecules: structure optimization, visualization of orbitals, charge & spin densities

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Wann? 16.11.2012, 11:30-13:00

Wo? KIT Campus Nord, Flachbau Physik, Geb. 30.22, Computerpool, Raum FE-6

Overview

- Structure optimization, visualization of molecular orbitals and charge densities
  - Examples: benzene, pyridine

- Open shell systems, Jan-Teller distortions
  - Example: cobaltocene

Preparing for the hands-on session 2 …

- Log into **intact** cluster (have a look at a separate sheet of paper with instructions)
- Switch to a working directory:

```
cd ~/ABC_of_DFT/hands-on-sessions/
```

- Copy a script `session2` from **dft20** account:

```
cp ~/../dft20/ABC_of_DFT/session2 .
```

- Type from a command line:

```
./session2
```

- Examples (with this tutorial) will be imported to a directory

```
~/ABC_of_DFT/hands-on-sessions/session2
```

Example 1 – Benzene: structure visualization

- Go to a directory with example 1 (benzene):

```
cd ~/ABC_of_DFT/hands-on-
               sessions/session.2/example.1.benzene
```

- Create you own directory where you are going to run a calculation:

```
cp -r structure.benzene my.benzene
cd my.benzene
```

- Your directory contains a file `coord` with atomic positions:

```
cat coord
```

```
$coord
    2.27353301545502     -1.31262489848446      0.00000000000000      c
    2.27353301545502      1.31262489848446      0.00000000000000      c
    0.00000000000000      2.62524979696891      0.00000000000000      c
   -2.27353301545502      1.31262489848446      0.00000000000000      c
   -2.27353301545502     -1.31262489848446      0.00000000000000      c
    0.00000000000000     -2.62524979696891      0.00000000000000      c
    4.03777188872899     -2.33120868688398      0.00000000000000      h
    4.03777188872899      2.33120868688398      0.00000000000000      h
    0.00000000000000      4.66241737376797      0.00000000000000      h
   -4.03777188872899      2.33120868688398      0.00000000000000      h
   -4.03777188872899     -2.33120868688398      0.00000000000000      h
    0.00000000000000     -4.66241737376797      0.00000000000000      h
$end
```

Example 1 – Benzene: structure visualization

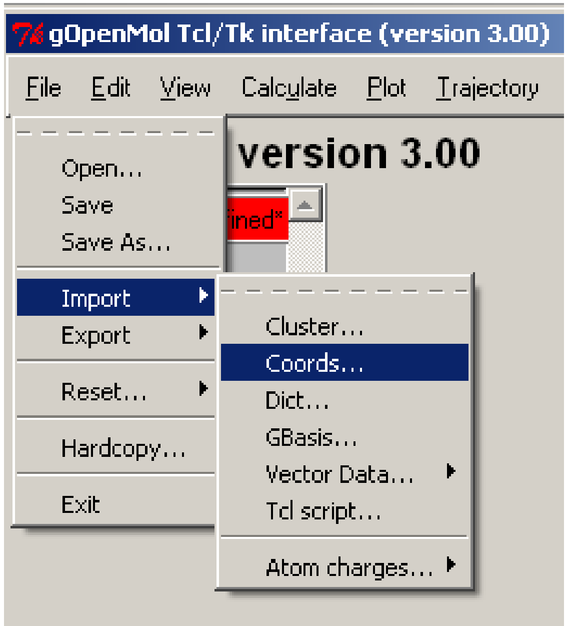
- Convert file `coord` to the .xyz format:

  `t2x coord > coord.xyz`
- Start a visualization program gOpenMol:

  `rungOpenMol &`

- Load in coordinates by using a menu of gOpenMol:

  `File -> Import -> Coords...`
- You will get a sub-menu where you can select coordinates from. Load the `coord.xyz` file from your directory and click on the `<Apply>` buttom.

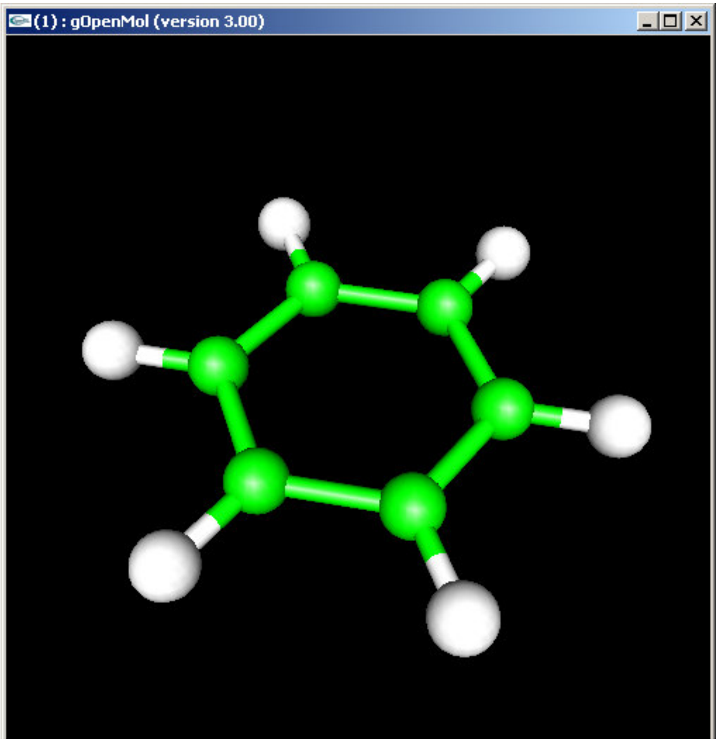


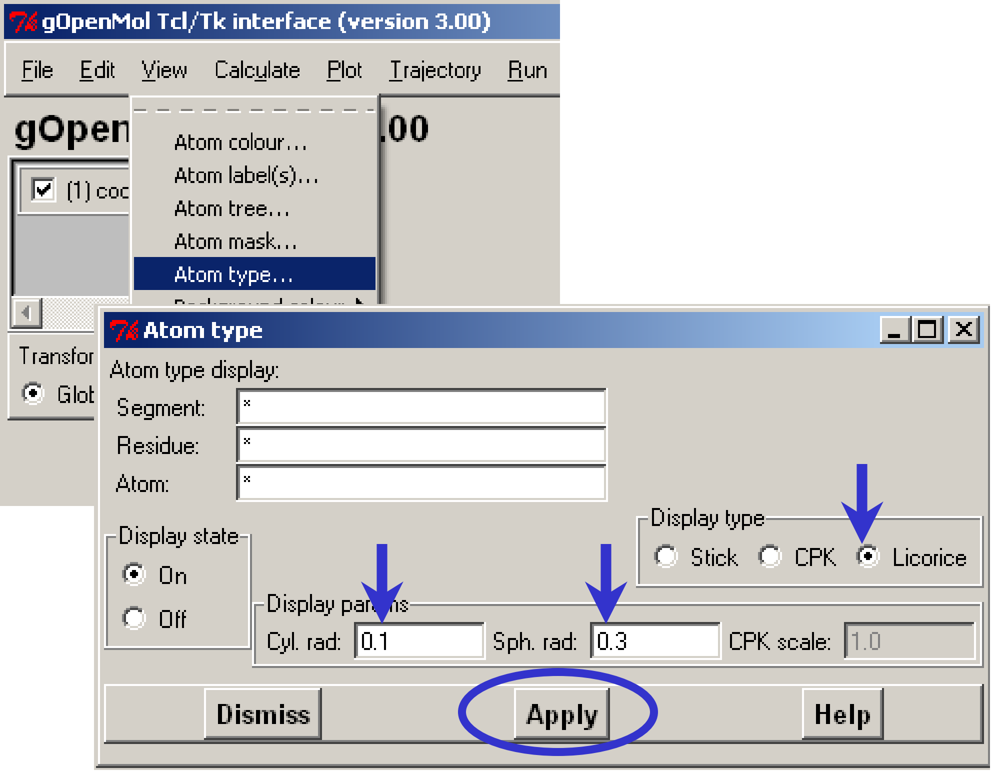
Example 1 – Benzene: structure visualization

- You can tune the way your structure is viewed by selecting

  `View -> Atom type...`

  and by choosing in the upcoming window `Licorice` with parameters `Cyl.rad = 0.1; Sph.rad = 0.3` followed by the `<Apply>` button.





Atom type display:

Segment: *

Residue: *

Atom: *

Display state: ● On ○ Off

Display type: ○ Stick ○ CPK ● Licorice

Display params: Cyl. rad: 0.1 Sph. rad: 0.3 CPK scale: 1.0

Example 1 – Benzene: creating an input (step 1)

- Call an interactive module **define** from the directory `my.benzene`:

```
define
  ...
DATA WILL BE WRITTEN TO THE NEW FILE control
IF YOU WANT TO READ DEFAULT-DATA FROM ANOTHER control-TYPE FILE,
THEN ENTER ITS LOCATION/NAME OR OTHERWISE HIT >return<.
```

- Hit `<Enter>` for the name of input file

-
  ```
   INPUT TITLE OR
  ENTER & TO REPEAT DEFINITION OF DEFAULT INPUT FILE
  ```

  Type e.g. `benzene` for the title, followed by `<Enter>`

- You will get the „molecular geometry“ menu

```
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=0     SYMMETRY=c1  )
YOU MAY USE ONE OF THE FOLLOWING COMMAND
sy <group> <eps> : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
desy <eps>       : DETERMINE MOLECULAR SYMMETRY AND ADJUST
                   COORDINATES (default for eps=1d-6)
susy             : ADJUST COORDINATES FOR SUBGROUPS
ai               : ADD ATOMIC COORDINATES INTERACTIVELY
a <file>         : ADD ATOMIC COORDINATES FROM FILE <file>
 ....
```

Type `a coord <Enter>` to append your structure

Example 1 – Benzene: creating an input (step 2)

- You will see that 12 atoms have been added:

```
CARTESIAN COORDINATES FOR  12 ATOMS HAVE SUCCESSFULLY
BEEN ADDED.
   ....
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=12    SYMMETRY=c1   )
 YOU MAY USE ONE OF THE FOLLOWING COMMAND
 sy <group> <eps> : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
 desy <eps>       : DETERMINE MOLECULAR SYMMETRY AND ADJUST
                    COORDINATES (default for eps=1d-6)
 susy             : ADJUST COORDINATES FOR SUBGROUPS
   ....
```

- Switch on the symmetry detection by entering

```
desy <Enter>
```

... symmetry detection will print out Schönflies symbol, group generators and the main menu with correct symmetry D_{6h}

```
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=12    SYMMETRY=d6h )
YOU MAY USE ONE OF THE FOLLOWING COMMANDS :
  ...
```

Example 1 – Benzene: creating an input (step 3)

- Next step is to provide internal coordinates (bonds, angles, etc...) required for a geometry optimization; type

```
ired <Enter>
```

```
JUST FOUND ISOLATED RING OF SIZE  6 :
   1    2    3    4    5    6
    GEOSPY: NBDIM:        2  NDEGR:        2
     Lowest Eigenvalue of BmBt is:          0.3819660113
     GEOSPY: ATTENTION!
     natural internals not linearly independent?
      Decoupling with "globtry"=    0.9999999999000000
     Lowest Eigenvalue of projected BBt           0.3819660113 No:     2
     Quotient of Eigenvalues           1.0000000000
    OCCUPATION OF BLOCKS:    2    0    0    0    0

SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=12    SYMMETRY=d6h )
YOU MAY USE ONE OF THE FOLLOWING COMMANDS :
   ....
```

- We are done with the molecular geometry menu; to proceed, type

```
* <Enter>
```

Example 1 – Benzene: creating an input (step 4)

- Next is the „atomic attributes“ menu:

```
ATOMIC ATTRIBUTE DEFINITION MENU  ( #atoms=12    #bas=12    #ecp=0     )

b    : ASSIGN ATOMIC BASIS SETS
bb   : b RESTRICTED TO BASIS SET LIBRARY
bl   : LIST ATOMIC BASIS SETS ASSIGNED
....
```

- You may check that a default basis set def-SV(P) is assigned:

```
bl <Enter>
```

```
------------------------------------------------------------
INDEX | BASIS SET NICKNAME
------------------------------------------------------------
   1  | c def-SV(P)
   2  | h def-SV(P)
------------------------------------------------------------
```

- You may switch to other basis (e.g. def-TZVP, of triple-ζ quality):

```
b all def-TZVP <Enter>
```

- To proceed for the next menu, type

```
* <Enter>
```

Example 1 – Benzene: creating an input (step 5)

- The next menu is the one where **define** determines initial molecular orbitals with, e.g., an extended Hückel guess.

```
OCCUPATION NUMBER & MOLECULAR ORBITAL DEFINITION MENU

CHOOSE COMMAND
infsao      : OUTPUT SAO INFORMATION
eht         : PROVIDE MOS && OCCUPATION NUMBERS FROM EXTENDED HUECKEL GUESS
use <file>  : SUPPLY MO INFORMATION USING DATA FROM <file>
man         : MANUAL SPECIFICATION OF OCCUPATION NUMBERS
hcore       : HAMILTON CORE GUESS FOR MOS
&           : MOVE BACK TO THE ATOMIC ATTRIBUTES MENU
THE COMMANDS  use  OR  eht  OR  *  OR q(uit) TERMINATE THIS MENU !!!
FOR EXPLANATIONS APPEND A QUESTION MARK (?) TO ANY COMMAND
```

To choose the Hückel guess, type

```
eht <Enter>
```

- You will be asked a lot questions: accept all defaults

Example 1 – Benzene: creating an input (step 6)

- There are **two important** questions during that procedure:

```
ENTER THE MOLECULAR CHARGE  (DEFAULT=0)
```

If you have a charged system, you have to tell that **define** at this point. For now, we accept a neutral molecule by hitting `<Enter>`

- The second question is about occupation numbers

```
AUTOMATIC OCCUPATION NUMBER ASSIGNMENT ESTABLISHED !
FOUND CLOSED SHELL SYSTEM !
HOMO/LUMO-SEPARATION :  0.167139
ORBITAL  SYMMETRY      ENERGY     DEFAULT
(SHELL)    TYPE                  OCCUPATION
   11      3e1u       -0.51863       4
   12      1b1u       -0.50821       2
   13      1e1g       -0.48203       4
   14      3e2g       -0.43095       4
   15      1e2u       -0.26381       0
   16      1b1g       -0.08611       0
   17      4e1u        0.39013       0

DO YOU ACCEPT THIS OCCUPATION ?  DEFAULT=y
```

For our case, the restricted single occupation is OK, press `<Enter>`

Example 1 – Benzene: creating an input (step 7)

- We will get the last “general menu”:

```
GENERAL MENU : SELECT YOUR TOPIC
scf     : SELECT NON-DEFAULT SCF PARAMETER
mp2/cc2: OPTIONS AND DATA GROUPS FOR MP2, CC2, ETC.
ex      : EXCITED STATE AND RESPONSE OPTIONS
prop    : SELECT TOOLS FOR SCF-ORBITAL ANALYSIS
drv     : SELECT NON-DEFAULT INPUT PARAMETER FOR EVALUATION
          OF ANALYTICAL ENERGY DERIVATIVES
          (GRADIENTS, FORCE CONSTANTS)
rex     : SELECT OPTIONS FOR GEOMETRY UPDATES USING RELAX
stp     : SELECT NON-DEFAULT STRUCTURE OPTIMIZATION PARAMETER
e       : DEFINE EXTERNAL ELECTROSTATIC FIELD
dft     : DFT Parameters
 ...
```

- Choose DFT, by entering `dft <Enter>` , and then `on <Enter>`

```
STATUS OF DFT_OPTIONS:
DFT is used
  functional b-p
   ....
Just <ENTER>, q or '*' terminate this menu.
```

Type `q <Enter>` to quit and go back to the general menu

Example 1 – Benzene: creating an input (step 8)

- General menu allows further options to control over the calculation

```
 GENERAL MENU : SELECT YOUR TOPIC
     ....
ri      : RI Parameters
rijk    : RI-JK-HF Parameters
trunc   : USE TRUNCATED AUXBASIS DURING ITERATIONS
marij   : MULTIPOLE ACCELERATED RI-J
dis     : DISPLAY MOLECULAR GEOMETRY
list    : LIST OF CONTROL FILE
&       : GO BACK TO OCCUPATION/ORBITAL ASSIGNMENT MENU
* or q  : END OF DEFINE SESSION
```

- Calculations for larger molecules can be substantially accelerated if one employs a so-called resolution of the identity (RI) approximation for the evaluation of Coulomb energy integral, where the charge density is expanded over the auxiliary basis set.

Example 1 – Benzene: creating an input (step 9)

- To activate RI approximation, type `ri <Enter>`, followed by `on <Enter>` in the upcoming sub-menu.

- After done so, you will find

```
 STATUS OF RI-OPTIONS:
RI IS USED
Memory for RI:           200 Mb
Filename for auxbasis: auxbasis
   ....
Use <ENTER>, q, end, or '*' to leave this menu
```

- Type `q <Enter>` to go back to the general menu, followed by `q <Enter>` to finish define session.

Example 1 – Benzene: creating an input (remarks)

- After **define** session is finished, you'll find following files in your directory: `control, basis, auxbasis, mos.`
- File `control` contains all settings to control over your calculation.
- Files `basis & auxbasis` contain information about basis functions (contracted Gaussian type orbitals) and auxiliary basis set to be used for wave functions (molecular orbitals = MOs) and charge density expansions, respectively.
- File `mos` contains MO energies and expansion coefficients of MOs over the basis functions.
- Files `control` and `mos` will be updated during the calculation.

Example 1 – Benzene: running calculation

- To run a DFT calculation, call from the current directory

```
ridft > ridft.out &
```

- After a minute, scroll up the output file: you’ll find the energy diminishes within the self-consistent cycle, and is converged after 9 iterations:

```
ITERATION  ENERGY          1e-ENERGY        2e-ENERGY     NORM[dD(SAO)]  TOL
        .....
  4   -232.06592645088    -715.02052527     278.59415462    0.000D+00 0.327D-09
        .....
  5   -232.07193048496    -715.42066923     278.98829454    0.000D+00 0.327D-09
        .....
  6   -232.07269666729    -715.66752979     279.23438892    0.000D+00 0.327D-09
        .....
  7   -232.07272816194    -715.63626449     279.20309213    0.000D+00 0.327D-09
        .....
  8   -232.07273547481    -715.68122603     279.24804636    0.000D+00 0.327D-09

ENERGY CONVERGED !
        .....
  9   -232.07253692230    -715.67741588     279.24443476    0.000D+00 0.327D-09
        .....
  convergence criteria satisfied after    9 iterations
```

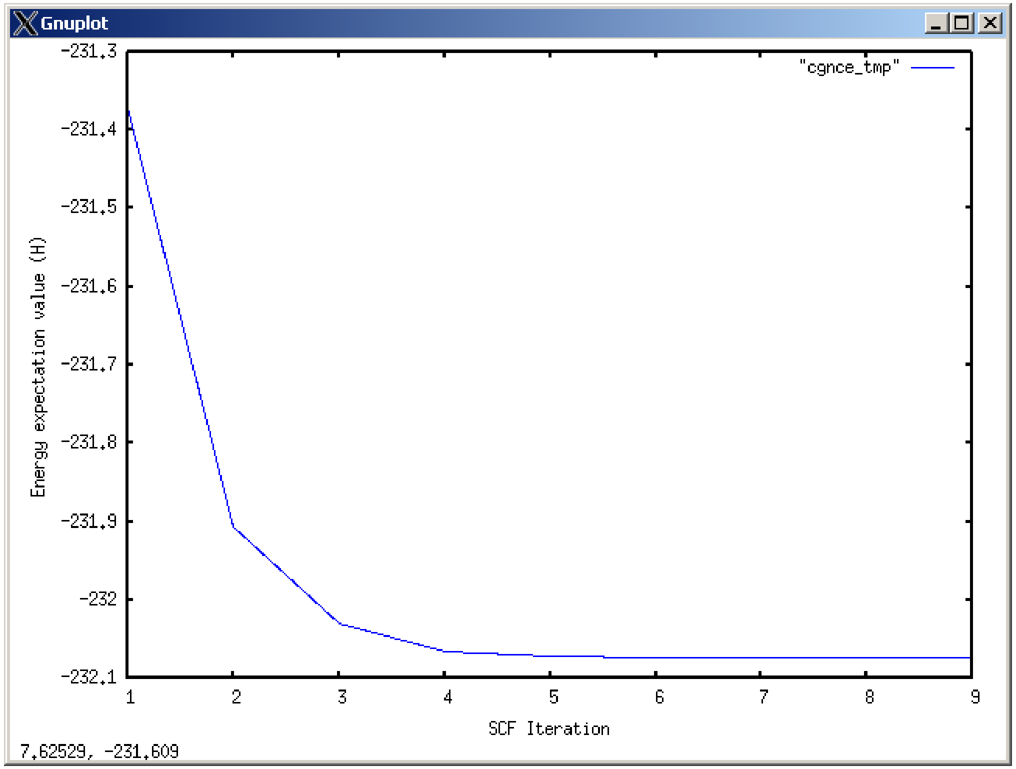
Reason for a slightly different value:
a denser grid for a numerical integration is used !

Example 1 – Benzene: checking convergence

- To check convergence of the energy, you can use script `cgnce`, which exports output info to `gnuplot`. Type

  `cngce ridft.out`

  The window on the right will show up (press `<Enter>` to quit)



- The converged ground state energy (in Hartree units) is appended to file `energy` (first column):

```
$energy      SCF                SCFKIN              SCFPOT
     1 -232.0725369223    229.7317088723    -461.8042457946
$end
```

Example 1 – Benzene: data post-processing

- Data post-processing script `eiger` provides information about orbital energies and occupations. Type `eiger > molecular.levels.dat` and afterwards `cat molecular.levels.dat`

```
 benzene : bp-86, def-SV(P)
Total energy =   -232.0725369223 H =     -6315.0186312 eV

 HOMO-LUMO Separation
   HOMO:     14.      1 e1g   -0.23145578 H =     -6.29824 eV
   LUMO:     15.      1 e2u   -0.03736717 H =     -1.01681 eV
   Gap :                      +0.19408861 H =     +5.28142 eV

Number of MOs=     64, Electrons=     42.00, Symmetry: d6h

   Nr.   Orbital    Occupation        Energy
      ....
   16.      4 a1g                  +0.043231 H =       +1.176 eV
   15.      1 e2u                  -0.037367 H =       -1.017 eV
   14.      1 e1g      4.000       -0.231456 H =       -6.298 eV
   13.      3 e2g      4.000       -0.304977 H =       -8.299 eV
   12.      1 a2u      2.000       -0.333260 H =       -9.068 eV
   11.      3 e1u      4.000       -0.378680 H =      -10.304 eV
   10.      1 b1u      2.000       -0.401898 H =      -10.936 eV
       ....
```

2x degenerate LUMO

2x degenerate HOMO

Example 1 – Benzene: structure optimization

- To perform geometry optimization of benzene, make a new directory:

```
cd ~/ABC_of_DFT/hands-on-
              sessions/session.2/example.1.benzene
cp -r my.benzene my.benzene.relaxed
cd my.benzene.relaxed
```

- Call from the current directory `jobex` script:

```
jobex -ri -grad -c 25
```

`-ri` tells the script to use modules with RI implementation;

`-grad` tells to perform a gradient evaluation as the first step;

`-c <number>` accounts for a maximum amount of relaxation steps

- Further information can be obtained via `jobex -h`

Example 1 – Benzene: structure optimization

- At each step of optimization procedure, information on the energy is appended to the file `energy`; type: `cat energy`

```
$energy      SCF                SCFKIN             SCFPOT
     1 -232.0725369223     229.7317088723     -461.8042457946
     2 -232.0764088838     229.3325106808     -461.4089195645
     3 -232.0765621000     229.3004492613     -461.3770113613
     4 -232.0765632300     229.2972414010     -461.3738046309
     5 -232.0765631460     229.2967217448     -461.3732848908
     6 -232.0765631243     229.2965858552     -461.3731489795
$end
```

- Information on gradient and new coordinates is appended to the file `gradient`; type: `grep cycle gradient`

```
cycle =      1    SCF energy =   -232.0725369223   |dE/dxyz| =  0.042942
cycle =      2    SCF energy =   -232.0764088838   |dE/dxyz| =  0.016091
cycle =      3    SCF energy =   -232.0765621000   |dE/dxyz| =  0.001375
cycle =      4    SCF energy =   -232.0765632300   |dE/dxyz| =  0.000194
cycle =      5    SCF energy =   -232.0765631460   |dE/dxyz| =  0.000021
```

- Question: what are the C-C and C-H bond lengths that you've got? How well do these values compare with experimental data?

Example 1 – Benzene: visualization of orbitals

- Go to your directory with the calculation for benzene, e.g.

```
cd ~/ABC_of_DFT/hands-on-
  sessions/session.2/example.1.benzene/my.benzene.relaxed
```

- Call `eiger` script to get info about orbital energies
- You'll see HOMO is orbital #14, LUMO is #15, etc …
- To plot frontier orbitals, add to `control` file a line (before `$end`)

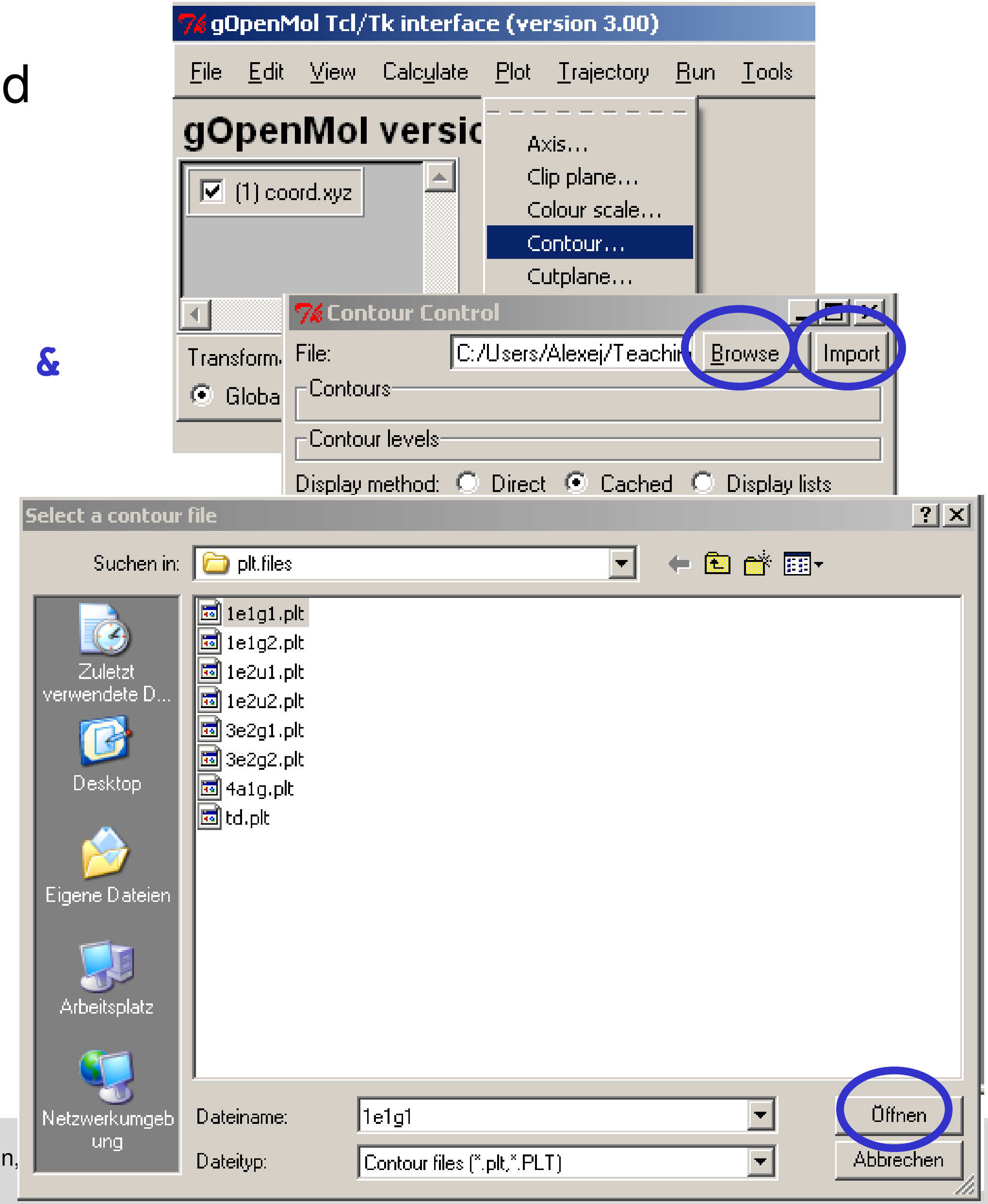
```
$pointval mo 13-16
```

  and call: `ridft -proper`

- You'll see four `*.plt` files on output. Each file name is associated with one orbital
- To plot a charge density, a line `$pointval dens` is required in `control` file

Example 1 – Benzene: visualization of orbitals

- **`*.plt`** files can be visualized with gOpenMol.
- Call it from a command line: **`rungOpenMol coord.xyz &`**
- Go to the menu: **`Plot -> Contour...`**
- You will get the window where you can load in the **`*.plt`** files: first click on **`Browse`**, load the file, then press **`Import`**



☑ (1) coord.xyz

File: C:/Users/Alexej/Teachin

Display method: ○ Direct ● Cached ○ Display lists

Suchen in: plt.files

Dateiname: 1e1g1

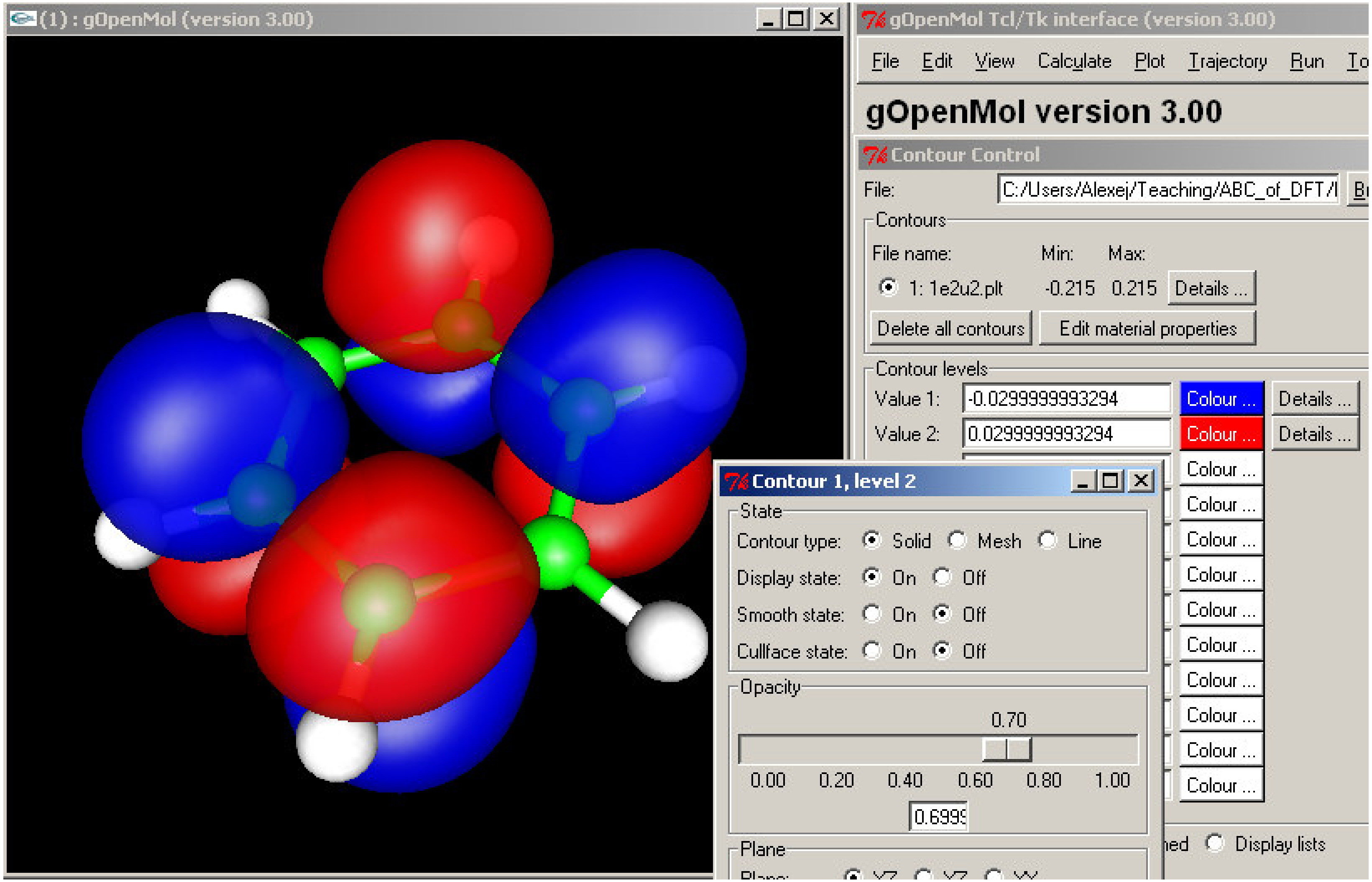
Dateityp: Contour files (*.plt,*.PLT)

Example 1 – Benzene: visualization of orbitals

- The Contour Control Window will expand, writing out the minimum and maximum value of the wave function amplitude (or density) that has been read in.
- For each of the 10 fields, called Value 1 till Value 10, you can now enter a value that will define the iso-surface of the wave function's amplitude (or density iso-surface, if charge density is plotted).
- With **`Colour...`** and **`Details...`** you can change the color and the opacity of each contour.
- Do not forget to click on the **`Apply`** button.

Example 1 – Benzene: visualization of orbitals

- Example shows one of the antibonding (π*-like) LUMOs of benzene



gOpenMol version 3.00

File: C:/Users/Alexej/Teaching/ABC_of_DFT/I

Contours

File name:	Min:	Max:
● 1: 1e2u2.plt	-0.215	0.215

Contour levels

Value 1: -0.0299999993294

Value 2: 0.0299999993294

State

Contour type: ● Solid ○ Mesh ○ Line

Display state: ● On ○ Off

Smooth state: ○ On ● Off

Cullface state: ○ On ● Off

Opacity

0.70

0.00 0.20 0.40 0.60 0.80 1.00

0.6999

ned ○ Display lists

Example 1 – Benzene: visualization of orbitals

- Exercise: plot two degenerate HOMOs of benzene. Convince yourself that these two orbitals form an aromatic π-electron system, delocalized over the entire ring.

- Userful remark: your pictures can be exported to graphics files. For that, use the menu of gOpenMol

  `File -> Hardcopy ...`

  where an upcoming window allows to choose among graphics formats.

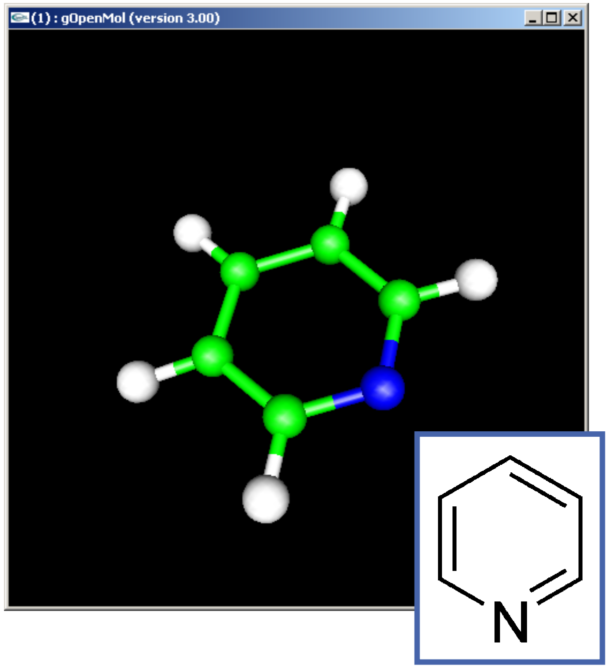
Example 2 – Pyridine (exercise)

- Consider a pyridine molecule, C_5H_5N, which is structurally related to benzene, with one CH group replaced by N atom. Look at `~/ABC_of_DFT/hands-on-sessions/session.2/example.2.pyridine/structure.pyridine`

- Visualize atomic structure of the molecule.

- Compute electronic structure of pyridine, assuming a default C_{2v} symmetry.

- Perform atomic structure relaxation.



Example 2 – Pyridine (exercise)

- Visualize frontier molecular orbitals of pyridine (few occupied and few unoccupied ones).

- Questions:

1. N atom has a single “lone pair” pointing outwards the ring. One of the σ-type molecular orbitals resembles this lone pair. Which orbital is that?
2. Due to a structural similarity, the some frontier molecular orbitals of pyridine resemble double degenerate HOMO (π) and LUMO (π*) of benzene. Can you show, which are these orbitals? Why degeneracy is lifted in case of pyridine?

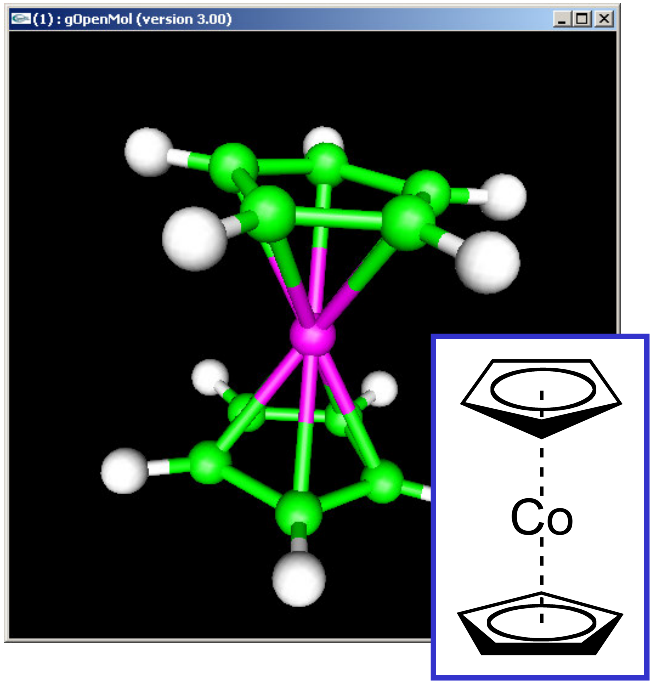
Example 3 – Cobaltocene (open shell: step 1)

- Structure of $Co(C_5H_5)_2$ can be found at `~/ABC_of_DFT/hands-on-sessions/session.2/example.3.open-shell.cobaltocene.d5d/structure.cobaltocene`

- When creating an input with define, impose a high D_{5d} symmetry (`desy 0.3`)

- Due to orbital energies degeneracy, automatic occupation of Hückel's orbitals will fail.

- Help define by choosing an open shell occupation for a charge neutral complex with **7 unpaired spins as a starting guess** **(please, look at the next slide …)**



Example 3 – Cobaltocene (open shell: step 2)

- After you’ve specified a zero charge on the complex, you’ll get …

```
NUMBER OF ELECTRONS IN YOUR MOLECULE IS   97

 YOU HAVE TO ASSIGN OCCUPATION NUMBERS MANUALLY
 >> UHF << : ALPHA AND BETA SHELLS  (a,b)
 >> RHF << : CLOSED AND OPEN SHELLS (c,o)

 OCCUPATION NUMBER ASSIGNMENT MENU  ( #e=97  #c=0  #o=0)

 s         : CHOOSE UHF SINGLET OCCUPATION
 t         : CHOOSE UHF TRIPLET OCCUPATION
 u <int>   : CHOOSE UHF WITH <int> UNPAIRED ELECTRONS
 ...
 ENTER COMMAND
```

Type `u 7 <Enter>`

(1, 3, or 5 unpaired spins will not be accepted)

- Proceed further with define, setting up DFT, RI, MARI-J options

Example 3 – Cobaltocene (open shell: step 3)

- After define session is finished, you'll find two files, `alpha` and `beta`, accounting for MOs with α ("up") and β ("down") spins

- Open shell systems (and, also, large systems) require electronic temperature smearing of occupation numbers within first steps of self-consistent cycle to encourage convergence.

- That is done with help of `mkfermi` script, which modifies your `control` file by adding (among others) the following line:

  ```
  $fermi tmstrt=300 tmend=10 tmfac=0.8 hlcrt=0.5 stop=1.0E-3
  ```

  The initial temperature 300 K is reduced at each cycle by the factor 0.8 until it reaches the value 10 K

- To run calculation, type

  ```
  mkfermi
  ridft | tee cobaltocene.out
  ```

Example 3 – Cobaltocene (open shell: step 4)

- After single-point energy calculation is finished, scroll up the output file. You'll find the DFT ground state with one unpaired spin:

```
 ITERATION  ENERGY          1e-ENERGY        2e-ENERGY     NORM[dD(SAO)]  TOL
  60  -1769.6462134688   -4216.3089987     1552.3456264    0.000D+00 0.170D-09
                            Exc = -117.556943916     Coul =  1669.90257029
                         Ntotal = 96.999988223       Nspin = 1.0000005307
                             Na = 48.999994377          Nb = 47.999993846
                            current damping = 9.900
          ...

 End of SCF iterations

   convergence criteria satisfied after   60 iterations
```

Number of unpaired spins

- Proceed further with geometry optimization: set electronic temperature to 10 K by modifying (red) one line in `control` file to

  `$fermi tmstrt=10 tmend=10 tmfac=1.0 hlcrt=0.5 stop=1.0E-3`

  Perform structure relaxation:

  `nohup jobex -ri -grad -c 50 > jobex.out &`

Example 3 – Cobaltocene (open shell: step 5)

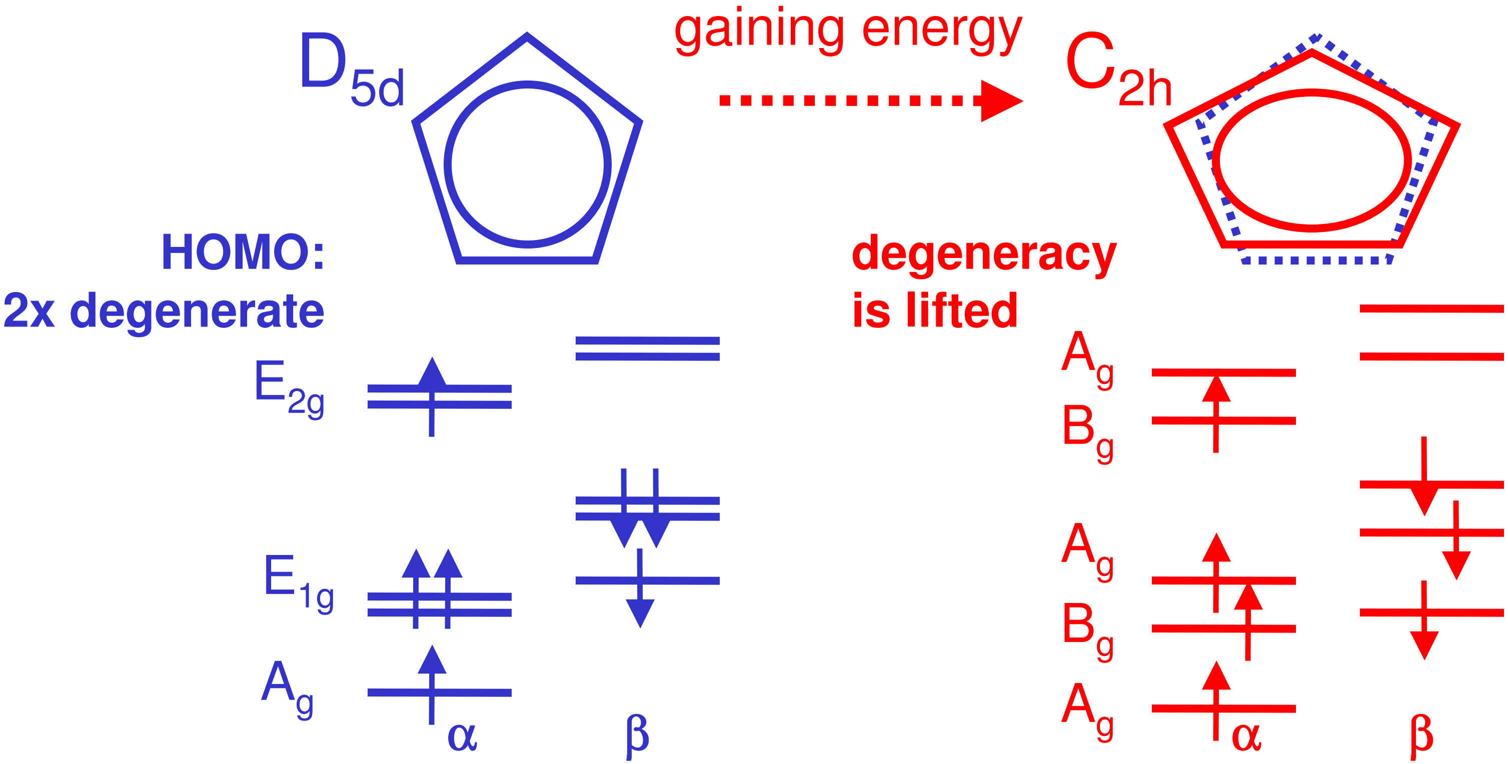
- Get information about orbital energies (`eiger` script)

```
 cobaltocene d5d
Total energy =  -1769.6597050510 H =    -48154.9180980 eV

 HOMO-LUMO Separation
   HOMO:     63. a   5 e2g   -0.09829840 H =     -2.67484 eV
   LUMO:     64. b   5 e2g   -0.06691752 H =     -1.82092 eV
   Gap :                     +0.03138089 H =     +0.85392 eV
Number of MOs=    226, Electrons=     97.00, Symmetry: d5d

   Nr.    Orbital    Occupation       Energy
     ...

   65. a   4 e2u                    +0.021386 H =       +0.582 eV
   64. b   5 e2g                    -0.066918 H =       -1.821 eV
   63. a   5 e2g     1.000          -0.098298 H =       -2.675 eV
   62. b   4 e1g     2.000          -0.162209 H =       -4.414 eV
   61. b   8 a1g     1.000          -0.174730 H =       -4.755 eV
   60. a   4 e1g     2.000          -0.179628 H =       -4.888 eV
   59. a   8 a1g     1.000          -0.187986 H =       -5.115 eV
```

HOMO : double degenerate α level (E_{2g} symmetry) is occupied by one electron

Example 4 – Cobaltocene (Jahn-Teller effect)

- In nature, orbital energies degeneracy is lifted due to Jahn-Teller distortions: a non-linear molecule with a degenerate electronic ground state will undergo a geometrical distortion, which removes that degeneracy, because the distortion lowers the overall energy of the complex.



Example 4 – Cobaltocene (Jahn-Teller effect)

- **Exercise: illustrate Jahn-Teller effect with your calculation**

- Take a structure of Co(C_5H_5)$_2$ at `~/ABC_of_DFT/hands-on-sessions/session.2/example.4.open-shell.cobaltocene.c2h/structure.cobaltocene`
- Within define session, choose C_{2h} symmetry.
- For a charge neutral complex, approve an open shell occupation with one unpaired spin.
- Perform a DFT calculation, and a subsequent structural relaxation: do not forget about the Fermi smearing (**`mkfermi`** script) !

Example 4 – Cobaltocene (Jahn-Teller effect)

- Estimate energy difference for structures with D_{5d} and C_{2h} symmetry.
  Answer: GS DFT energy for the C_{2h} structure is lower by ~ 0.11 eV
  (value is given for the def-SV(P) basis, “b-p” BP86 functional)

- Compare KS spectrum of complexes with different symmetries. You’ll find, the “HOMO doublet” splits to HOMO (occupied) and LUMO (unoccupied) levels. What is the splitting?
  Answer: ~ 0.4 eV (def-SV(P) basis, “b-p” BP86 functional)

- Hint: you can compare output of your calculations for the two cases with those at
  D_{5d}: `.../session.2/example.3.open-shell.cobaltocene.d5d/output.cobaltocene/output.jobex`
  C_{2h}: `.../session.2/example.4.open-shell.cobaltocene.c2h/output.cobaltocene/output.jobex`

Example 4 – Cobaltocene: charge & spin densities

- **Exercise:** Plot charge and spin densities of cobaltocene: show that unpaired spin is localized mainly on Co atom. That may look like …