```
      --------------------------
  1   :     1.7561      2.2540
  2   :    -1.7562      2.2541
  3   :     0.0001      0.9800
```

The output from this calculation shows the expected results, with the local site spins being close to their ideal value 2.5 which would hold for a high-spin Fe(III) ion.

5.1.11 Population Analysis of UNOs

Population analyses for *UHF natural Orbitals* can be requested via the respective print options in the `%output` block:

```
%output
  Print[ P_UNO_OccNum      ] = 1;         # Occupation numbers
  Print[ P_UNO_AtPopMO_M  ] = 0;          # Mulliken atom pop. per UNO
  Print[ P_UNO_OrbPopMO_M] = 0;           # Mulliken orbital pop. per UNO
  Print[ P_UNO_ReducedOrbPopMO_M] = 0;  # Mulliken reduced orbital pop. per UNO
  Print[ P_UNO_AtPopMO_L  ] = 0;          # Loewdin atom pop. per UNO
  Print[ P_UNO_OrbPopMO_L] = 0;           # Loewdin orbital pop. per UNO
  Print[ P_UNO_ReducedOrbPopMO_L] = 0;  # Loewdin reduced orbital pop. per UNO
end
```

5.1.12 Keywords

A collection of useful keywords in the context of population analyses is given in Table 5.1, Table 5.2, Table 5.3, and Table 5.4.

Table 5.1: Simple input keywords for population analyses.

Keyword	Description
AllPop	Activates all population analyses
NoPop	Deactivates all population analyses
ReducedPop	Prints reduced orbital populations per MO
NoReducedPop	Deactivates printing of reduced orbital populations
Mulliken	Activates *Mulliken* population analysis
NoMulliken	Deactivates Mulliken population analysis
Loewdin	Activates *Löwdin* population analysis
NoLoewdin	Deactivates Löwdin population analysis
Mayer	Activates *Mayer* population analysis
NoMayer	Deactivates Mayer population analysis
NPA	Activates *NPA*. NBO program required
NBO	Activates *NPA* and *NBO* analyses. NBO program required
NoNBO	Deactivates NBO
NoNPA	Deactivates NPA and NBO
MBIS	Activates *MBIS* population analysis
CHELPG	Requests calculation of *CHELPG* charges
CHELPG(LARGE)	Requests calculation of *CHELPG* charges with large grid

Table 5.2: `%output` block input keywords and options for population analyses.

Keyword	Option	Description
Print[<option>]	P_Mayer	Print Mayer population analysis (Default = on)
	P_NatPop	Print Natural population analysis (Default = off)

Table 5.2 – continued from previous page

Keyword	Option	Description
	P_NPA	Print Natural population analysis (Default = off)
	P_Hirshfeld	Print Hirshfeld population analysis (Default = off)
	P_MBIS	Print MBIS population analysis (Default = off)
	P_Mulliken	Print Mulliken population analysis (Default = on)
	P_AtCharges_M	Print Mulliken atomic charges
	P_OrbCharges_M	Print Mulliken orbital charges
	P_FragCharges_M	Print Mulliken fragment charges
	P_FragBondOrder_M	Print Mulliken fragment bond orders
	P_BondOrder_M	Print Mulliken bond orders
	P_ReducedOrbPop_M	Print Mulliken reduced orbital charges
	P_FragPopMO_M	Print Mulliken fragment population for each MO
	P_FragOvlMO_M	Print Mulliken overlap populations per fragment pair
	P_AtPopMO_M	Print Mulliken atomic charges in each MO
	P_OrbPopMO_M	Print Mulliken orbital population for each MO
	P_ReducedOrbPopMO_M	Print Mulliken reduced orbital population for each MO
	P_Loewdin	Print Loewdin population analysis (Default = on)
	P_AtCharges_L	Print Loewdin atomic charges
	P_OrbCharges_L	Print Loewdin orbital charges
	P_FragCharges_L	Print Loewdin fragment charges
	P_FragBondOrder_L	Print Loewdin fragment bond orders
	P_BondOrder_L	Print Loewdin bond orders
	P_ReducedOrbPop_L	Print Loewdin reduced orbital charges
	P_FragPopMO_L	Print Loewdin fragment population for each MO
	P_FragOvlMO_L	Print Loewdin overlap populations per fragment pair
	P_AtPopMO_L	Print Loewdin atomic charges in each MO
	P_OrbPopMO_L	Print Loewdin orbital population for each MO
	P_ReducedOrbPopMO_L	Print Loewdin reduced orbital population for each MO
	P_Fragments	Print fragment information
	P_GUESSPOP	Print initial guess populations
	P_UNO_FragPopMO_M	Print Mulliken fragment population per UNO
	P_UNO_OrbPopMO_M	Print Mulliken orbital pop. per UNO
	P_UNO_AtPopMO_M	Print Mulliken atomic charges per UNO
	P_UNO_ReducedOrbPopMO_M	Print Mulliken reduced orbital pop. per UNO
	P_UNO_FragPopMO_L	Print Loewdin fragment population per UNO
	P_UNO_OrbPopMO_L	Print Loewdin orbital pop. per UNO
	P_UNO_AtPopMO_L	Print Loewdin atomic charges per UNO
	P_UNO_ReducedOrbPopMO_L	Print Loewdin reduced orbital pop. per UNO
	P_UNO_OccNum	Print occupation numbers per UNO

Table 5.3: `%method` block input keywords and options for population analyses.

Keyword	Option	Description
LOEWDIN_BONDORDEI	<real>	Sets printing threshold for Löwdin bond orders (default = 0.05)
MAYER_BONDORDERTI	<real>	Sets printing threshold for Mayer bond orders (default = 0.1)
MBIS_CHARGETHRES	<real>	Sets convergence threshold for MBIS charges (default = 10^{-6})
MBIS_LARGEPRINT	true/false	Activate printing of *MBIS Quantities* (default = false)
MBIS_ORIGIN_MULT	CenterOfCoor(	Sets origin for MBIS properties to center of coordinate system (0,0,0)
	CenterOfMass	Sets origin for MBIS properties to center of mass
	CenterOfNucCh	Sets origin for MBIS properties to center of nuclear charge
	CenterXYZ	Sets origin for MBIS properties to arbitrary position, set coordinates with MBIS_ORIMULT_XYZ
	CenterOfEachA	Sets origin for MBIS properties to center of each atom (default)
MBIS_ORIMULT_XYZ	<x,y,z>	Set the coordinates, otherwise 0,0,0 (unit: Angstrom)

Table 5.4: `%chelpg` block input keywords and options for CHELPG charges.

Keyword	Option	Description
GRID	<real>	Spacing of the regular grid in Å (default = 0.3)
RMAX	<real>	Maximum distance of all atoms to any gridpoint in Å (default = 2.8)
VDWRADII	COSMO	Activates usage of COSMO VdW radii of Atoms (default)
	BW	Activates usage of Breneman, Wiberg radii
DIPOLE	false/true	If true, the charges also reproduce the total dipole moment (default = false)

5.2 Natural Bond Orbital (NBO) Analysis

A popular and useful method for population analysis is the natural bond orbital analysis due to Weinhold and co-workers. It is implemented in the **NBO** program which is distributed in older versions via the CCL list and in newer versions via the University of Wisconsin/Madison. Information about the NBO program can be found at http://www.chem.wisc.edu/~nbo7. In order to use it together with ORCA you need a version of the stand-alone executable. Starting with version 3.1.x ORCA can only be used with NBO6 or NBO7. To specify the NBO executable the environment variable NBOEXE=/full/name/of/nbo7-executable has to be set. As the NBO part of the interface is not independent of the integer data-type width (i4 or i8), the NBO executable which will be used together with ORCA has to be compiled using i4!

ORCA features two methods to interface with the **NBO** program: ! NBO keyword and the `%nbo`-block. The following example illustrates the use for formaldehyde:

```
#
# Test the interface to the NBO program
#
! RHF SVP NBO

* xyz 0 1
  C     0.000000    0.000000    0.000000
  O     1.200000    0.000000    0.000000
  H    -0.550000    0.952628    0.000000
  H    -0.550000   -0.952628   -0.000000
*
```

This produces the following output:

```
Now starting NBO....

********************************** NBO 7.0 **********************************
           N A T U R A L   A T O M I C   O R B I T A L   A N D
         N A T U R A L   B O N D   O R B I T A L   A N A L Y S I S
*********************** development version (D000000) ***********************
  (c) Copyright 1996-2018 Board of Regents of the University of Wisconsin System
      on behalf of the Theoretical Chemistry Institute.  All rights reserved.

         Cite this program [NBO 7.0.0 (15-Nov-2018)] as:

         NBO 7.0.  E. D. Glendening, J. K. Badenhoop, A. E. Reed,
         J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou,
         C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute,
         University of Wisconsin, Madison, WI (2018)


      /NPA    / : Natural Population Analysis
      /NBO    / : Natural Bond Orbital Analysis
      /AONBO  / : Checkpoint the AO to NBO transformation
      /ARCHIVE/ : Write the archive file to lfn47

 Job title:  ORCA Job: NBO_1


 NATURAL POPULATIONS:  Natural atomic orbital occupancies

  NAO Atom No lang    Type(AO)    Occupancy      Energy
 -------------------------------------------------------
   1   C  1  s      Cor( 1s)     1.99997      -11.34329
   2   C  1  s      Val( 2s)     1.01533       -0.17540
   3   C  1  s      Ryd( 3s)     0.00701        0.61376
   4   C  1  px     Val( 2p)     0.81697        0.08822
   5   C  1  px     Ryd( 3p)     0.01268        0.63900
   6   C  1  py     Val( 2p)     1.09795       -0.01243
   7   C  1  py     Ryd( 3p)     0.00055        0.80803
   8   C  1  pz     Val( 2p)     0.66003       -0.03464
   9   C  1  pz     Ryd( 3p)     0.00283        0.62824
  10   C  1  dxy    Ryd( 3d)     0.00576        2.75039
  11   C  1  dxz    Ryd( 3d)     0.00375        2.25746
  12   C  1  dyz    Ryd( 3d)     0.00000        2.08566
  13   C  1  dx2y2  Ryd( 3d)     0.00337        2.74845
  14   C  1  dz2    Ryd( 3d)     0.00114        2.40647

  15   O  2  s      Cor( 1s)     1.99998      -20.56485
  16   O  2  s      Val( 2s)     1.70725       -0.92198
  17   O  2  s      Ryd( 3s)     0.00171        1.55322
  18   O  2  px     Val( 2p)     1.62177       -0.42255
  19   O  2  px     Ryd( 3p)     0.00079        1.29654
  20   O  2  py     Val( 2p)     1.91529       -0.46844
  21   O  2  py     Ryd( 3p)     0.00383        1.41052
  22   O  2  pz     Val( 2p)     1.32984       -0.28626
  23   O  2  pz     Ryd( 3p)     0.00011        1.30080
  24   O  2  dxy    Ryd( 3d)     0.00213        3.26414
  25   O  2  dxz    Ryd( 3d)     0.00340        3.20490
  26   O  2  dyz    Ryd( 3d)     0.00000        2.98918
  27   O  2  dx2y2  Ryd( 3d)     0.00406        3.55008
  28   O  2  dz2    Ryd( 3d)     0.00119        3.17511

  29   H  3  s      Val( 1s)     0.88576        0.07107
  30   H  3  s      Ryd( 2s)     0.00298        0.41181
  31   H  3  px     Ryd( 2p)     0.00030        2.18260
  32   H  3  py     Ryd( 2p)     0.00159        2.49146
```

```
 33    H  3  pz    Ryd( 2p)    0.00002         1.85643


 34    H  4  s     Val( 1s)    0.88576         0.07107
 35    H  4  s     Ryd( 2s)    0.00298         0.41181
 36    H  4  px    Ryd( 2p)    0.00030         2.18260
 37    H  4  py    Ryd( 2p)    0.00159         2.49146
 38    H  4  pz    Ryd( 2p)    0.00002         1.85643



Summary of Natural Population Analysis:

                                 Natural Population
               Natural    ---------------------------------------------
 Atom No        Charge       Core      Valence    Rydberg      Total
----------------------------------------------------------------------
   C  1        0.37265     1.99997     3.59028    0.03709     5.62735
   O  2       -0.59134     1.99998     6.57415    0.01720     8.59134
   H  3        0.10934     0.00000     0.88576    0.00489     0.89066
   H  4        0.10934     0.00000     0.88576    0.00489     0.89066
======================================================================
* Total * -0.00000        3.99995    11.93596    0.06408    16.00000


                           Natural Population
-----------------------------------------------------------
  Core                      3.99995 ( 99.9988% of    4)
  Valence                  11.93596 ( 99.4664% of   12)
  Natural Minimal Basis    15.93592 ( 99.5995% of   16)
  Natural Rydberg Basis     0.06408 (  0.4005% of   16)
-----------------------------------------------------------


   Atom No          Natural Electron Configuration
-----------------------------------------------------------------------------
    C  1       [core]2s( 1.02)2p( 2.57)3s( 0.01)3p( 0.02)3d( 0.01)
    O  2       [core]2s( 1.71)2p( 4.87)3d( 0.01)
    H  3             1s( 0.89)
    H  4             1s( 0.89)



NATURAL BOND ORBITAL ANALYSIS:

                      Occupancies       Lewis Structure     Low   High
         Max   Occ    ------------------ ----------------    occ   occ
 Cycle  Ctr  Thresh   Lewis    non-Lewis  CR  BD  nC  LP     (L)   (NL)
=============================================================================
   1     2    1.90   15.89671   0.10329    2   4   0   2      0     0
-----------------------------------------------------------------------------


Structure accepted: No low occupancy Lewis orbitals


----------------------------------------------------------
  Core                      3.99995 ( 99.999% of    4)
  Valence Lewis            11.89676 ( 99.140% of   12)
 =================         ============================
  Total Lewis              15.89671 ( 99.354% of   16)
----------------------------------------------------------
  Valence non-Lewis         0.07835 (  0.490% of   16)
  Rydberg non-Lewis         0.02493 (  0.156% of   16)
 =================         ============================
  Total non-Lewis           0.10329 (  0.646% of   16)
----------------------------------------------------------
```

```
   (Occupancy)   Bond orbital / Coefficients / Hybrids
---------------- Lewis ------------------------------------------------------
 1. (1.99997) CR ( 1) C  1            s(100.00%)
                                      1.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000
 2. (1.99998) CR ( 1) O  2            s(100.00%)
                                      1.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000
 3. (1.98853) LP ( 1) O  2            s( 56.22%)p 0.78( 43.73%)d 0.00(  0.05%)
                                      0.0000  0.7496 -0.0170  0.6612  0.0069
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000 -0.0201  0.0100
 4. (1.91757) LP ( 2) O  2            s(  0.00%)p 1.00( 99.89%)d 0.00(  0.11%)
                                      0.0000  0.0000  0.0000 -0.0000 -0.0000
                                      0.9994 -0.0098  0.0000 -0.0000 -0.0330
                                     -0.0000  0.0000  0.0000 -0.0000
 5. (1.99996) BD ( 1) C  1- O  2
         ( 33.33%)   0.5773* C  1 s(  0.00%)p 1.00( 99.44%)d 0.01(  0.56%)
                                      0.0000 -0.0000 -0.0000  0.0000 -0.0000
                                     -0.0000  0.0000  0.9951 -0.0652 -0.0000
                                      0.0750  0.0000 -0.0000  0.0000
         ( 66.67%)   0.8165* O  2 s(  0.00%)p 1.00( 99.75%)d 0.00(  0.25%)
                                      0.0000 -0.0000  0.0000  0.0000 -0.0000
                                     -0.0000  0.0000  0.9987 -0.0090  0.0000
                                     -0.0505  0.0000  0.0000 -0.0000
 6. (1.99975) BD ( 2) C  1- O  2
         ( 32.59%)   0.5709* C  1 s( 32.18%)p 2.09( 67.35%)d 0.01(  0.46%)
                                      0.0000  0.5628  0.0714  0.8149  0.0973
                                     -0.0000 -0.0000 -0.0000 -0.0000 -0.0000
                                     -0.0000  0.0000  0.0618 -0.0286
         ( 67.41%)   0.8211* O  2 s( 43.84%)p 1.27( 55.85%)d 0.01(  0.31%)
                                      0.0000  0.6615  0.0284 -0.7470 -0.0215
                                     -0.0000  0.0000 -0.0000 -0.0000  0.0000
                                      0.0000  0.0000  0.0490 -0.0270
 7. (1.99548) BD ( 1) C  1- H  3
         ( 56.63%)   0.7526* C  1 s( 33.98%)p 1.94( 65.86%)d 0.00(  0.16%)
                                      0.0000  0.5826 -0.0192 -0.3995 -0.0029
                                      0.7063 -0.0087  0.0000 -0.0000 -0.0318
                                     -0.0000  0.0000 -0.0180 -0.0153
         ( 43.37%)   0.6585* H  3 s( 99.79%)p 0.00(  0.21%)
                                      0.9989 -0.0095  0.0184 -0.0416  0.0000
 8. (1.99548) BD ( 1) C  1- H  4
         ( 56.63%)   0.7526* C  1 s( 33.98%)p 1.94( 65.86%)d 0.00(  0.16%)
                                      0.0000  0.5826 -0.0192 -0.3995 -0.0029
                                     -0.7063  0.0087 -0.0000  0.0000  0.0318
                                      0.0000  0.0000 -0.0180 -0.0153
         ( 43.37%)   0.6585* H  4 s( 99.79%)p 0.00(  0.21%)
                                      0.9989 -0.0095  0.0184  0.0416 -0.0000
--------------- non-Lewis ---------------------------------------------------
 9. (0.00000) BD*( 1) C  1- O  2
         ( 66.67%)   0.8165* C  1 s(  0.00%)p 1.00( 99.44%)d 0.01(  0.56%)
         ( 33.33%)  -0.5773* O  2 s(  0.00%)p 1.00( 99.75%)d 0.00(  0.25%)
10. (0.00000) BD*( 2) C  1- O  2
         ( 67.41%)   0.8211* C  1 s( 32.18%)p 2.09( 67.35%)d 0.01(  0.46%)
         ( 32.59%)  -0.5709* O  2 s( 43.84%)p 1.27( 55.85%)d 0.01(  0.31%)
11. (0.03918) BD*( 1) C  1- H  3
         ( 43.37%)   0.6585* C  1 s( 33.98%)p 1.94( 65.86%)d 0.00(  0.16%)
                                      0.0000 -0.5826  0.0192  0.3995  0.0029
```

```
                                        -0.7063  0.0087 -0.0000  0.0000  0.0318
                                         0.0000  0.0000  0.0180  0.0153
            ( 56.63%)  -0.7526* H  3 s( 99.79%)p 0.00(  0.21%)
                                        -0.9989  0.0095 -0.0184  0.0416 -0.0000
 12. (0.03918) BD*( 1) C  1- H  4
            ( 43.37%)   0.6585* C  1 s( 33.98%)p 1.94( 65.86%)d 0.00(  0.16%)
                                         0.0000 -0.5826  0.0192  0.3995  0.0029
                                         0.7063 -0.0087  0.0000 -0.0000 -0.0318
                                        -0.0000  0.0000  0.0180  0.0153
            ( 56.63%)  -0.7526* H  4 s( 99.79%)p 0.00(  0.21%)
                                        -0.9989  0.0095 -0.0184 -0.0416  0.0000
 13. (0.00969) RY ( 1) C  1           s( 29.83%)p 2.30( 68.57%)d 0.05(  1.60%)
                                         0.0000 -0.0565  0.5432 -0.1169  0.8198
                                         0.0000 -0.0000  0.0000 -0.0000 -0.0000
                                         0.0000  0.0000  0.1087 -0.0648
 14. (0.00517) RY ( 2) C  1           s(  0.00%)p 1.00(  9.56%)d 9.46( 90.44%)
                                         0.0000  0.0000 -0.0000  0.0000 -0.0000
                                         0.0465  0.3057  0.0000 -0.0000  0.9510
                                         0.0000  0.0000 -0.0000 -0.0000
 15. (0.00001) RY ( 3) C  1           s( 20.02%)p 0.82( 16.47%)d 3.17( 63.52%)
 16. (0.00000) RY ( 4) C  1           s(  0.00%)p 1.00( 90.64%)d 0.10(  9.36%)
 17. (0.00000) RY ( 5) C  1           s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
 18. (0.00000) RY ( 6) C  1           s( 42.72%)p 0.35( 15.02%)d 0.99( 42.26%)
 19. (0.00000) RY ( 7) C  1           s(  0.00%)p 1.00(  0.56%)d99.99( 99.44%)
 20. (0.00000) RY ( 8) C  1           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 21. (0.00000) RY ( 9) C  1           s(  7.29%)p 0.09(  0.66%)d12.63( 92.05%)
 22. (0.00368) RY ( 1) O  2           s(  0.00%)p 1.00( 98.96%)d 0.01(  1.04%)
                                         0.0000 -0.0000 -0.0000  0.0000  0.0000
                                         0.0064  0.9948 -0.0000  0.0000 -0.1018
                                         0.0000  0.0000 -0.0000  0.0000
 23. (0.00014) RY ( 2) O  2           s( 35.10%)p 1.44( 50.60%)d 0.41( 14.30%)
                                         0.0000 -0.0178  0.5922  0.0556 -0.7091
                                         0.0000 -0.0000 -0.0000  0.0000 -0.0000
                                         0.0000  0.0000  0.3336 -0.1780
 24. (0.00000) RY ( 3) O  2           s( 56.05%)p 0.25( 13.79%)d 0.54( 30.17%)
 25. (0.00000) RY ( 4) O  2           s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
 26. (0.00000) RY ( 5) O  2           s(  0.00%)p 1.00(  1.14%)d86.35( 98.86%)
 27. (0.00000) RY ( 6) O  2           s(  0.00%)p 1.00(  0.25%)d99.99( 99.75%)
 28. (0.00000) RY ( 7) O  2           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 29. (0.00000) RY ( 8) O  2           s(  6.72%)p 5.27( 35.42%)d 8.61( 57.85%)
 30. (0.00000) RY ( 9) O  2           s(  2.07%)p 0.30(  0.61%)d47.00( 97.32%)
 31. (0.00308) RY ( 1) H  3           s( 99.42%)p 0.01(  0.58%)
                                         0.0096  0.9970 -0.0710 -0.0281  0.0000
 32. (0.00002) RY ( 2) H  3           s(  0.22%)p99.99( 99.78%)
 33. (0.00002) RY ( 3) H  3           s(  0.00%)p 1.00(100.00%)
 34. (0.00001) RY ( 4) H  3           s(  0.57%)p99.99( 99.43%)
 35. (0.00308) RY ( 1) H  4           s( 99.42%)p 0.01(  0.58%)
                                         0.0096  0.9970 -0.0710  0.0281  0.0000
 36. (0.00002) RY ( 2) H  4           s(  0.22%)p99.99( 99.78%)
 37. (0.00002) RY ( 3) H  4           s(  0.00%)p 1.00(100.00%)
 38. (0.00001) RY ( 4) H  4           s(  0.57%)p99.99( 99.43%)


 NHO DIRECTIONALITY AND BOND BENDING (deviation from line of nuclear centers at
                              the position of maximum hybrid amplitude)

      [Thresholds for printing:  angular deviation  >  1.0 degree]
                                 p- or d-character  > 25.0%
                                 orbital occupancy  > 0.10e

                  Line of Centers        Hybrid 1            Hybrid 2
```

```
               ---------------   -------------------   -------------------
       NBO             Theta  Phi   Theta  Phi   Dev   Theta  Phi   Dev
===============================================================================
  3. LP ( 1) O  2       --    --    90.0   0.0   --     --    --    --
  4. LP ( 2) O  2       --    --    90.0  90.7   --     --    --    --
  5. BD ( 1) C  1- O  2  90.0  0.0    3.0   0.0  87.0  178.7 180.0  88.7


SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

   Threshold for printing:   0.50 kcal/mol

                                               E(2) E(NL)-E(L) F(L,NL)
     Donor (L) NBO            Acceptor (NL) NBO    kcal/mol  a.u.   a.u.
===============================================================================

within unit  1
  3. LP ( 1) O  2         13. RY ( 1) C  1          8.58   1.40   0.098
  4. LP ( 2) O  2         11. BD*( 1) C  1- H  3   26.11   1.16   0.156
  4. LP ( 2) O  2         12. BD*( 1) C  1- H  4   26.11   1.16   0.156
  4. LP ( 2) O  2         14. RY ( 2) C  1          5.72   3.06   0.118
  4. LP ( 2) O  2         26. RY ( 5) O  2          0.73   3.75   0.047
  7. BD ( 1) C  1- H  3   12. BD*( 1) C  1- H  4    0.74   1.42   0.029
  7. BD ( 1) C  1- H  3   22. RY ( 1) O  2          2.25   2.12   0.062
  8. BD ( 1) C  1- H  4   11. BD*( 1) C  1- H  3    0.74   1.42   0.029
  8. BD ( 1) C  1- H  4   22. RY ( 1) O  2          2.25   2.12   0.062


NATURAL BOND ORBITALS (Summary):


                                        Principal Delocalizations
       NBO             Occupancy   Energy  (geminal,vicinal,remote)
===============================================================================
Molecular unit  1  (CH2O)
------ Lewis -----------------------------------
  1. CR ( 1) C  1         1.99997  -11.34329
  2. CR ( 1) O  2         1.99998  -20.56485
  3. LP ( 1) O  2         1.98853   -0.81352  13(v)
  4. LP ( 2) O  2         1.91757   -0.46975  11(v),12(v),14(v),26(g)
  5. BD ( 1) C  1- O  2   1.99996   -0.53505
  6. BD ( 2) C  1- O  2   1.99975   -1.23345
  7. BD ( 1) C  1- H  3   1.99548   -0.72703  22(v),12(g)
  8. BD ( 1) C  1- H  4   1.99548   -0.72703  22(v),11(g)
------ non-Lewis -------------------------------
  9. BD*( 1) C  1- O  2   0.00000    0.20704
 10. BD*( 2) C  1- O  2   0.00000    0.95146
 11. BD*( 1) C  1- H  3   0.03918    0.69317
 12. BD*( 1) C  1- H  4   0.03918    0.69317
 13. RY ( 1) C  1         0.00969    0.58169
 14. RY ( 2) C  1         0.00517    2.58837
 15. RY ( 3) C  1         0.00001    1.75652
 16. RY ( 4) C  1         0.00000    0.96046
 17. RY ( 5) C  1         0.00000    0.64510
 18. RY ( 6) C  1         0.00000    1.49223
 19. RY ( 7) C  1         0.00000    2.24615
 20. RY ( 8) C  1         0.00000    2.08566
 21. RY ( 9) C  1         0.00000    2.49414
 22. RY ( 1) O  2         0.00368    1.39676
 23. RY ( 2) O  2         0.00014    1.56107
 24. RY ( 3) O  2         0.00000    2.18160
 25. RY ( 4) O  2         0.00000    1.30222
 26. RY ( 5) O  2         0.00000    3.27920
```

```
   27. RY ( 6) O   2              0.00000    3.20505
   28. RY ( 7) O   2              0.00000    2.98918
   29. RY ( 8) O   2              0.00000    2.69359
   30. RY ( 9) O   2              0.00000    3.12898
   31. RY ( 1) H   3              0.00308    0.41874
   32. RY ( 2) H   3              0.00002    2.57996
   33. RY ( 3) H   3              0.00002    1.85643
   34. RY ( 4) H   3              0.00001    2.06898
   35. RY ( 1) H   4              0.00308    0.41874
   36. RY ( 2) H   4              0.00002    2.57996
   37. RY ( 3) H   4              0.00002    1.85643
   38. RY ( 4) H   4              0.00001    2.06898
              ------------------------------
                Total Lewis   15.89671  ( 99.3545%)
            Valence non-Lewis   0.07835  (  0.4897%)
            Rydberg non-Lewis   0.02493  (  0.1558%)
              ------------------------------
                 Total unit  1   16.00000  (100.0000%)
                Charge unit  1    0.00000


 $CHOOSE
   LONE 2 2 END
   BOND D 1 2 S 1 3 S 1 4 END
 $END


 NBO analysis completed in 0.05 CPU seconds (0 wall seconds)
 Maximum scratch memory used by NBO was 297106 words (2.27 MB)
Stopping NBO...Storing NBOs: NBO_1.nbo

                         *** returned from  NBO  program ***
```

Thus, in this example the NBO analysis of formaldehyde shows that a single Lewis structure is dominant with single bonds between C and H, a double bond between C and O and two lone pairs at the oxygen – just as ordinary chemical arguments would imply. In addition, the program produces the four corresponding valence antibonds. The remaining components of the basis set span the "Rydberg" space and lead to semilocalized, orthogonal orbitals that are assigned to single atoms (Note the nomenclature: BD = bond, BD* = antibond, LP = lone pair, CR = core orbital, RY= Rydberg orbital). The NPA analysis shows a patially negative oxygen and partially positive carbon and hydrogen atoms.

Additionally, the NBO orbitals are stored in the ORCA .gbw file format as `jobname.nbo`. This file can be used for further analysis and usage with ORCA e.g. for plotting orbitals via `orca_plot`.

The **NBO** program has many additional features and analysis tools. The features that are implemented in ORCA can be controlled via the `%nbo`-block

```
%nbo
NBOKEYLIST    = "$NBO     ... $END"
DELKEYLIST    = "$DEL     ... $END"
COREKEYLIST   = "$CORE    ... $END"
NRTSTRKEYLIST = "$NRTSTR  ... $END"
NPEPAKEYLIST  = "$NPEPA   ... $END"
end
```

The syntax of the respective keylists is given by the NBO6.x/NBO7.x manual.

Specifying the single `! NBO` keyword corresponds to the `%nbo`-block

```
%nbo
NBOKEYLIST    = "$NBO NBO NPA AONBO=C ARCHIVE $END"
end
```

The full set of features beyond those which can be give via the `%nbo` block can be accessed using the file `FILE.47`,

which is generated by the NBO program. This is an ascii file that can be edited with a text editor. Add or remove keywords in the corresponding blocks as needed and call the gennbo program like

```
gennbo < FILE.47 >jobname.nboout
```


(a) (a) π   (b) (b) π - LP   (c) (c) π*

(d) (d) σ   (e) (e) σ - LP   (f) (f) σ*
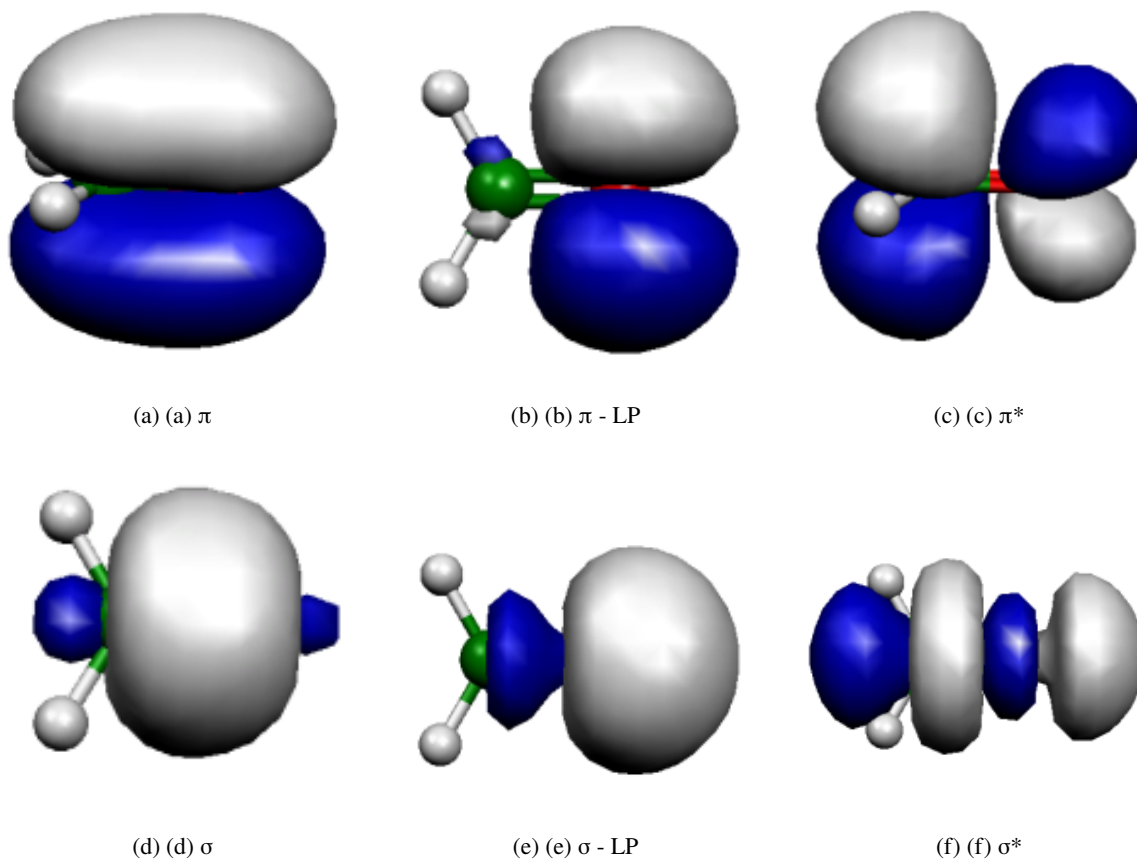
Fig. 5.1: Six NBOs of the H_2CO molecule. Shown are the occupied bonding π and σ orbitals (left) for C and O, the two oxygen lone pairs (middle) and the two π^* and σ^* antibonding orbitals (right).

The `FILE.47` file looks like:

```
$GENNBO   NATOMS=4   NBAS=38   UPPER   BODM   FORMAT   $END
 $NBO   $END
 $COORD
 ORCA Job: check
     6     6        0.000000        0.000000        0.000000
     8     8        2.267671        0.000000        0.000000
     1     1       -1.039349        1.800206        0.000000
     1     1       -1.039349       -1.800206        0.000000
 $END
 $BASIS
```

If you have no need for this (rather large) file, then you have to delete it manually!

5.2.1 NBO Deletions

An advanced feature, which has been implemented via the ORCA-NBO interface, is the possibility of using deletions.

```
! RHF 3-21G BOHRS TightSCF

%nbo
nbokeylist="$nbo nbo npa aonbo=c archive $end"
delkeylist="$del lewis delete 1 element 3 11 $end"
end


*xyz 0 1
 C            1.4089705283       0.0210567401       0.0000000000
 N           -1.3645072652      -0.1355759321       0.0000000000
 H            1.9849776453       1.9986808971       0.0000000000
 H            2.1492280974      -0.9096841007       1.6818209547
 H            2.1492280974      -0.9096841007      -1.6818209547
 H           -2.0504340036       0.7268536543      -1.5583845544
 H           -2.0504340036       0.7268536543       1.5583845544
*
```

The `DELKEYLIST` provides NBO with the task to perform certain deletions of orbitals/interactions. Per deletion ORCA calculates a new Fock matrix on basis of an NBO density corresponding to the deletions:

```
Stopping NBO...Starting NBO again for $del instructions...

 LEWIS: Delete all non-Lewis NBOs
 Deletion of the following orbitals from the NBO Fock matrix:
   10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28

 Orbital occupancies:

      Orbital                         No deletions  This deletion   Change
 ------------------------------------------------------------------------------
    1. CR ( 1) C  1                     1.99978        2.00000       0.00022
    2. CR ( 1) N  2                     1.99983        2.00000       0.00017
    3. LP ( 1) N  2                     1.97796        2.00000       0.02204
    4. BD ( 1) C  1- N  2               1.99846        2.00000       0.00154
    5. BD ( 1) C  1- H  3               1.99858        2.00000       0.00142
    6. BD ( 1) C  1- H  4               1.99406        2.00000       0.00594
    7. BD ( 1) C  1- H  5               1.99406        2.00000       0.00594
    8. BD ( 1) N  2- H  6               1.99440        2.00000       0.00560
    9. BD ( 1) N  2- H  7               1.99440        2.00000       0.00560
   10. BD*( 1) C  1- N  2               0.00009        0.00000      -0.00009
   11. BD*( 1) C  1- H  3               0.01567        0.00000      -0.01567
   12. BD*( 1) C  1- H  4               0.00763        0.00000      -0.00763
   13. BD*( 1) C  1- H  5               0.00763        0.00000      -0.00763
   14. BD*( 1) N  2- H  6               0.00424        0.00000      -0.00424
   15. BD*( 1) N  2- H  7               0.00424        0.00000      -0.00424
   16. RY ( 1) C  1                     0.00094        0.00000      -0.00094
   17. RY ( 2) C  1                     0.00034        0.00000      -0.00034
   18. RY ( 3) C  1                     0.00020        0.00000      -0.00020
   19. RY ( 4) C  1                     0.00001        0.00000      -0.00001
   20. RY ( 1) N  2                     0.00114        0.00000      -0.00114
   21. RY ( 2) N  2                     0.00044        0.00000      -0.00044
   22. RY ( 3) N  2                     0.00034        0.00000      -0.00034
   23. RY ( 4) N  2                     0.00001        0.00000      -0.00001
   24. RY ( 1) H  3                     0.00163        0.00000      -0.00163
   25. RY ( 1) H  4                     0.00079        0.00000      -0.00079
   26. RY ( 1) H  5                     0.00079        0.00000      -0.00079
   27. RY ( 1) H  6                     0.00117        0.00000      -0.00117
```

```
    28. RY ( 1) H  7                       0.00117       0.00000      -0.00117


 NEXT STEP:  Perform one SCF cycle to evaluate the energy of the new density
             matrix constructed from the deleted NBO Fock matrix.


    -------------------------------------------------------------------------
Copying NBO density...
Calculating new Fock-Matrix...
Calculating Fock-Matrix...done!


New NBO energy via Fock-Matrix: -94.629937



Starting NBO again for $del/return energy instructions...


    -------------------------------------------------------------------------
   Energy of deletion :         -94.629936711
     Total SCF energy :         -94.679444929
                              ------------------
         Energy change :          0.049508 a.u.,          31.067 kcal/mol
    -------------------------------------------------------------------------
```

Multiple deletions can also be specified, as can be seen for this example. The output then also contains the additional energy values:

```
Starting NBO again for $del instructions...

 Deletion of the following NBO Fock matrix elements:
     3, 11;

 Orbital occupancies:

       Orbital                        No deletions  This deletion   Change
    -------------------------------------------------------------------------
    1. CR ( 1) C  1                       1.99978       1.99978      -0.00000
    2. CR ( 1) N  2                       1.99983       1.99983      -0.00000
    3. LP ( 1) N  2                       1.97796       1.99348       0.01552
    4. BD ( 1) C  1- N  2                 1.99846       1.99860       0.00015
    5. BD ( 1) C  1- H  3                 1.99858       1.99845      -0.00014
    6. BD ( 1) C  1- H  4                 1.99406       1.99404      -0.00002
    7. BD ( 1) C  1- H  5                 1.99406       1.99404      -0.00002
    8. BD ( 1) N  2- H  6                 1.99440       1.99450       0.00011
    9. BD ( 1) N  2- H  7                 1.99440       1.99450       0.00011
   10. BD*( 1) C  1- N  2                 0.00009       0.00008      -0.00000
   11. BD*( 1) C  1- H  3                 0.01567       0.00042      -0.01525
   12. BD*( 1) C  1- H  4                 0.00763       0.00780       0.00017
   13. BD*( 1) C  1- H  5                 0.00763       0.00780       0.00017
   14. BD*( 1) N  2- H  6                 0.00424       0.00424       0.00000
   15. BD*( 1) N  2- H  7                 0.00424       0.00424       0.00000
   16. RY ( 1) C  1                       0.00094       0.00063      -0.00031
   17. RY ( 2) C  1                       0.00034       0.00034       0.00000
   18. RY ( 3) C  1                       0.00020       0.00032       0.00012
   19. RY ( 4) C  1                       0.00001       0.00002       0.00001
   20. RY ( 1) N  2                       0.00114       0.00115       0.00001
   21. RY ( 2) N  2                       0.00044       0.00044       0.00000
   22. RY ( 3) N  2                       0.00034       0.00034       0.00000
   23. RY ( 4) N  2                       0.00001       0.00001       0.00000
   24. RY ( 1) H  3                       0.00163       0.00092      -0.00072
   25. RY ( 1) H  4                       0.00079       0.00083       0.00005
   26. RY ( 1) H  5                       0.00079       0.00083       0.00005
   27. RY ( 1) H  6                       0.00117       0.00118       0.00000
```

```
   28. RY ( 1) H  7                      0.00117        0.00118        0.00000


 NEXT STEP:  Perform one SCF cycle to evaluate the energy of the new density
             matrix constructed from the deleted NBO Fock matrix.


     ---------------------------------------------------------------------------
Copying NBO density...
Calculating new Fock-Matrix...
Calculating Fock-Matrix...done!

New NBO energy via Fock-Matrix: -94.668383


Starting NBO again for $del/return energy instructions...


     ---------------------------------------------------------------------------
   Energy of deletion :        -94.668383268
     Total SCF energy :        -94.679444929
                              ------------------
        Energy change :           0.011062 a.u.,           6.941 kcal/mol
     ---------------------------------------------------------------------------
```

> **ⓘ Note**
>
> Note that deletions are only implemented for SCF methods!

5.2.2 NBO for Post-HF Densities

NBO analysis can be performed on all methods producing a density. In some methods the density generation has to be specified explictly, e. g. for MP2 calculations this would be:

```
! MP2 3-21G TightSCF BOHRS NBO

%MP2
density relaxed
end

*xyz 0 1
 C            1.4089705283       0.0210567401       0.0000000000
 N           -1.3645072652      -0.1355759321       0.0000000000
 H            1.9849776453       1.9986808971       0.0000000000
 H            2.1492280974      -0.9096841007       1.6818209547
 H            2.1492280974      -0.9096841007      -1.6818209547
 H           -2.0504340036       0.7268536543      -1.5583845544
 H           -2.0504340036       0.7268536543       1.5583845544
*
```

The output will contain both the NBO analysis of the SCF density as well as of the MP2 relaxed density. An NBO analysis of a density generated by the MDCI module can be specified as follows:

```
! CISD 3-21G TightSCF BOHRS NBO

%mdci
    density linearized
end

*xyz 0 1
 C        1.4089705283       0.0210567401       0.0000000000
```

```
 N        -1.3645072652        -0.1355759321         0.0000000000
 H         1.9849776453         1.9986808971         0.0000000000
 H         2.1492280974        -0.9096841007         1.6818209547
 H         2.1492280974        -0.9096841007        -1.6818209547
 H        -2.0504340036         0.7268536543        -1.5583845544
 H        -2.0504340036         0.7268536543         1.5583845544
*
```

Again, the output will contain both the NBO analysis of the SCF density as well as of the CISD linearized density.

5.2.3 Natural Chemical Shielding Analysis (NCS)

For closed-shell calculations of NMR chemical shielding at the SCF level (see sections *NMR Chemical Shifts* and *EPRNMR - keywords for magnetic properties*), the NCS analysis can be requested by adding `NCS` to the `NBOKEYLIST`. The `NCS` keyword accepts the arguments `U`, `I`, `CSA`, `XYZ`, and `MO` to analyze the "unperturbed", "induced", anisotropic, Cartesian, and canonical MO contributions to the shielding tensors, respectively, as well as a decimal number for the printing threshold (in ppm). For more information, consult the NBO manual and the original publication [587].

```
! PBE def2-TZVP NMR
%nbo
  NBOKeyList = "$NBO NCS=0.01,I,U,XYZ $END"
end
* xyz 0 1
  H    0.00    0.00    0.00
  C    1.06    0.00    0.00
  N    2.23    0.00    0.00
*
```

```
Summary of isotropic NMR chemical shielding
 Total Lewis (L) and non-Lewis (NL) contributions: (ppm)

        NBO          H  1    C  2    N  3
 ---------------    ------- ------- -------
   1.  C 2(cr)   L   -0.18  200.26    0.18
                 NL  -0.02    0.02    0.00
   2.  N 3(cr)   L   -0.03   -0.12  235.18
                 NL   0.00    0.01    0.02
   3.  N 3(lp)   L    1.02  -33.00 -151.92
                 NL  -1.04    1.81   12.18
   4.  H 1- C 2  L   25.75  -49.28  -20.30
                 NL  -1.24    6.10    2.26
   5.  C 2- N 3  L    2.29   15.40   13.66
                 NL   0.02    0.00   -0.00
   6.  C 2- N 3  L    2.29   15.40   13.66
                 NL   0.02    0.00   -0.00
   7.  C 2- N 3  L    0.46  -77.94 -151.00
                 NL   0.05   -4.41    0.95
 ---------------    ------- ------- -------
         Lewis       31.59   70.70  -60.53
     non-Lewis       -2.21    3.53   15.42
 ---------------    ------- ------- -------
         Total       29.38   74.23  -45.11
```

5.3 Fractional Occupation Number Weighted Density (FOD)

Many approximate QC methods do not yield reliable results for systems with significant static electron correlation (SEC) and moreover it is often difficult to predict if the system in question suffers from SEC or not. Existing scalar SEC diagnostics (e.g., the T_1 diagnostic) do not provide any information where the SEC is located in the molecule. Furthermore, often quite expensive calculations have to be performed first (e.g., CCSD) in order to judge the reliability of the results based on a single value. Molecular systems with strong SEC (e.g. covalent bond-breaking, biradicals, open-shell transition metal complexes) are usually characterized by small energy gaps between frontier orbitals, and hence, the existence of many equally important determinants in their electronic wavefunction. This finding is used in the fractional occupation number weighted density (FOD) analysis proposed by Hansen and Grimme.[588] The FOD analysis is based on *finite temperature KS-DFT* where the *fractional occupation numbers* are determined from the Fermi distribution ("Fermi smearing").

$$f_i = \frac{1}{e^{(\varepsilon_i - E_F)/kT_{el}} + 1} \tag{5.25}$$

The central quantity of the FOD analysis is the fractional occupation number weighted electron density (ρ^{FOD}), a real-space function of the position vector r:

$$\rho^{FOD}(r) = \sum_i^N (\delta_1 - \delta_2 f_i)|\varphi_i(r)|^2 \tag{5.26}$$

(δ_1 and δ_2 are unity if the level is lower than E_F while they are 0 and -1, respectively, for levels higher than E_F). The f_i represent the fractional occupation numbers ($0 \leq f_i \leq 1$; sum over all electronic single-particle levels obtained by solving self-consistently the KS-SCF equations minimizing the *free*-electronic energy).

$\rho^{FOD}(r)$ can be plotted using a pre-defined contour surface value (see Section *FOD Plots*). The integration of ρ^{FOD} over all space yields as additional information a single size-extensive number termed N_{FOD} which correlates well with other scalar SEC diagnostics and can be used to globally quantify SEC effects in the molecule. Accordingly, FOD analysis and plots represent a cost-effective and robust way to identify the 'hot' (strongly correlated) electrons in a molecule and to choose appropriate approximate quantum chemical methods for a subsequent computational study of the systems in question. Based on our experience, the following rules of thumb can be derived:

- no significant ρ^{FOD}: use (double)-hybrid functionals or (DLPNO-)CCSD(T) (single-reference electronic structure)

- significant but rather localized ρ^{FOD}: use semi-local GGA functionals (or hybrid functional with low Fock-exchange, avoid HF or MP2; slight multi-reference character)

- significant *and* delocalized ρ^{FOD}: use multi-reference methods (or finite temperature DFT; strong multi-reference character)

> ⚠️ **Warning**
>
> Even though the FOD is intuitive and easy-to-use, it is not a 100% safe diagnostic for MR character and should only be used as a first indication. We recommend to always combine the FOD analysis with more sophisticated multi-reference diagnostics.

> 💡 **Tip**
>
> Mulliken reduced orbital charges based on $\rho^{FOD}(r)$ (see *Mulliken Population Analysis*) offer a fast alternative to get the information of the FOD plot (cf. *Example: p-Benzyne*).

5.3.1 Basic Usage

The FOD analysis is a very efficient and practicable tool to get information about the amount and localization of SEC in the system of question and can be invoked via the `!FOD` simple input keyword.

```
! FOD
```

This will perform the analysis at the default TPSS/def2-TZVP (`TightSCF`) level that was chosen since it is fast and robust. Besides the standard analysis output (cf. Section 5.3.3), ρ^{FOD} is stored in the file `basename.scfp_fod` file which is included in the general `basename.densities` container (for plotting the FOD, see Section 5.3.2).

The FOD analysis can be customized via simple input and the `%scf` block.

```
! B3LYP def2-TZVP TightSCF

%scf
 SmearTemp 9000
end
```

> **Ⅱ Important**
>
> - ρ^{FOD} (and N_{FOD}) strongly depend on the orbital energy gap which itself depends almost linearly on the amount of the non-local Fock exchange admixture a_x (cf. *hybrid DFT*). The following (empirical) function of the optimal electronic temperature T_{el} on a_x
>
> $$T_{el} = 20000\,\text{K} \times a_x + 5000\,\text{K} \tag{5.27}$$
>
> is used to ensure that similar results of the FOD analysis are obtained with various functionals. For example, the `SmearTemp` has to be 5000 K for TPSS ($a_x = 0$), 9000 K for B3LYP ($a_x = 20\%$), 10000 K for PBE0 ($a_x = 25\%$), and 15800 K for M06-2x ($a_x = 54\%$).

> **ⓘ Some Notes on FOD**
>
> - The FOD analysis is not strongly dependent on the employed basis set (see supplementary information of the original publication[588]).
> - The FOD analysis will be always printed (including Mulliken reduced orbital charges based on ρ^{FOD}) if `SmearTemp > 0 K`.
> - Since the $\hat{S}^2$ expectation value is not defined for fractional occupation numbers, its printout is omitted.
> - The FOD analysis may also be useful for finding a suitable active space for e.g. in *CASSCF* calculations.

5.3.2 FOD Plots

The fractional occupation number weighted electron density (ρ^{FOD}, see *Fractional Occupation Number Weighted Density (FOD)*) can be plotted in 3D for a pre-defined contour surface value which, after extensive testing, was set to the default value of $\sigma = 0.005$ e/Bohr^3. In order to allow comparison of various systems this value should be kept fix (in critical cases, one may also check the FOD plot with a a smaller value of $\sigma = 0.002$ e/Bohr^3 for comparison). The FOD is strictly positive in all space and resembles orbital densities (e.g., π-shape in large polyenes) or the total charge density for an ideal 'metal' with complete orbital degeneracy in simple cases.

Basically, ρ^{FOD} can be plotted analogously to an electron density using the *orca_plot* utility program and the generated `basename.scfp_fod` density file that is stored in the `basename.scfp_fod` is stored in the `basename.densities` container.

To do so call `orca_plot` in interactive mode via

```
orca_plot basename.gbw -i
```

The interface will now show various plot options.

```
PlotType        ... MO-PLOT
MO/Operator     ... 0 0
Output file     ... (null)
Format          ... Grid3D/Binary
Resolution      ... 40 40 40
Boundaries      ...  -22.359392     16.311484 (x direction)
                     -12.628859     13.574504 (y direction)
                      -7.001812      7.002006 (z direction)


      1 - Enter type of plot
      2 - Enter no of orbital to plot
      3 - Enter operator of orbital (0=alpha,1=beta)
      4 - Enter number of grid intervals
      5 - Select output file format
      6 - Plot CIS/TD-DFT difference densities
      7 - Plot CIS/TD-DFT transition densities
      8 - Set AO(=1) vs MO(=0) to plot
      9 - List all available densities
     10 - Perform Density Algebraic Operations

     11 - Generate the plot
     12 - exit this program
Enter a number:
```

To check all available densities in the `basename.densities` container one can use the `9 - List all available densities` option.

```
--------------------
List of density names
--------------------


Index:                          Name of Density
-----------------------------------------------------
   0:                      basename.scfp_fod  <--- required for FOD plot
   1:                          basename.scfp
   2:                          basename.scfr
```

The most general way to create the FOD plot is now to create a `.cube` file that can be visualized with many external programs like ChimeraX or Chemcraft (cf. *Graphical User Interfaces*).

To do so we use the following subsequent user inputs to `orca_plot`:

```
1 (type of plot)
2 (electron density)
n (default name: no)
basename.scfp_fod (name of the FOD file)
4 (number of grid intervals)
120 (NGrid)
5 (output file format)
7 (cube)
10 (generate plot)
11 (exit)
```

> ⚠️ **Warning**
>
> Note that producing `.cube` files can become very large and their generation with `orca_plot` may take a considerable amount of time for larger molecules. This is particularly the case if high quality plots using tight

> grid resolution settings (i.e., 120x120x120 resolution) are used for publication purposes.

It is also possible to generate `*.cube` files from ρ^{FOD} (analogously to electron density plots) with other programs that can read ORCA's `baseame.gbw` and electron density files by simply using the `basename.scfp_fod` file instead of the `basename.scfp` file.

An example FOD plot for Ni(bis-dithiolene) is shown below (Fig. 5.2). It was generated with ChimeraX and a `.cube` file generated by `orca_plot` and clearly shows the strong FOD on the metal center and the adjacent ligands. This observation is in line with various studies on the multi-reference character of this complex.
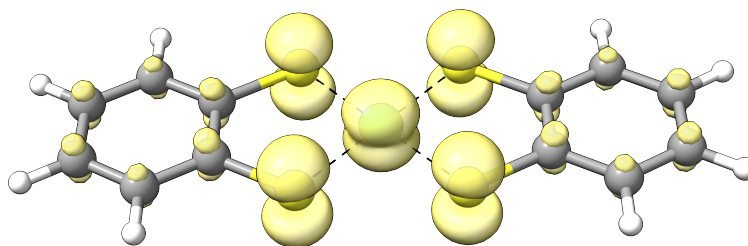
Fig. 5.2: FOD plot at $\sigma = 0.005$ e/Bohr^3 (TPSS/def2-TZVP (T = 5000 K) level) for the NiBDT complex (FOD depicted in yellow).

More examples of FOD plots generated with the same setup can be found in the original publication and corresponding supplementary information.[588]

5.3.3 Example: *p*-Benzyne

In this example, the FOD analysis for the ground state of *p*-Benzyne is performed.

```
! FOD

* xyz 0 1
C 0.0000000  1.2077612  0.7161013
C 0.0000000  0.0000000  1.3596219
C 0.0000000 -1.2077612  0.7161013
C 0.0000000 -1.2077612 -0.7161013
C 0.0000000  0.0000000 -1.3596219
C 0.0000000  1.2077612 -0.7161013
H 0.0000000  2.1606260  1.2276695
H 0.0000000 -2.1606260  1.2276695
H 0.0000000 -2.1606260 -1.2276695
H 0.0000000  2.1606260 -1.2276695
*
```

The respective output reads:

```
--------------------------------------------------------------------------------
↪--------
                              ORCA LEAN-SCF
                        memory conserving SCF solver
```
(continues on next page)

```
--------------------------------------------------------------------------------
↪--------

-------------------------------------D-I-I-S-----------------------------------
↪--------
Iteration     Energy (Eh)           Delta-E   RMSDP     MaxDP     DIISErr   Damp ␣
↪Time(sec)
--------------------------------------------------------------------------------
↪--------
              ***  Starting incremental Fock matrix formation  ***
   1    -230.8982516003082139     0.00e+00  5.01e-03  1.01e-01  1.12e-01  0.700 ␣
↪1.7
Warning: op=0 Small HOMO/LUMO gap (  -0.021) - skipping pre-diagonalization
        Will do a full diagonalization
   2    -230.9463607195993120    -4.81e-02  1.15e-03  2.59e-02  4.06e-02  0.700 ␣
↪1.6
                        ***Turning on AO-DIIS***
 ... etc.
  12    -231.0033984839932089    -5.02e-09  3.33e-07  7.37e-06  7.95e-06  0.000 ␣
↪1.1
              **** Energy Check signals convergence ****

FOD:
 Fermi smearing:E(HOMO(Eh)) = -0.201252 MUE = -0.179318 gap=  1.119 eV

 N_FOD =  0.920364
```

The high N_{FOD} already indicates strong SEC and checking the Mulliken reduced orbital charges based on $\rho^{FOD}(r)$ (see *Mulliken Population Analysis*) gives a first impression about the localization of hot electrons in the molecule. The printout for the first carbon atom is given below:

```
------------------------------------------
FOD BASED MULLIKEN REDUCED ORBITAL CHARGES
------------------------------------------
  0 C s       :      0.006371  s :     0.006371
    pz        :      0.016375  p :     0.030785
    px        :      0.009893
    py        :      0.004516
    dz2       :      0.004248  d :     0.010308
    dxz       :      0.000254
    dyz       :      0.004855
    dx2y2     :      0.000860
    dxy       :      0.000091
    f0        :      0.000006  f :     0.000378
    f+1       :      0.000014
    f-1       :      0.000309
    f+2       :      0.000002
    f-2       :      0.000006
    f+3       :      0.000010
    f-3       :      0.000032
```

If other population analysis printouts are wanted the user is referred to the Löwdin analysis (*Löwdin Population Analysis*) which is turned on by default using the total SCF density of the calculation, also in the case of finite electronic temperature.

The plot the ρ^{FOD} for *p*-Benzyne clearly shows the significant and rather delocalized FOD (^1A_g), thus indicating that multi-reference methods would be needed for reliable computational study of this molecule.
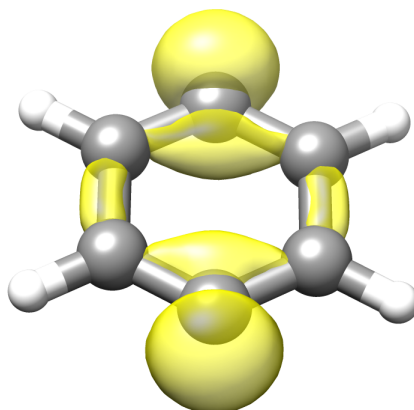
Fig. 5.3: FOD plot at $\sigma = 0.005$ e/Bohr^3 (TPSS/def2-TZVP (T = 5000 K) level) for the ^1A_g ground state of p-benzyne (FOD depicted in yellow).

5.4 Excited States Calculations

A plethora of methods to compute excited states exists in ORCA. Here we give a brief overview of the main methods, with focus on the basic usage and current capabilities of each. Detailed documentation for each method is indicated in each subsection.

Multi-reference methods, such as NEVPT2 or MRCI, are described elsewhere (*N-Electron Valence State Perturbation Theory (NEVPT2)*, *Multireference Configuration Interaction and Pertubation Theory (uncontracted)*) in the manual.

5.4.1 Excited States with RPA, CIS, TD-DFT and SF-TDA

ORCA features a module to perform TD-DFT, single-excitation CI (CIS) and RPA. The module works with either closed-shell (RHF or RKS) or unrestricted (UHF or UKS) reference wavefunctions. For DFT models the module automatically chooses TD-DFT and for HF wavefunctions the CIS model. If the RI approximation is used in the SCF part it will also be used in the excited states calculation. A detailed documentation is provided in section *Excited States via RPA, CIS, TD-DFT and SF-TDA*

General Use

In its simplest form it is only necessary to provide the number of roots sought:

```
! BP86 def2-SVP TightSCF

%tddft
  Nroots   10
  triplets true
end

*xyz 0 1
  C     0.016227   -0.000000    0.000000
  O     1.236847    0.000000   -0.000000
  H    -0.576537    0.951580   -0.000000
  H    -0.576537   -0.951580   -0.000000
end
```

Which gives the following output: