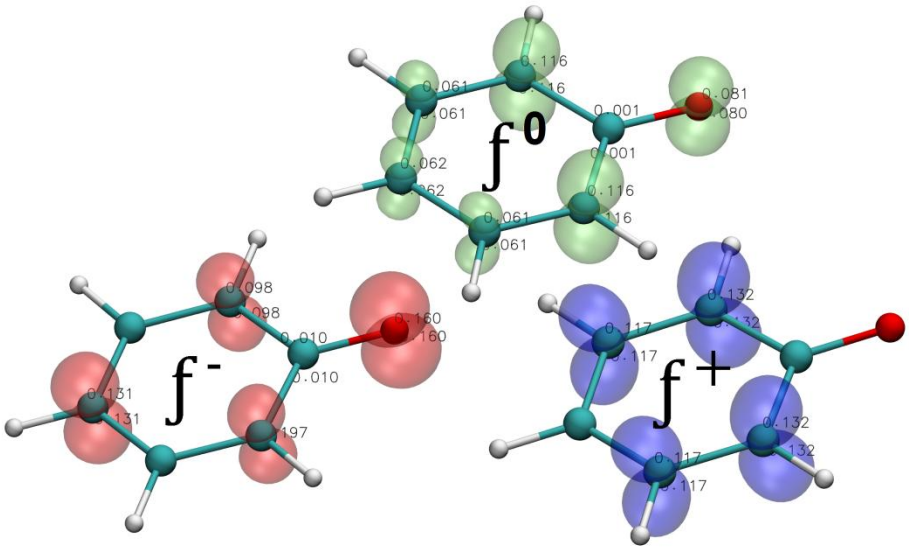
TAFF

Topological Analysis of Fukui Function

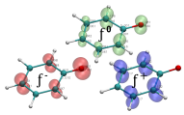
Pipeline software Manual

2015-Oct-22



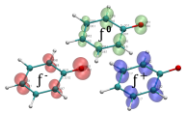
Tiznado Lab.

Doctorado en Fisicoquímica Molecular
Facultad de Ciencias Exactas
Universidad Andrés Bello
República 275, Santiago, Chile



CONTENTS

	Page
1. INTRODUCTION	3
2. PRELIMINARY CONSIDERATIONS	4
3. INSTALLATION AND USE OF TAFF	6
4. EXAMPLES	11
5. REFERENCES	14
6. ATTACHED	15



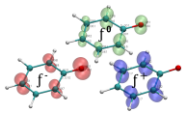
1. INTRODUCTION

The TAFF pipeline has been designed in order to "condense" the Fukui function according to it's topological analysis. This function is defined as the electronic density response when modifying the number of electrons (N), providing information about the reactive sites

Global Chemical Reactivity Properties

	Koopmans' theorem	*Finite Differenceapproximation*	*Ref.*
IonizationPotential (I)	$I = -\epsilon_H$	$I = \epsilon_{N-1} - \epsilon_N$	1,2
Electroaffinity (A)	$A = -\epsilon_L$	$A = \epsilon_N - \epsilon_{N+1}$	1,2
Chemical Potential (μ)	$\mu \approx \frac{1}{2}(\epsilon_L + \epsilon_H)$	$\mu \approx -\frac{1}{2}(I + A)$	1,3–7
Global Hardness (η)	$\eta \approx \frac{1}{2}(\epsilon_L - \epsilon_H)$	$\eta \approx \frac{1}{2}(I - A)$	1,4–8
Global Softness (S)	$S \approx \frac{1}{2\eta} \approx (\epsilon_L - \epsilon_H)^{-1}$	$S \approx \frac{1}{2\eta} \approx (I - A)^{-1}$	9–11
Electronegativity (χ)	$\chi \approx -\frac{1}{2}(\epsilon_L + \epsilon_H)$	$\chi \approx \frac{1}{2}(I + A)$	8,12,13
Electrophilicity (ω)	$\omega = \frac{\mu^2}{2\eta} \approx \frac{(\epsilon_L + \epsilon_H)^2}{2(\epsilon_L - \epsilon_H)}$	$\omega = \frac{\mu^2}{2\eta} \approx \frac{(I + A)^2}{2(I - A)}$	14
Electron Acceptor (ω^+)	$\omega^+ = \frac{(\epsilon_L + 3\epsilon_H)^2}{16(\epsilon_L - \epsilon_H)}$	$\omega^+ = \frac{(I + 3A)^2}{16(I - A)}$	14
Electron Donator (ω^-)	$\omega^- = \frac{(3\epsilon_L + \epsilon_H)^2}{16(\epsilon_L - \epsilon_H)}$	$\omega^- = \frac{(3I + A)^2}{16(I - A)}$	14
Net Electrophilicity($\Delta\omega^\pm$)	$\Delta\omega^\pm = \omega^+ + \omega^-$	$\Delta\omega^\pm = \omega^+ + \omega^-$	15

Table N°1. Equations for global reactivity indexes calculated by TAFF pipeline.



2. PRELIMINARY CONSIDERATIONS

2.1. Input file: The TAFF pipeline uses a formatted checkpoint file (.fch) as input. This file can be retrieved after formatting a binary Gaussian checkpoint file (.chk) which, in turn, has been obtained after a Gaussian09 or Gaussian03 calculation has been completed:

```
$ formchk filename.chk filename.fch
```

NOTE: The atomic positions of the neutral, cationic and anionic species need tobe the same when calculating the Fukui function by means of the finite difference approximation. Therefore, the use of the keyword "NOSYMM" in the route section of the Gaussian input file is suggested (See section 3.3.).

2.2. Multiwfn download and installation: Multiwfn program needs to be installed on your computer. If not, please follow the instructions bellow:

- Download the Multiwfn program from the following link: https://multiwfn.codeplex.com/.
  NOTE:
  The Linux or Windows version must be downloaded according to the version of TAFF to be used.

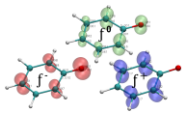
- Installation of Multiwfn:
  ForLinux:
  Open a terminal window and execute the following commands:

```
$ unzip Multiwfn_version_bin_linux.zip
$ cd Multiwfn_version_bin_linux
$ chmod 777 Multiwfn libiomp4.so
$ sudo apt-get install libmotif4
```

  Modify the *.bashrc* file (Environment variables) adding the following lines, using nano or any other text editor

```
$ nano .bashrc

export KMP_STACKSIZE=64000000
```



```
export LD_LIBRARY_PATH=/home/user/Multiwfn_version_bin_linux/
```

And then, execute the following command:

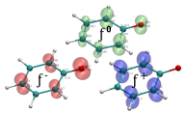
```
$ source .bashrc
```

For Windows:

Decompress the program package.

The “Multiwfn.exe” executable file and the “libiomp5md.dll” .dll file must be inside the decompressed folder.

In order to verify that the Multiwfn is running properly, open a cmd terminal, navigate to the directory (where the Multiwfn.exe file was decompressed); then, write Multiwfn.exe and press Enter.



3. INSTALLATION AND USE OF TAFF

In order to run TAFF, just execute the binary file of the corresponding operative system:

TAFF32.exe	*Executable version for 32bits Windows OS.*
TAFF64.exe	*Executable version for 64bits Windows OS.*
TAFF	*Executable version for 64bits Linux OS.*

NOTE:

*The **TAFF32.exe**, **TAFF64.exe** and **TAFF** executables will be named **TAFF** in this tutorial.*

3.1. Files needed for the execution of TAFF pipeline

Linux OS

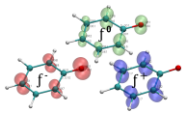
TAFF	*TAFF pipeline executable file.*
Multiwfn	*Multiwfn executable file*
libiomp5.so	*Intel OpenMPRuntimelibrary.*

32bits Windows OS

TAFF32.exe	*TAFF pipeline executable file for 32bits.*
route.txt	*File containing the directory where the Multiwfn executable is located.*
Multiwfn	*Multiwfn executable file.*
libiomp5md.dll	*Intel OpenMP Run time library.*
cygstdc++-6.dll	*Dynamic Link Library.*
cygwin1.dll	*Dynamic Link Library.*
disdll_d.dll	*Dynamic Link Library.*
cyggcc_s-1.dll	*Dynamic Link Library for 32 bits module.*

64bits Windows OS

TAFF64.exe	*TAFF pipeline executable file for 64bits.*



route.txt	*File containing the directory where the Multiwfn executable is located.*
Multiwfn	*Multiwfn executable file.*
libiomp5md.dll	*Intel OpenMP Run time library.*
cygstdc++-6.dll	*Dynamic Link Library.*
cygwin1.dll	*Dynamic Link Library.*
disdll_d.dll	*Dynamic Link Library.*
cyggcc_s-seh-1.dll	*Dynamic Link Library for 64 bits module.*

NOTE:

In red words ***Multiwfn package*** *and blue words* ***TAFF pipeline package****.*

Rudimentary help for certain parts of TAFF is retrieved by executing:

```
$ TAFF -h
```

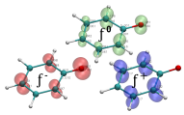
Which prints the following information:

`$ TAFF -k [compute]` print type keywords Koopmans Approach (according to equation 2 in the main article)

`$ TAFF -fd [compute]` print type keywords Finites Differences Approach (according to equation 3 in the article)

`$ TAFF -w [compute]` print type keywords Orbital-Weighted Local Reactivity Descriptor (according to equation 5 in the main article)

`[compute] = -f`	To compute Fukui function condensation in basins by integrating the scalar function.
`[compute] = -e`	To compute electron density in Fukui function condensation in basins.
`[compute] = -all`	To compute both (-e and -f).



3.2. Input/output file descriptions:

Input files

Extension file	Description
inputfile.fch	*Gaussian formatted checkpoint file.*

NOTE:

Contents of TAFF folder should be in the same directory as the Gaussian formatted checkpoint file (.fch).

Output files

Extension file	Description
outputfile.cube	*Cube file contains volumetric data as well as atom positions. It originates from the Gaussian software package.*
outputfile.dat	*Results of the Fukui function condensation in basins by integrating the scalar function (view attached N°2).*
outputfile.vmd	*Basin display in software VMD (view attached N°3).*

NOTE:

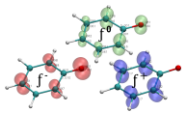
When the software execution is completed, two folders are created and named after the method and the file extension (i.e. koopmann_cube and koopmann_dat). In the first folder files with extension .vmd and .cube are placed, and in the second only the files with the .dat extension are placed.

3.3. Use of TAFF pipeline for topogical analysis of different Fukui function approximations

- **Koopman's Approximation:**

```
$ TAFF -k [compute] inputfile.fch
```

NOTE:



Calculation of Electrophilic, Nucleophilic and Radical Fukui Functions. The file inputfile.fch must correspond to a single point calculation of the molecule for which the Fukui function is to be calculated.

- **Finite Difference Approximation:**

```
$ TAFF -fd [compute] inputfile_neutral.fch inputfile_cation.fch inputfile_anion.fch
```

NOTE:

Calculation for Electrophilic, Nucleophilic and Radical Fukui functions. The inputfile_neutral.fch, inputfile_cation.fch, inputfile_anion.fch files must correspond to single point calculations on the neutrally, positively and negatively charged molecule in the geometry of the neutral molecule. The use of the keyword "NOSYMM" in the route section of the Gaussian single point calculation input file is suggested, as it is required that the atomic positions of the neutral cationic and anionic species be the same when calculating the Fukui function.

```
$ TAFF -fd [compute] inputfile_neutral.fch inputfile_cation.fch 0
```

NOTE:

Nucleophilic Fukui function does not require the anionic system file. To obtain this function, put 0 *at the end of the command.*

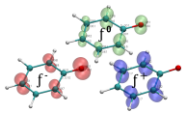
```
$ TAFF -fd [compute] inputfile_neutral.fch 0 inputfile_anion.fch
```

NOTE:

Electrophilic Fukui Function does not require cationic_system file. To obtain this function, put 0 *after the inputfile_neutral.fch.*

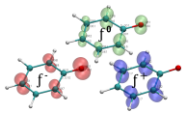
- **Orbital-weighted Fukui Function Approximation:**

```
$ TAFF -w [compute] filename.fch 0.1
```



NOTE:

0.1 is the width of the Gaussian function. The 0.1 value is recommended.



4. EXAMPLES

Here, we will calculate the Fukui Function in Koopman's and Orbital-weighted Local Reactivity Descriptor approximations

4.1. Obtaining Fukui Function using Koopman's approximation

Execute:

```
$ TAFF-k -all neutral.fch
```

NOTE:

Electrophilic, Nucleophilic and Radical Fukui Function are calculated.

Fukui Function cube files are generated, also files with the condensation information (.dat), and finally VMD file (.vmd) for visualization in VMD software

4.2. Obtaining Fukui Function using Finite Differences approximation

Execute:

```
$ TAFF -fd -all neutral.fch cation.fch anion.fch
```

NOTE:

In this case, Electrophilic, Nucleophilic and Radical Fukui Function is calculated.

Fukui Function cube files are generated, also file with the condensation information (.dat), and finally VMD file (.vmd) for visualization in VMD software

4.3.Obtaining Orbital-weighted Fukui Function Approximation.

Execute:

```
$ TAFF -w -all filename.fch 0.1
```

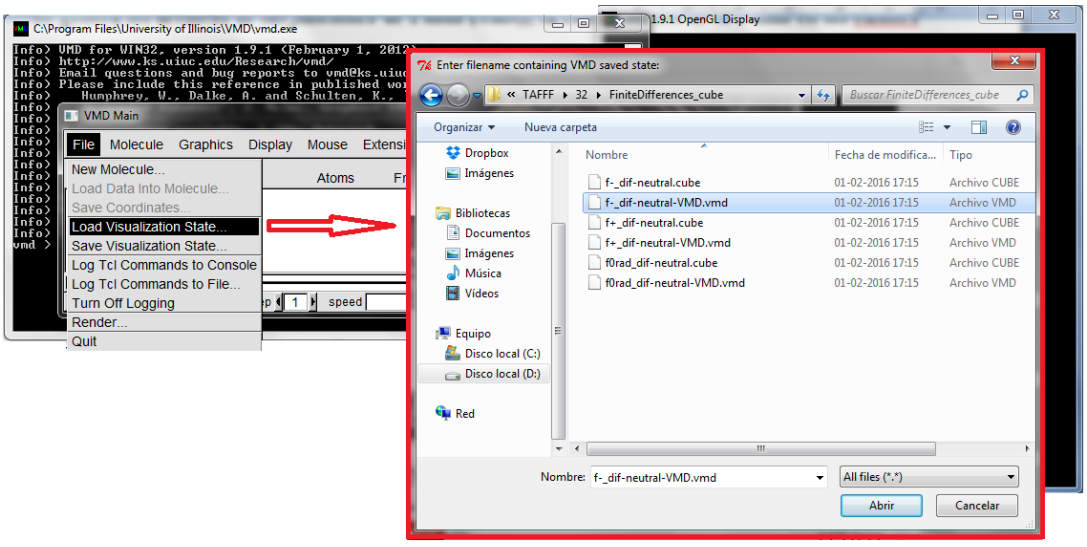
NOTE:

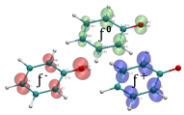
Nucleophilic Fukui Function is calculated, where the recommenden value (0.1) is used.

Fukui Function cube files are generated, also file for condensation files (.dat), and finally VMD file (.vmd) for visualization in VMD software

4.4. Basin Visualization using VMD Software

VMD software needs to be installed on your pc (can be downloaded in this link http://www.ks.uiuc.edu/Development/Download/download.cgi?PackageName=VMD). For the molecular structure and condensations values, we should open the *.vmd* file. After the software is installed we must perform the following steps:

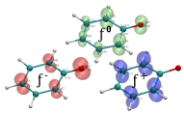




1- Open VMD.
2- Click on file→Load Visualization State.
3- Looking for *.vmd* file.
4- Finally open the file (view attached N°3).

NOTE:

For the visualization of basins and condensed values .cube and .dat files need to be in the same directory than .vmd file



5. REFERENCES

1 T. Koopmans, *Physica*, 1934, **1**, 104–113.

2 R. G. Pearson, *Proc. Natl. Acad. Sci. U. S. A.*, 1986, **83**, 8440–8441.

3 R. G. Parr, R. A. Donnelly, M. Levy and W. E. Palke, *J. Chem. Phys.*, 1978, **68**, 3801.

4 E. G. Lewars, *Computational Chemistry-Introduction to the Theory and Applications of Molecular and Quantum Mechanics*, Springer Netherlands, New York, 2011.

5 D. C. Young, *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*, John Wiley & Sons, New York, 2002.

6 F. Jensen, *Introduction to Computational Chemistry*, John Wiley & Sons, New York, 2nd editio., 2006.

7 C. J. Cramer, *Essentials of Computational Chemistry: Theories and Models*, John Wiley & Sons, New York, 2nd editio., 2004.

8 R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.*, 1983, **105**, 7512–7516.

9 W. Benchouk and S. M. Mekelleche, *J. Mol. Struct. THEOCHEM*, 2008, **852**, 46–53.

10 H. Chermette, *J. Comput. Chem.*, 1999, **20**, 129–154.

11 P. Geerlings, F. De Proft and W. Langenaeker, *Chem. Rev. (Washington, DC, United States)*, 2003, **103**, 1793–1873.

12 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533–3539.

13 R. G. Pearson, *Chemical Hardness*, Wiley, New York, 2005.

14 J. L. Gázquez, A. Cedillo and A. Vela, *J. Phys. Chem. A*, 2007, **111**, 1966–70.

15 P. K. Chattaraj, A. Chakraborty and S. Giri, *J. Phys. Chem. A*, 2009, **113**, 10068–74.

6. ATTACHED

```
 _________   ____    ________   ________
 \__   __/  /    \  |  _____/  |  _____/
    | |    / /__\ \ | |        | |
    | |    | |__| | | |___     | |___
    | |    |  __  | |  ___/    |  ___/
    | |    | |  | | | |        | |
    |_|    |_|  |_| |_|        |_|
# # # # # # # # # # # # # # # # # # # # # # # # # #
# Topological Analysis of Fukui Functions (TAFF)  #
# DATE: 2016-07-07.12:14:14                       #
# TiznadoLab                                      #
# # # # # # # # # # # # # # # # # # # # # # # # # #


Koopman's approximation selected

HOMO energy:                    -2.86170637E-01
LUMO energy:                    -3.20930535E-02
GAP :                           0.254078
Total electronic energy:        -568.842041

...:::Global reactivity indexes:::...

Ionization potential :          0.2861706316
Electroaffinity :               0.03209305182
Chemical potential :            -0.159131839871
Global Hardness :               0.127038791776
Global Softness :               3.93580579758
Electronegativity :             0.159131839871
Electrophilicity Index (w):     0.0996661782265
w+ Electron Acceptor:           0.035980116576
w- Electron Donator:            0.195111975074
Electrophilicity Net:           0.231092095375

Program finished correctly
CPU TIME: 57 seconds
```

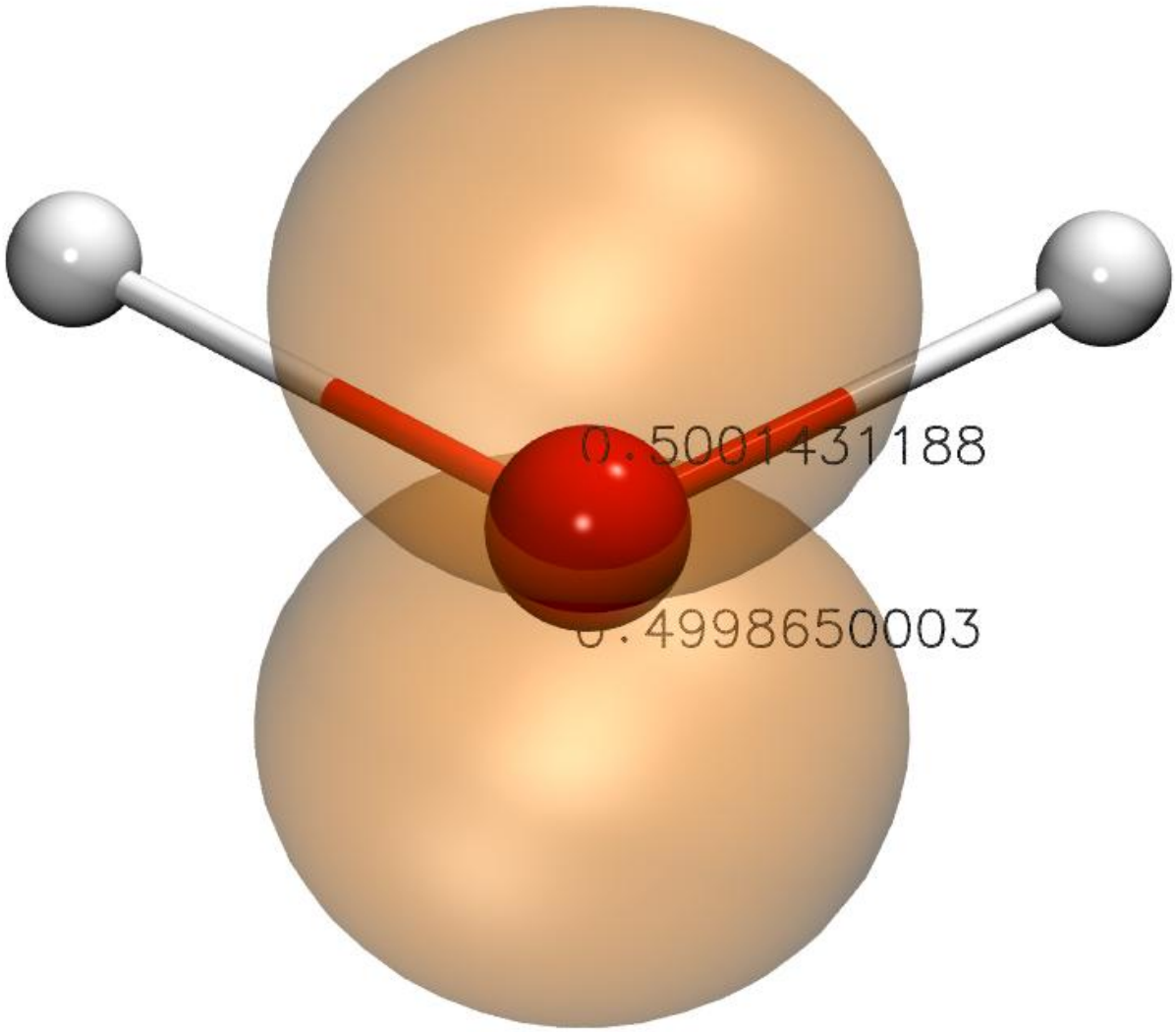
Attached N°1. Output text of Global Chemical Reactivity Properties (see table N°1) to screen from console.

```
TAFF
# # # # # # # # # # # # # # # # # # # # # # # # # #
# Topological Analysis of Fukui Functions (TAFF)  #
# DATE: 2016-07-07.12:14:48                        #
# TiznadoLab                                       #
# # # # # # # # # # # # # # # # # # # # # # # # # #
```

BASIN	VOLUME	INTEGRAL	<X>	<Y>	<Z>	VALUE
1	596.96295001	0.0274429886	-2.12814346	-1.22136279	-0.26699426	0.101512000E-01
2	301.24955498	0.0708662829	-0.76134213	-1.22136279	-0.26699426	0.212401000E-01
3	800.02980196	0.0723851534	-0.76134213	-1.22136279	0.24555624	0.213502000E-01
4	501.56094738	0.0035679959	1.97226054	-1.05051262	-0.69411968	0.855606000E-02
5	307.64811067	0.1496188210	-0.07794146	-0.02541162	-0.26699426	0.553522000E-01
6	528.26156078	0.1410706579	-2.81154412	-0.02541162	-0.26699426	0.566062000E-01
7	238.10956656	0.0563205772	-0.76134213	1.25596463	-0.26699426	0.174416000E-01
8	677.54857318	0.0412617041	-2.12814346	1.25596463	-0.26699426	0.132244000E-01
9	442.45528829	0.0029025925	1.97226054	1.17053955	-0.52326951	0.701311000E-02
10	719.23383837	0.0581094189	-0.76134213	1.25596463	0.24555624	0.177225000E-01
11	17.18060582	0.0049070371	1.88683546	-0.87966245	-0.69411968	0.999564000E-02
12	19.22090793	0.0037668182	1.88683546	0.99968938	-0.60869460	0.843732000E-02
13	3.42434210	0.0035241024	1.37428496	-0.02541162	-0.35241935	0.613360000E-02
14	792.61740543	0.1412118284	-2.81154412	-0.02541162	0.24555624	0.560619000E-01
15	199.08721114	0.1317155129	-0.07794146	-0.02541162	0.24555624	0.549394000E-01
16	5.24168336	0.0035542000	1.37428496	-0.02541162	0.24555624	0.570949000E-02
17	157.33884382	0.0269404141	-2.04271837	-1.22136279	0.33098132	0.100693000E-01
18	540.75998877	0.0078727373	1.97226054	-0.11083670	1.27065724	0.287357000E-01
19	14.09701520	0.0125882285	1.71598529	-0.11083670	1.18523215	0.245739000E-01
20	241.39929079	0.0403770815	-2.12814346	1.25596463	0.24555624	0.130332000E-01
TOTAL		1.00000415				

THE MEMBERS OF DEGENERATED ATTRACTOR

Attached N°2. The data shown in the table represent the number of basins, volume, value of integration for each of them, Cartesian coordinates and the value of each basin. Furthermore, the degenerate are attractors shown if the molecule under study had.



Attached N°3. Graphical visualization in software VMD of the Nucleophilic Fukui function for H_2O using the Koopman's approximation (isosurface value: 0.01) also the condensed values are shown.