Adaptive Natural Density Partitioning (AdNDP 2.0) User's Manual

Contents

1. Introduction.

Adaptive Natural Density Partitioning (AdNDP) is a tool for obtaining patterns of chemical bonding in systems of the most general type. The AdNDP is based on the concept of the electron pair as the main element of chemical bonding models. Thus, it represents the electronic structure in terms of *n*-center two electrons (nc–2e) bonds. With *n* spanning the interval from one to the total number of atoms in the particular atomic assembly, AdNDP recovers both Lewis bonding elements (1c-2e and 2c-2e objects, corresponding to the core electrons and lone pairs, and two-center two-electron bonds, respectively) and delocalized bonding elements, which are associated with the concepts of aromaticity and antiaromaticity. From this point of view, AdNDP achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. Essentially, AdNDP is a very efficient and visual approach to the interpretation of the molecular orbital-based wave functions. The AdNDP analysis can be used for the assignment of aromaticity/antiaromaticity on the basis of counting rules (Note: the method does not provide any quantitative characteristics of the electron delocalization).

Novel features of the new version of AdNDP algorithm such as: distance restrictions, symmetric direct search, bonding analysis for open shell cases, and exited states bonding analysis are greatly expand the applicability of the method. AdNDP 2.0 was written using Python3.7 programming language. *The NumPy package should be installed for the program to work correctly.* Here, we pleased to show a brief manual for a new AdNDP 2.0 code.

2. Theoretical Background.

The AdNDP is a generalization of the Natural Bonding Orbital Analysis (NBO) proposed by Weinhold. The algorithm is based on the analysis of the first-order reduced density matrix in the basis of Natural Atomic Orbitals (NAO). In the course of the analysis *n*-center sub-block density matrices are formed with respect to the distance restrictions, and the eigenproblem is solved for each of them. If the eigenvalues (occupation numbers) of the found eigenvectors (bonds) are close to the maximum value 2.00 |e| (within the tolerance range, determined by the occupation number threshold), the vectors are accepted, the density matrix is depleted of the density associated with the accepted vectors, and the search continues for (n+1)-atomic blocks. The detailed description of the algorithm as well as the description of features of AdNDP 2.0 code can be found in the original papers introducing AdNDP and AdNDP 2.0 (see Citations section).

3. How to Use.

3.1. Preliminary calculations.

The current version of AdNDP requires output files of certain preliminary calculations performed using Gaussian 09 or Gaussian 16 software packages. These calculations include:

1) NBO analysis as implemented in Gaussian 09 and Gaussian 16 for generating the matrix of the transformation between the regular atomic basis set and the Natural Atomic Orbital basis set (AONAO), and the first-order reduced density matrix in the basis of NAOs (DMNAO). Due to the new option of “Distance Restriction” distance matrix should be calculated in NBO-file too.
2) Printing out molecular orbitals (MO-file) in the format suitable for visualization using MOLDEN or ChemCraft software.

For the convenience of the reader we will show how to prepare NBO and MO files:

NBO-file

#<method>/<basis set> **pop(nboread) geom=distance**

Comment line

<charge><multiplicity>
<optimized geometry>

$nbo aonao dmnao $end

MO-file

#<method>/<basis set> **iop(6/7=3) gfinput**

Comment line

<charge><multiplicity>
<optimized geometry>

3.2. AdNDP.in and Distance.in files

It will be convenient to consider a real example of AdNDP analysis. In this section we will build a bonding pattern picture for a $C_2H_4^+$ molecule, MO and NBO files were calculated at CASSCF(7,9)/aug-cc-pvdz level of theory. After the preparation of NBO and MO files, AdNDP_2.py script should be placed in the same folder. After the launching of the script, four possible options are available:

```
(base) D:\Manual\CASSCF_C2H4_example>python AdNDP_2.py
1) Create AdNDP.in and Distance.in files.
2) AdNDP analysis.
3) AdNDP direct search.
4) Quit.
```

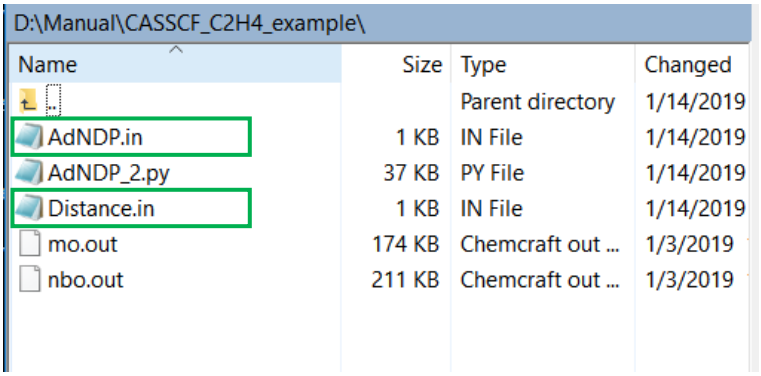
First, we need to create input files (AdNDP.in and Distance.in), so we will pick the first option:

```
1
Is the density matrix calulated separetely for Alpha and Beta electron? (Y/N):
```

For unrestricted (or restricted open shell) methods two different density matrices (for alpha and beta electrons) are created in NBO file. However, unrestricted open shell example will be considered later. So, for now we will just pick 'NO' option because RCASSCF method was used. After that we need to enter NBO and MO file names.

```
Is the density matrix calulated separetely for Alpha and Beta electron? (Y/N): N
Enter NBO file name: nbo.out
Enter MO file name: mo.out
```

Now we can check that input files have been created:



Let's look at these files:

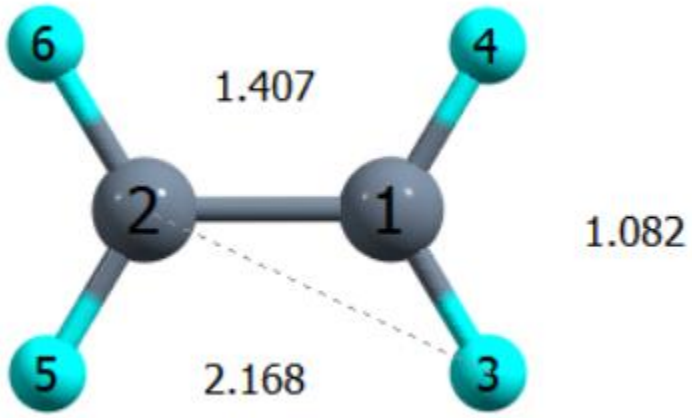
```
0 0 0 0 0 0
Mode(LD-Late Depleting, FC-"Found-Cut", LDFC-hybrid): LD
Save Residual Density Matrix: T
```

The Distance.in file contains three lines. In the first line the user should put the information about “Distance Restriction” parameters. In the second line one should choose the mode. In the last, the user needs to decide whether the Residual Density Matrix will be created (T or F). By the default, there is no distance restrictions (zero in the i^{th} position means that we ignore distance restriction for *i*c-2e bond); the default mode is LD (it corresponds to a standard depletion process). Other modes will be discussed in future versions of the manual.

In our example, let us put 1.5 Å “Distance Restriction” parameter for 2c-2e bond (replace the second “0” in the first line with “1.5”).

```
0 1.5 0 0 0 0
Mode(LD-Late Depleting, FC-"Found-Cut", LDFC-hybrid): LD
Save Residual Density Matrix: T
```

Now, the AdNDP algorithm will build 2-center sub-block matrices only for the atomic pairs which distance is less than 1.5 Å. For example, C1-C2 pair and C1-H3 pair will be checked during AdNDP analysis, but C2-H3 pair will not.

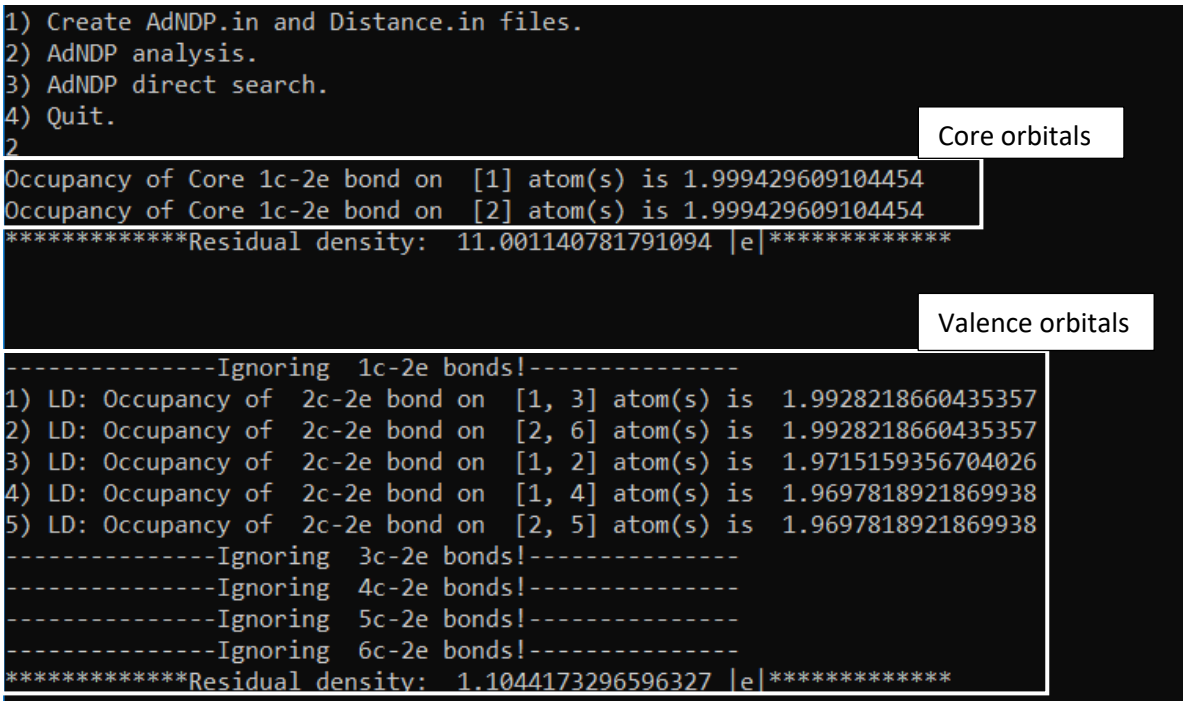


The AdNDP.in file is the main input file. It contains information about: NBO and MO file names, number of atoms, number of valence electron pairs, total number of electron pairs, total number of basis functions, number of basis functions on each atom and the occupation number (ON) thresholds. However, all this information (except ON thresholds) is created automatically from the NBO file. The only parameter that should be set up is the values of ON thresholds. For our case, we are looking for 2c-2e bonds with ON>1.9 |e|. The AdNDP.in file is shown below:

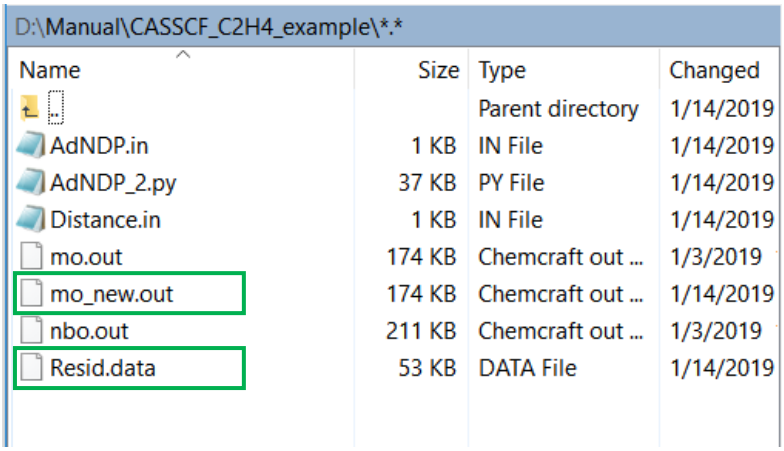
```
NBO filename
nbo.out
Number of atoms
6
Amount of valence electronic pairs
5
Total amount of electronic pairs
7
Total amount of basis functions
82
Amount of basis functions on each atom
23
23
9
9
9
9
Occupation number thresholds
0.
0.1
0.
0.
0.
0.
CMO filename
mo.out
```

3.3 AdNDP general analysis

To conduct AdNDP nalysis we need to pick the second option in the main menu of the AdNDP 2.0 script:

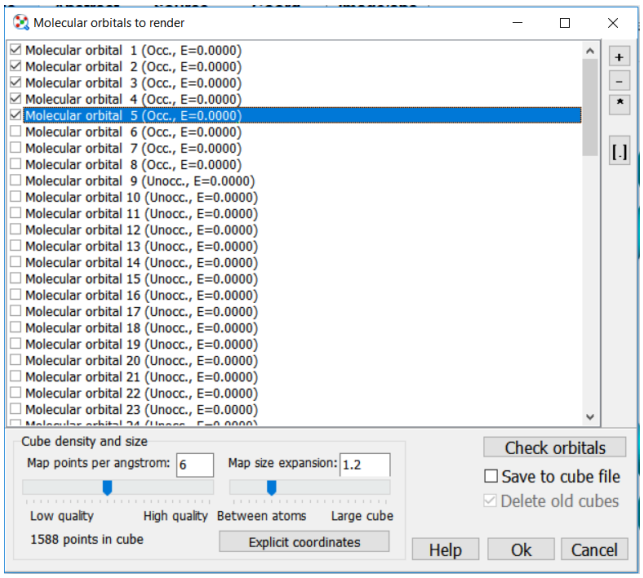


Two core orbitals and five valence bonds have been found. Occupation numbers are shown for each bond. For instance, for 2c-2e C1-C2 bond occupation number is 1.97 |e|. Also, two new files have been created:

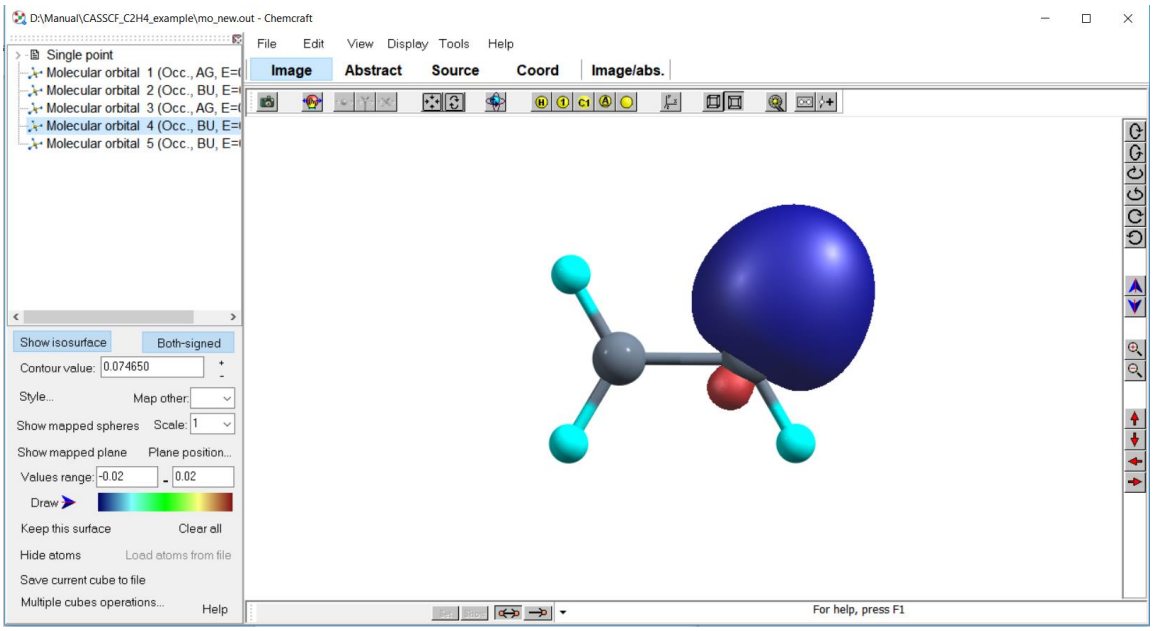


The Resid.data file contains information about the depleted Residual Density Matrix obtained after AdNDP analysis. ***Without this file we can not perform AdNDP direct search analysis.*** The mo_new.out file is created for the visualization of valence bonds. It should be noted

that the AdNDP_2.py script does not visualize core orbitals. Since we found five valence bonds, we need to visualize the first five orbitals in the mo_new.out file:



For example, the visualization of 2c-2e C1-H4 σ-bond with ON=1.97 |e| is shown below:



3.4 AdNDP direct search

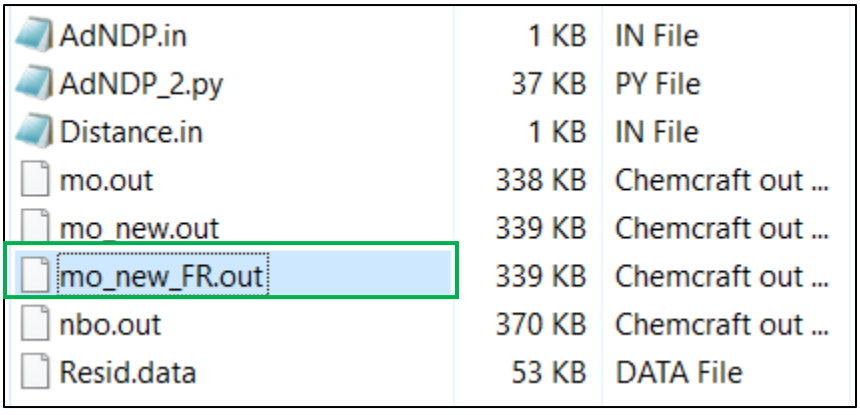
To localize remaining electron density, we need to use the AdNDP direct search option (please, make sure that Resid.data file has been created).

```
1) Create AdNDP.in and Distance.in files.
2) AdNDP analysis.
3) AdNDP direct search.
4) Quit.
3
---------------Residual density:  1.1044173296596327 |e|----------------

Symmetry search?(Y/N):
```

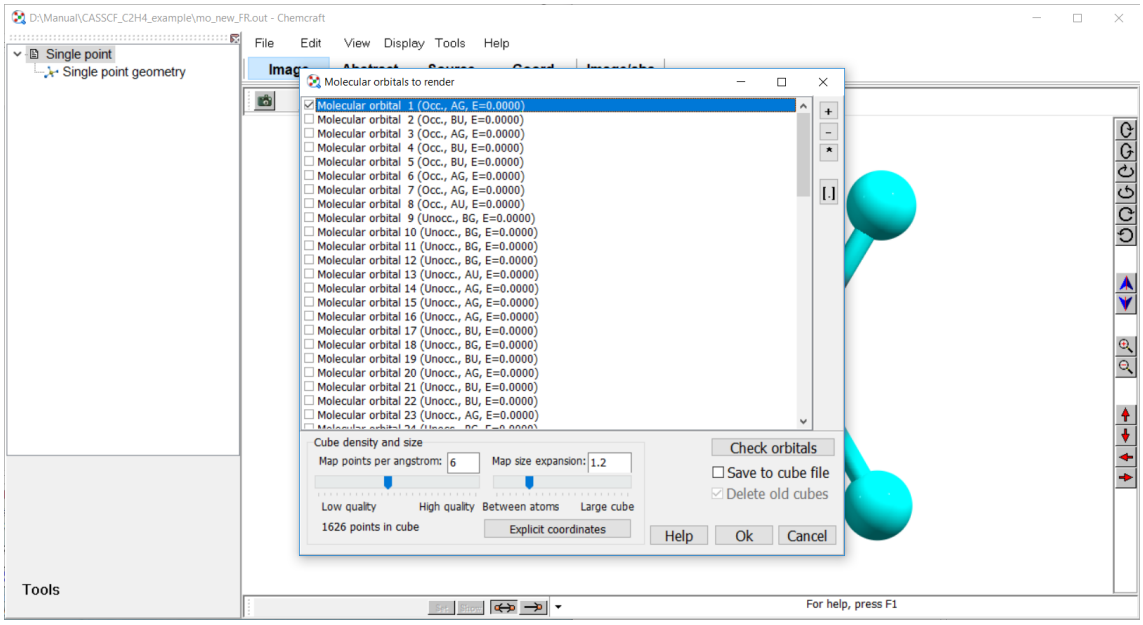
Since we want to find one fragment, it is not necessary to pick the "Symmetry search" option. This option will be useful for localizing more than one symmetric fragment using the exact atomic centers. Consequently, we will type "N". Then, we need to enter the number of fragments. Since we have one electron, we are expecting to find a bond on one fragment. We hope that our remaining electron will sit on C1 and C2 atoms, thus we will type "1 2" as centers for our bond. Then we need to choose the number of orbitals on this fragment. We will choose "1".

```
Symmetry search?(Y/N): N
Enter the number of Fragments: 1
Enter centers for 1 Fragment: 1 2
Enter the number of orbitals in the fragment: 1
Direct search on Fragment  0 : Occupancy of 2c-2e bond on  [1, 2] atom(s) is 0.990426984065663

---------------Residual density:  0.1139903455939697 |e|----------------
Do you want to rewrite Resid.data?(Y/N): Y
```

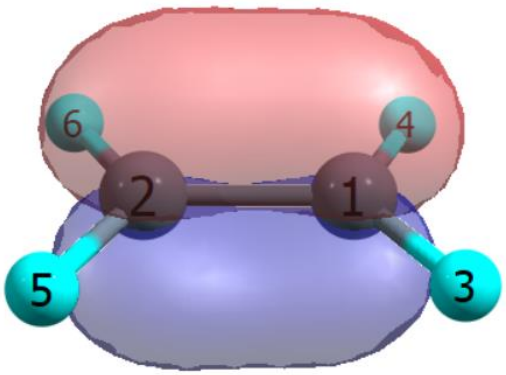
After the direct search analysis, we can see that 0.99 |e| is localized on C1 and C2 centers. We also can notice that a new "mo_new_FR.out" file has been created. It contains information for the visualization of the new bond.



To visualize new bond, let us open this file with ChemCraft software.



Since we have only one bond, visualization information is written instead of the first MO.



We can see that this bond is exactly C1-C2 π-bond with ON=0.99|e|.

4. Unrestricted AdNDP analysis

Now let us look at the example of Open Shell system calculated with the unrestricted method. Our molecule of interest is the $C_6H_6^-$ at the geometry of the C_6H_6. NBO and MO files were

calculated at UPBE0/6-311G level of theory. To create input files, we are going to use the first option, but now we have DMNAO calculated separately for alpha and beta electrons.

```
1) Create AdNDP.in and Distance.in files.
2) AdNDP analysis.
3) AdNDP direct search.
4) Quit.
1
Is the density matrix calulated separetely for Alpha and Beta electron? (Y/N): Y
Enter NBO file name: nbo.out
Enter MO file name: mo.out
```

After that you will see this message:

```
Switching to Open Shell mode preparing mode...
Alpha and Beta folders with proper MO, NBO, AdNDP.in and Distance.in files have been created. To perform AdNDP analysis
for openshell system, please, follow the standart procedure of AdNDP analysis using files in created folders!
```

Also, two new folders have been created:

alpha		File folder
beta		File folder
AdNDP_2.py	37 KB	PY File
mo.out	339 KB	Chemcraft out ...
nbo.out	471 KB	Chemcraft out ...

These folders contain AdNDP.in, Distance.in, mo.out files for alpha and beta electrons separately. NBO-files has been modified and contain only alpha or only beta DMNAO. Now we need to conduct alpha and beta analyses separately. For this reason, we need to duplicate a script file to the alpha and beta folders.

AdNDP.in	1 KB	IN File
AdNDP_2.py	37 KB	PY File
Distance.in	1 KB	IN File
mo.out	339 KB	Chemcraft out ...
nbo.out	309 KB	Chemcraft out ...

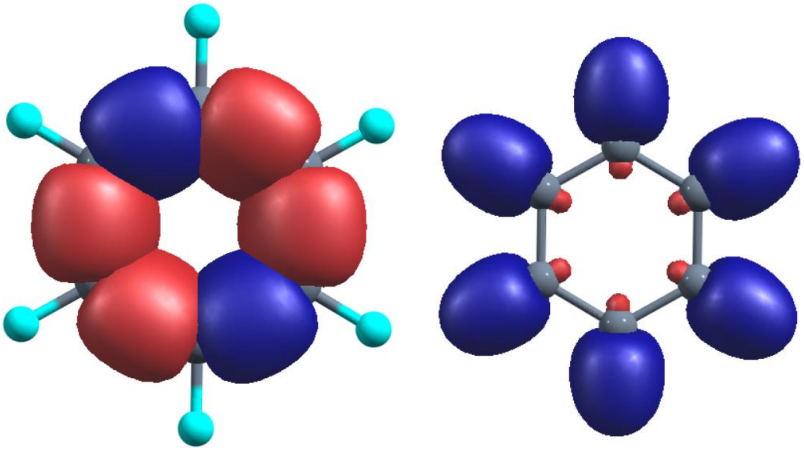
The main difference between the unrestricted and restricted methods is that we need to use thresholds greater than one. Let us try to find 2c-2e bonds for alpha electron with ON>0.98|e| and "Distance restriction" 1.5 Å.

```
Occupation number thresholds
0.
1.02
0.
0.
0.
0.
0.
0.
0.
0.
0.
0.
```

```
(base) D:\Manual\Benzene_example\alpha>python AdNDP_2.py
1) Create AdNDP.in and Distance.in files.
2) AdNDP analysis.
3) AdNDP direct search.
4) Quit.
2
Occupancy of Core 1c-2e bond on  [1] atom(s) is 0.9996167607242396
Occupancy of Core 1c-2e bond on  [2] atom(s) is 0.9996130329587345
Occupancy of Core 1c-2e bond on  [3] atom(s) is 0.9996130329587345
Occupancy of Core 1c-2e bond on  [6] atom(s) is 0.9996130329587345
Occupancy of Core 1c-2e bond on  [7] atom(s) is 0.9996130329587345
Occupancy of Core 1c-2e bond on  [10] atom(s) is 0.9996167607242396
************Residual density:  16.00231434671658 |e|************
```

```
---------------Ignoring  1c-2e bonds!---------------
1) LD: Occupancy of  2c-2e bond on  [6, 10] atom(s) is  0.9920600037381052
2) LD: Occupancy of  2c-2e bond on  [7, 10] atom(s) is  0.9920600037381052
3) LD: Occupancy of  2c-2e bond on  [1, 2] atom(s) is  0.9920600037381049
4) LD: Occupancy of  2c-2e bond on  [1, 3] atom(s) is  0.9920600037381049
5) LD: Occupancy of  2c-2e bond on  [2, 6] atom(s) is  0.9917423043596689
6) LD: Occupancy of  2c-2e bond on  [3, 7] atom(s) is  0.9917423043596689
7) LD: Occupancy of  2c-2e bond on  [1, 12] atom(s) is  0.9909956736362554
8) LD: Occupancy of  2c-2e bond on  [10, 11] atom(s) is  0.9909956736362554
9) LD: Occupancy of  2c-2e bond on  [2, 4] atom(s) is  0.9905269190797255
10) LD: Occupancy of  2c-2e bond on  [3, 5] atom(s) is  0.9905269190797255
11) LD: Occupancy of  2c-2e bond on  [6, 8] atom(s) is  0.9905269190797255
12) LD: Occupancy of  2c-2e bond on  [7, 9] atom(s) is  0.9905269190797255
---------------Ignoring  3c-2e bonds!---------------
---------------Ignoring  4c-2e bonds!---------------
---------------Ignoring  5c-2e bonds!---------------
---------------Ignoring  6c-2e bonds!---------------
---------------Ignoring  7c-2e bonds!---------------
---------------Ignoring  8c-2e bonds!---------------
---------------Ignoring  9c-2e bonds!---------------
---------------Ignoring  10c-2e bonds!---------------
---------------Ignoring  11c-2e bonds!---------------
---------------Ignoring  12c-2e bonds!---------------
************Residual density:  4.10649069945341 |e|************
```

We found twelve 2c-2e bonds. Now let us visualize them.



Analogically, the same procedure should be done for beta electrons.

5. Citations

Please, provide the following citations for the AdNDP 2.0 code if using it:

N. V. Tkachenko and A. I. Boldyrev, *"Chemical bonding analysis of excited states using the Adaptive Natural Density Partitioning method"*, *Phys. Chem. Chem. Phys.*, **2019**, *21*, 9590-9596.

D. Yu. Zubarev and A. I. Boldyrev, *"Developing paradigms of chemical bonding: adaptive natural density partitioning" Phys. Chem. Chem. Phys.,* **2008**, *10*, 5207–5217.