

# **Multiwfn**

**- A Multifunctional Wavefunction Analyzer -**

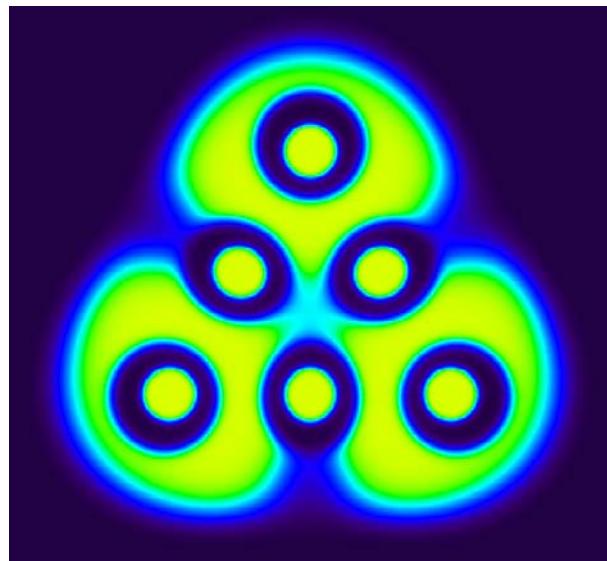
## **Software Manual**

**with abundant tutorials and examples in Chapter 4**

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<http://sobereva.com/multiwfn>



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# !!!!!! ALL USERS MUST READ !!!!!!!

I know, most people, including myself, are unwilling to read lengthy manual. Since Multiwfn is a heuristic and very user-friendly program, it is absolutely unnecessary to read through the whole manual before using it. However, you should never skip reading following content!

1. The BEST way to get started quickly is first reading Chapter 1, Section 2.1~2.5 of Chapter 2, and then follow the tutorials in Chapter 4. After that if you want to learn more about theoretical backgrounds and details of Multiwfn, then read Section 2.6~2.8 of Chapter 2 and Chapter 3. Note that the tutorials and examples given in Chapter 4 only cover the most important and frequently used functions rather than all functions of Multiwfn. Some application skills are described in Chapter 5, which may be useful for you.
2. Different functions of Multiwfn require different type of input file, please read Section 2.5 for explanation.
3. If you do not know how to copy the output of Multiwfn from command-line window to a plain text file, consult Section 5.4. If you do not know how to enlarge screen buffer size of command-line window of Windows system, consult Section 5.5.
4. If the error “No executable for file 11.exe” appears in screen when Multiwfn is invoking Gaussian, you should set up Gaussian environment variable first. For Windows version, you can refer Appendix 1. (Note: Most functions in Multiwfn DO NOT require Gaussian installed on your local machine)
5. The so-called “current directory” in this manual is the path where you are invoking Multiwfn. If you boot up Multiwfn by clicking the icon of executable file in Windows, the “current directory” is the position of the executable file. For the case of command-line mode, if you are in “D:\study\” directory when invoking Multiwfn, then “D:\study” is “current directory”.
6. Please often check Multiwfn website and update the program to the latest version. Multiwfn is always in active development, useful functions are continuously added, bugs are continuously fixed and efficiency is continuously improved.
7. Please feel free to ask any question about using Multiwfn by emailing me (sobereva@sina.com), but please ensure that you have read this manual carefully to find solution, and you have updated your Multiwfn to the latest version. I would like to provide as much help as I can for any Multiwfn user. \(^{\circ}\forall^{\circ})/

# **Linux and Mac OS USERS MUST READ**

1. See Section 2.1.2 and 2.1.3 on how to install Linux and Mac OS versions of Multiwfn, respectively.
2. When graphical user interface (GUI) appears, the graph cannot be shown automatically, you have to do something to active the graph, e.g. clicking "up" button or dragging a scale bar in the GUI.
3. Transparent style does not work when showing isosurfaces in GUI window. But if you choose to save the picture, the transparent isosurfaces can be rendered normally in the resulting graphical file.

# About the manual

This manual is organized as following sequence:

Chapter 1 Overview: Briefly describes what is Multiwfn and what Multiwfn can do.

Chapter 2 General information: Introduces all aspects beyond specific functions of Multiwfn, such as how to install, how to use, supported file types, etc.

Chapter 3 Functions: Describes all functions and related theories of Multiwfn in detail.

Chapter 4 Tutorials and examples: Plenty of practical examples are provided for helping users to use Multiwfn.

Chapter 5 Skills: Some useful skills in using Multiwfn.

Appendix

In general, italics font is used for input commands and journal name throughout this manual. Very important contents are highlighted by red color.

You can directly jump to specific section by choosing corresponding entry in bookmark window of your pdf reader.

The purpose of this manual is not only helping users to use Multiwfn, but also introducing related theories. I hope any quantum chemist can benefit from this manual.

Albeit I have tried to write this manual as readable as possible for beginners, some topics request the readers have basic knowledges of quantum chemistry. If the readers have carefully read the book "Quantum Chemistry 7ed" written by Ira. Levine, then they will never encounter any difficulty during reading through the whole manual.

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# 1 Overview

Multiwfn is an extremely powerful wavefunction analysis program, it supports almost all of the most important wavefunction analysis methods. Multiwfn is free, open-source, high-efficient, very user-friendly and flexible. 64 bit Windows, Linux and Mac OS platforms are supported. Multiwfn can be downloaded at Multiwfn official website <http://sobereva.com/multiwfn>.

## **Input files supported by Multiwfn**

Multiwfn accepts several kinds of files for loading wavefunction information: .wfn/.wfx (Conventional / Extended PROAIM wavefunction file), .fch (Gaussian formatted check file), .molden (Molden input file), .31~.40 (NBO plot files) and .gms (GAMESS-US output file). Other type of files such as Gaussian output file, .cub file, DMol3 .grd file, .pdb file, .xyz file can be used for specific functions.

## **Special points of Multiwfn**

- (1) Comprehensive functions. Almost all of the most important wavefunction analysis methods (except for NBO methods) are supported by Multiwfn.
- (2) Very user-friendly. Multiwfn is designed as an interactive program, prompts shown on screen in each step clearly tell users what should do next, Multiwfn also never prints obscure messages, hence there is no barrier even for beginners. In addition, there are about 100 well-written tutorials in the manual, which are very helpful for new users.
- (3) High efficiency. The code of Multiwfn is substantially optimized. Most parts are parallelized by OpenMP technology. For computationally intensive tasks, the efficiency of Multiwfn exceeds analogous programs significantly.
- (4) Results can be visualized directly. A high-level graphical library DISLIN is invoked internally and automatically by Multiwfn for visualizing results, most plotting parameters are controllable in interactive interface. This remarkably simplified wavefunction analysis, especially for studying distribution of real space functions.

## **Primary functions of Multiwfn**

- 1) Showing molecular structure and viewing orbitals (MO, NBO, natural orbital, etc.).
- 2) Outputting all supported real space functions at a point.
- 3) Outputting real space function in a line and plot it as curve map.
- 4) Outputting real space function in a plane and plot it as graph. Supported graph types include filled-color map, contour map, relief map (with/without projection), gradient map, vector field map.
- 5) Outputting real space function in a spatial scope, data can be exported to Gaussian-type grid file (.cub) and can be visualized as isosurface.
- 6) For the calculation of real space functions in one-, two- and three-dimensions, user can

define the operations between the data generated from multiple wavefunction files. Therefore one can calculate and plot such as Fukui function, dual descriptor and density difference very easily. Meanwhile promolecule and deformation properties for all real space functions can be calculated directly.

- 7) Topology analysis for electron density (AIM analysis), Laplacian, ELF/LOL etc. Critical points and gradient paths can be searched and visualized in terms of 3D or plane graph. Interbasin surfaces can be drawn. Values of real space functions can be calculated at critical points or along topology paths.
- 8) Checking and modifying wavefunction. For example print orbital and basis function information, manually set orbital occupation number and type, translate and duplicate system, discard wavefunction information from specified atoms.
- 9) Population analysis. Hirshfeld, Hirshfeld-I, VDD, Mulliken, Löwdin, Modified Mulliken (including three methods: SCPA, Stout & Politzer, Bickelhaupt), Becke, ADCH (Atomic dipole moment corrected Hirshfeld), CHELPG, Merz-Kollmann and AIM methods are supported.
- 10) Orbital composition analysis. Mulliken, Stout & Politzer, SCPA, Hirshfeld, Hirshfeld-I, Becke and natural atomic orbital (NAO) methods are supported to obtain orbital composition.
- 11) Bond order analysis. Mayer bond order, multi-center bond order (up to 12-centers), Wiberg bond order in Löwdin orthogonalized basis and Mulliken bond order are supported. Mayer and Mulliken bond order can be decomposed to orbital contributions.
- 12) Plotting Total/Partial/Overlap population density-of-states (TDOS, PDOS, OPDOS), up to 10 fragments can be very flexibly and conveniently defined. Local DOS (LDOS) can also be plotted for a point as curve map or for a line as color-filled map.
- 13) Plotting IR/Raman/UV-Vis/ECD/VCD spectrum. Abundant parameters (broadening function, FWHM, etc.) can be determined by users, individual contribution from each transition to the spectrum can be easily studied. Conformational weighted spectrum as well as spectra of all conformations can be very conveniently plotted together.
- 14) Quantitative analysis of molecular surface. Surface properties such as surface area, enclosed volume, average value and std. of mapped functions can be computed for overall molecular surface or local surfaces; local minima and maxima of mapped functions on the surface can be located. Becke and Hirshfeld surface analysis, as well as fingerprint analysis are also supported.
- 15) Processing grid data (can be loaded from .cub/.grd or generated by Multiwfn). User can perform mathematical operations on grid data, set value in certain range, extract data in specified plane, plot integral curve, etc.
- 16) Adaptive natural density partitioning (AdNDP) analysis. The interface is interactive and the AdNDP orbitals can be visualized directly.
- 17) Analyzing real space functions in fuzzy atomic spaces (defined by Becke, Hirshfeld or Hirshfeld-I partitions). Integral of selected real space function in atomic spaces or in overlap regions of atomic spaces, atomic multipole moments, atomic overlap matrix (AOM), localization and delocalization index (DI), condensed linear response kernel, multi-center DI, as well as four aromaticity indices, namely FLU, FLU-pi, PDI and PLR can be computed.

- 18) Charge decomposition analysis (CDA) and extended CDA analysis. Orbital interaction diagram can be plotted. Infinite number of fragments can be defined.
- 19) Basin analysis. Attractors can be located for any real space function, corresponding basins can be generated and visualized at the same time. All real space functions can be integrated in the generated basins. Electric multipole moments, orbital overlap matrix, localization index and delocalization index can be calculated for the basins. Atomic contribution to basin population can be obtained.
- 20) Electron excitation analysis, including: Visualizing and analyzing hole-electron distribution, transition density, transition electric/magnetic dipole moment and charge density difference; calculating Coulomb attractive energy between hole and electron; Calculating atomic transition charges; decomposing transition dipole moment to MO pair contribution or basis function/atom contribution; analyzing charge-transfer by the method proposed in JCTC, 7, 2498; plotting transition density matrix as color-filled map; calculating  $\Delta r$  index to reveal electron excitation mode; calculating transition dipole moments between all excited states; generating natural transition orbitals (NTOs).
- 21) Other useful functions or utilities involved in quantum chemistry studies: Weak interaction analysis via RDG method (including fluctuation environment analysis); plotting scatter map for two functions in specific spatial scope; integrating a real space function over the whole space by Becke's multi-center method; evaluating overlap integral between alpha and beta orbitals; evaluating overlap and centroid distance between two orbitals; monitoring SCF convergence process; generating Gaussian input file with initial guess from converged wavefunction or multiple fragment wavefunctions; calculating van der Waals volume; calculating HOMA and Bird aromaticity indices; calculating LOLIPOP index; calculating intermolecular orbital overlap; Yoshizawa's electron transport route analysis; calculating atomic and bond dipole moment in Hilbert space; plotting radial distribution function for real space functions; plotting iso-chemical shielding surface (ICSS); calculating overlap integral between orbitals in two different wavefunctions; parsing output of (hyper)polarizability task of Gaussian; calculating polarizability and 1st/2nd/3rd hyperpolarizability by sum-over-states (SOS) method; outputting various kinds of integrals between orbitals; calculating center; the first and second moments and radius of gyration for a real space function; exporting wavefunction to .wfn, .wfx, .molden, .fch, NBO .47 and GAMESS-US input file with \$VEC; calculating bond polarity index (BPI); evaluating oxidation state; Pipek-Mezey orbital localization; perform integration within isosurface defined by a real space function and so on.

### The real space functions supported by Multiwfn

Real space function analysis is one of the most powerful feature of Multiwfn, about 100 real space functions are supported and listed below, detailed descriptions can be found in Section 2.6 and 2.7 of the manual:

- 1 Electron density
- 2 Gradient norm of electron density
- 3 Laplacian of electron density

- 4 Value of orbital wavefunction
- 5 Electron spin density
- 6 Hamiltonian kinetic  $K(r)$
- 7 Lagrangian kinetic  $G(r)$
- 8 Electrostatic potential from nuclear / atomic charges
- 9 Electron localization function (ELF) defined by Becke and the one defined by Tsirelson
- 10 Localized orbital locator (LOL) defined by Becke and the one defined by Tsirelson
- 11 Local information entropy
- 12 Electrostatic potential (ESP)
- 13 Reduced density gradient (RDG) with/without promolecular approximation
- 15 Sign( $\lambda_2$ )\*rho (The product of the sign of the second largest eigenvalue of electron density Hessian matrix and electron density) with/without promolecular approximation
- 17 Exchange-correlation density, correlation hole and correlation factor
- 18 Average local ionization energy
- 19 Source function
- 20 Others: Such as potential energy density, electron energy density, shape function, local temperature, bond metallicity, linear response kernel, local electron affinity/electronegativity/hardness, ellipticity of electron density, eta index, on-top pair density, numerous DFT exchange-correlation potential, Weizsäcker potential, Fisher information entropy, Ghosh/Shannon entropy density, integrand of Rényi entropy, steric energy/potential/charge, Pauli potential/force/charge, quantum potential/force/charge, PAEM, density overlap regions indicator (DORI), region of slow electrons (RoSE), PS-FID, single exponential decay detector (SEDD), electron linear momentum density, electric/magnetic dipole moment density, local electron correlation function.

Implementing a new real space function into Multiwfn is extremely easy, as illustrated in Section 2.7 of the manual.

## Citing Multiwfn

If Multiwfn is used in your research, this paper should be cited:

Tian Lu, Feiwu Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comp. Chem.* **33**, 580-592 (2012)

If quantitative molecular surface analysis module of Multiwfn is involved, citing below paper is also highly welcomed, in which the algorithm was described in detail

Tian Lu, Feiwu Chen, Quantitative analysis of molecular surface based on improved Marching Tetrahedra algorithm, *J. Mol. Graph. Model.*, **38**, 314-323 (2012)

If orbital composition analysis module of Multiwfn is involved, citing below paper is recommended, in which different orbital composition calculation methods are detailedly discussed

Tian Lu, Feiwu Chen, Calculation of Molecular Orbital Composition, *Acta Chim. Sinica*, **69**, 2393-2406 (2011) (in Chinese)

If CDA module of Multiwfn is involved, citing below paper is recommended, in which the

## 1 Overview

generalized CDA method that implemented in Multiwfn is introduced

Meng Xiao, Tian Lu, Generalized Charge Decomposition Analysis (GCDA) Method, *Journal of Advances in Physical Chemistry*, **4**, 111-124 (2015) (in Chinese)  
<http://dx.doi.org/10.12677/JAPC.2015.44013>

Citing Multiwfn website in your work is also highly welcomed, but please *do not ONLY* cite the website, thanks!

### Discussion zone

This is the official Multiwfn discussion zone (in Chinese, but using English is also completely OK). Before post users need to register

<http://bbs.keinsci.com/forum.php?mod=forumdisplay&fid=112>

## 2 General information

### 2.1 Install

#### 2.1.1 Windows version

What you need to do is just uncompressing the program package. You can place Multiwfn anywhere, however the name of the path (including file name) should less than 80 characters, otherwise some unexpected problems may occur. A few functions in Multiwfn rely on Gaussian, you may need to setup environment variable for Gaussian manually, see Appendix 1.

Multiwfn is compatible with 32 or 64bit version of Windows XP/Vista/7/8/10.

#### 2.1.2 Linux version

1 Uncompress the program package to for example /sob/Multiwfn. Notice that the path (including file name) should less than 80 characters.

2 Make sure that you have installed openmotif package, which provides libXm.so.4, Multiwfn cannot boot up without this file. The openmotif is freely available at <http://motif.ics.com/motif/downloads>. If you are a CentOS/RHEL user, download corresponding rpm package (e.g. motif-2.3.4-1.x86\_64\_0.rpm); if you are a Ubuntu user, download corresponding deb package (e.g. libmotif4\_2.3.4-1\_amd64.deb). Then install the package.

3 Add below sentence to your .bashrc file, e.g. /root/.bashrc, then reboot your shell

```
export KMP_STACKSI ZE=64000000
```

KMP\_STACKSIZE defines stacksize (in bytes) for each thread in parallel implementation, see Section 2.4 for detail.

4 Run `/sbin/sysctl -a/grep shmmmax` to check if the size of SysV shared memory segments is large enough (unit is in bytes), if the value is too small, Multiwfn may crashes when analyzing big wavefunction. In order to enlarge the size, for example you can add `kernel.shmmmax = 512000000` to /etc/sysctl.conf and reboot system, then the upper limit will be enlarged to about 512MB.

5 If you prefer to boot up Multiwfn from different folders, you'd better set `Multiwfnpnpath` environment variable, so that Multiwfn can find settings.ini file properly (see Section 2.3 for more detail about this file). For example, the executable file of Multiwfn is `/sob/Multiwfn_3.3.8_bin_Linux/Multiwfn`, then `Multiwfnpnpath` should be set to `/sob/Multiwfn_3.3.8_bin_Linux`.

Linux version of Multiwfn works well on Red Hat Enterprise Linux 6 & 7, CentOS 6 & 7 and Ubuntu 12. I can not guarantee that the program is completely compatible with all other Linux distributions. If system prompts you that some dynamical link libraries (.so files) are missing when booting up Multiwfn, try to find and install the packages which contain corresponding .so files.

If you are using Ubuntu and Multiwfn crashes when dealing with large systems, try adding "ulimit -s unlimited" in your .bashrc file to set the available stacksize to be formally unlimited. Because Ubuntu is one of the most foolish systems that I have ever used, its default stacksize is quite small (8MB in some versions)!

If you encounter difficulty when running/compiling Multiwfn due to missing or incompatibility of some

graphical related library files, and in the meantime you don't need visualization functions in Multiwfn, you can run/compile Multiwfn without GUI supported, all functions irrelevant to GUI and map plotting will still work normally. Please check document of compilation method in source code package on how to compile this version, the pre-compiled binary of this version can also be downloaded from Multiwfn website (termed as noGUI version).

### 2.1.3 Mac OS version

If you are using relatively old Mac OS version, e.g. OS X 10.8, please follow the instruction given in this section. If you intend to install Multiwfn in relatively new Mac OS systems, such as OS X 10.11 EI Capitan and macOS 10.12 Sierra, please follow steps in this page: <https://wiki.ch.ic.ac.uk/wiki/index.php?title=Mod:multiwfn>.

1 Uncompress the program package to for example /Users/sob/Multiwfn. Notice that the path (including file name) should less than 80 characters.

2 Download .dmg file of Mac OS version of openmotif from [http://www.ist-inc.com/downloads/motif\\_download.html](http://www.ist-inc.com/downloads/motif_download.html) and then install it. The openmotif package I installed is openmotif-compat-2.1.32\_IST.macosx10.5.dmg.

If your system does not natively support X11 (i.e. OS X Mountain Lion), you should download XQuartz from <http://xquartz.macosforge.org/landing> and install it.

3 Add below sentence to your .profile file (e.g. /Users/sob/.profile) to make them take effect automatically, then reboot your terminal. If the .profile is unexisting, you should create it manually.  
export KMP\_STACKSI ZE=64000000

KMP\_STACKSIZE defines stacksize (in bytes) for each thread in parallel implementation, see Section 2.4 for detail.

4 Run *sysctl -a/grep shmax* to check if the size of SysV shared memory segments is large enough (unit is in bytes), if the value is too small, Multiwfn may crashes when analyzing big wavefunction. In order to enlarge the size, you should edit or create the file /etc/sysctl.conf, and add *kern.sysv.shmax = 512000000* to it and reboot system, then the upper limit will be enlarged to about 512MB.

5 Move libdislin\_d.11.dylib in the Multiwfn package to /usr/local/lib folder.

6 Set *Multiwfnprefix* environment variable if needed, see point 5 of Section 2.1.2.

Now enjoy!

## 2.2 Using Multiwfn

Using Multiwfn is very easy, simply read the prompts printed on screen, you will know what should input next. If you are stuck, please read corresponding section carefully in Chapter 3 or corresponding tutorials in Chapter 4.

The first thing to do after boot up Multiwfn is inputting the path of the input file, e.g. *E:\ltwd\bitboys.wfn*. If the input file is in current directory, you can input file name without the path of directory. If the input file is just the one that last time used, you can simply input the letter *o*. (The path of the input file successfully read at last time was recorded in settings.ini). If the input file is in the same path as the one last time used, for convenience, the path can be replaced by symbol ?. For example, last time you loaded *c:\sob\wives\K-ON\Mio.wfn*, this time you can simply input *?Azusa.fch* to load *c:\sob\wives\K-ON\Azusa.fch*.

You can press CTRL+C or click “×” button at right-top of command-line window any time to

exit Multiwfn. When graphical window is showing on screen, you can click “RETURN” button to close the window, if there is no such button, click right mouse button on the graph to close it. Another way to exit Multiwfn is selecting option -10 (an hidden option) in main function menu.

If you want to load another file into Multiwfn, you can reboot Multiwfn or start a new Multiwfn task. Alternatively, in main function menu you can select option -11 (a hidden option) to re-initialize Multiwfn and load a new file.

Multiwfn also supports silent mode, by which users needn’t to click any button during running, it is useful for batch process or repeating similar tasks, please consult Chapter 5.

All involved theories and options in Multiwfn are introduced in Chapter 3. Numerous tutorials, which cover most important functions of Multiwfn are provided in Chapter 4.

## 2.3 The files of Multiwfn

You will find following files after uncompressing Multiwfn package, only the bolded files are indispensable for running Multiwfn:

**Multiwfn.exe** (Windows) or **Multiwfn** (Linux/Mac OS) : The executable file of Multiwfn.

**libomp5md.dll** (Windows) : Intel OpenMP Runtime library.

settings.ini : All detail parameters for running Multiwfn are recorded here, most of them do not need to be frequently modified. When booting up, Multiwfn will try to find and use this file in current folder, if it is not presented in current folder, the file in the path defined by "Multiwfnpnpath" environment variable will be used; if the file still cannot be found, default settings will be used instead. The meanings of all parameters in settings.ini are not documented in this manual systematically, since they have already been commented in detail, only those important will be mentioned in this manual. I suggest you read through settings.ini and find out the ones useful for you.

“examples” folder : Some useful files and input files of examples in Chapter 4.

## 2.4 Parallel implementation

Most time-consuming codes of Multiwfn have been parallelized by OpenMP. If your computer is SMP architecture, you can feel much benefit from parallelization (For grid calculation, the speed up ratio versus the number of CPU cores is nearly linear). To enable parallel mode, just modify “nthreads” parameter in settings.ini to your situation. For example, your computer have a 12-cores CPU installed, then change “nthreads” to 12.

If Multiwfn crashes during parallel calculation, try to enlarge “ompstacksize” in settings.ini (for Windows version) or enlarge the value of the environment variable KMP\_STACKSIZE (for Linux or Mac OS version).

## 2.5 Input files and wavefunction types

Wavefunction types supported by Multiwfn include restricted/unrestricted single-determinant wavefunction, restricted open-shell wavefunction and post-HF wavefunction (in natural orbital

formalism).

For basis function, Cartesian or spherical harmonic Gauss functions with angular moment up to  $\mathbf{h}$  are supported.

There is no upper limit of the number of atoms / basis functions / GTFs / orbitals in Multiwfn, the actual upper limit is only decided by available memory on your computer.

Multiwfn determines the input file type by file extension. Notice that different function need different types of information, you should choose proper type of input file, see the table below. For example, the wavefunction represented by GTFs is enough for Hirshfeld population, so you can use .fch/.molden/.gms/.31~.40/.wfn/.wfx file as input, but .pdb, .xyz, .chg, .cub and .grd files do not carry any wavefunction information hence cannot be used. While generating grid data of RDG function with promolecular approximation only requires atom coordinates, so all supported file formats can be used (except for plain text file). The requirements of information types by each function are described at the end of corresponding section in Chapter 3 by red text.

File Format	Contained information types			
	Basis functions	GTFs	Atom coordinates	Grid data
.fch/.fchk	✓	✓	✓	✗
.molden	✓	✓	✓	✗
.gms	✓	✓	✓	✗
.31~.40	✗	✓	✓	✗
.wfn	✗	✓	✓	✗
.wfx	✗	✓	✓	✗
.pdb .xyz	✗	✗	✓	✗
.chg	✗	✗	✓	✗
.cub/.cube	✗	✗	✓	✓
DMol3 .grd	✗	✗	✗	✓
Plain text file	✗	✗	✗	✗

**1 PROAIM wavefunction file (.wfn) :** This format was first introduced by Bader's AIMPAC program, and currently supported by a lot of mainstream quantum chemistry softwares, such as Gaussian, GAMESS-US/UK, Firefly, Q-Chem. The information of .wfn files include atomic coordinates/types, orbital energies, occupation numbers, expansion coefficients of Cartesian Gauss type functions (GTF). Supported angular momentum of GTF is up to  $f$ . The wfn file does not contain any virtual orbital. The generation method of .wfn file is documented at the beginning of Chapter 4.

Note: Although GTFs with angular moment of  $g$  and  $h$  are not formally supported by original .wfn format, if  $g$  and  $h$ -type GTFs are recorded in following manner, then Multiwfn is able to recognize them: 21~35 in "TYPE ASSIGNMENT" correspond to YZZZ, XYYY, XXYY, XYZZ, YZZZ, XYYZ, XXXX, XXXY, XZZZ, XXYZ, XXXZ, XXZZ, YYYY, YYYZ, ZZZZ, respectively. 36~56 correspond to ZZZZZ, YZZZZ, YYZZZ, YYYZZ, YYYYZ, YYYYY, XZZZZ, XYZZZ, XYYZZ, XYYYY, XXZZZ, XXYZZ, XXYYZ, XXYYY,

## 2 General information

XXXZZ, XXXYZ, XXXYY, XXXXZ, XXXXY, XXXXX, respectively. The sequence shown here in fact is also the sequence used in the .wfn outputted by Molden2AIM and Gaussian09 since B.01.

**2 AIM extended wavefunction files (.wfx) :** This is a newly introduced format as an extension of .wfn, the file can be generated by Gaussian09 since B.01 revision. Relative to .wfn format, .wfx supports higher data precision and infinite high angular moment of GTF. The most special point is the newly added electron density function (EDF) field, that is using multiple GTFs to represent inner core electron density of the wavefunction in which effective core potential (ECP) is used. Thus, the results of electron density analysis of the wavefunction used ECP are nearly identical to full electron wavefunction. Currently the real space functions supported EDFs in Multiwfn include: electron density, its gradient and Laplacian, local information entropy, reduced density gradient as well as  $\text{Sign}(\lambda_2(\mathbf{r}))$ . Meanwhile topology analyses of electron density and its Laplacian also take into account EDFs. **Notice that EDF informations have neither effect on ESP nor the real space functions that relied on wavefunction (e.g. kinetic energy density, ELF).** If you want to analyze these properties for heavy elements, you should use full-electrons basis-sets, at least small-core ECP. Currently the only supported GTF type in EDF field is S-type (actually S-type is enough for fitting inner density, since which is nearly spherical symmetry). Like .wfn, Multiwfn does not allow virtual orbitals presented in .wfx file.

Notice that for certain version of Gaussian (e.g. G09 B.01), I found that the EDF field recorded in .wfx for rare cases is problematic, namely the number of electrons represented by EDF field is unequal to the actual number of core electrons exhibited by ECP. In order to verify if the EDF field is correct, you can use subfunction 4 in main function 100 to obtain the integral of total electron density over the whole space, if the result is approximately equal to the total number of electrons (core+valence electrons), that means the EDF field is correct.

Multiwfn has a powerful built-in EDF library, as long as the input file contains GTF information (e.g. .fch and .wfn ...), Multiwfn always automatically loads EDF information from this library for the atoms using pseudopotential basis set. Only when you use .wfx file as input and the .wfx itself already contains EDF field, the EDF information will be loaded from the .wfx file rather than from EDF library. See Appendix 4 for more details.

**3 Gaussian formatted checkpoint file (.fch/.fchk) :** Checkpoint file of Gaussian program (.chk) can be converted to formatted checkpoint file (.fch/.fchk) via *formchk* utility in Gaussian package. There is no any difference between .fch and .fchk. "fch" ("fchk") is the default extension generated by Windows (Linux) version of *formchk*.

.fch/.fchk contains richer information than .wfn/.wfx files, virtual orbital wavefunctions are also recorded, and meanwhile it provides basis function information for Multiwfn. If you want to use .fch/.fchk file as carrier for post-HF wavefunction, read the beginning of Chapter 4 carefully!

Notice that for single-determinant wavefunctions, before some calculations involving real space function (e.g. main function 2, 4, 5), virtual orbitals higher than LUMO+10 will be deleted automatically to speed up calculations, therefore you cannot analyze those orbitals after the calculation, unless you reboot Multiwfn. If you want to disable this treatment, **set "idelvirorb" in settings.ini to 0.**

The .fch file generated by Q-Chem can also be used as input file of Multiwfn, however, since I am not a Q-Chem user, I am unable to guarantee the correctness of the analysis result.

**4 Molden input file (.molden) :** Currently, a wide variety of quantum chemistry packages, such as Molpro/Molcas/ORCA/Q-Chem/CFour/Turbomole/PSI are able to produce input file of Molden visualization program. This type of file records atomic coordinates, basis-set definition, information of all occupied and virtual orbitals (including expansion coefficient of basis functions, occupation number, spin, energy and symmetry), meanwhile there is no information only specific for Molden. So in fact, Molden input file can be regarded as a standard and general file format for exchanging wavefunction information. For Multiwfn, this type of file can provide atomic coordinate, basis function information and GTF information.

Beware that the Molden input files produced by a lot of program are quite non-standard, currently Multiwfn only supports the Molden input file generated by Molpro, ORCA (up to f angular moment), deMon2k and BDF. If the Molden input file you used is generated by other programs, the analysis result may or may not be correct, you should first use the methods described in Appendix 5 to check if the wavefunction has been correctly loaded.

Hint: Multiwfn fully supports the Molden input file standardized by molden2aim utility (see Section 5.1 for detail), which is able to properly recognize Molden input files generated by many other quantum chemistry codes, such as CFOUR, Molcas and ORCA up to g angular moment.

Although Molden input file also supports Slater type orbital (STO), Multiwfn can only utilize the Molden input file recording Gauss type basis functions.

One drawback of Molden input file is that it does not explicitly record nuclear charges as other formats such as wfn and fch, therefore the results relying on nuclear charges (e.g. electrostatic potential) will be problematic when pseudo-potential is used. To address this problem, Multiwfn loads atomic indices in the file (i.e. the third column in [Atoms] field) as nuclear charges, thus if you manually change the atomic index as the number of atomic valence electrons that explicitly represented in the quantum chemistry calculation, then the result will be correct. (Note that Multiwfn determines element of each atom according to atomic name in .molden file, therefore even after above modification, the elements can still be correctly identified)

A disadvantage of Molden input file as wavefunction carrier is that its format is not as compact as .fch. Due to this fact, for the same wavefunction, the loading speed of .molden file is much slower than .fch. Therefore, if you need to frequently analyze a .molden file, I suggest you use subfunction 2 of main function 100 to convert it to .fch format.

In analogy to .fch file, Multiwfn may delete virtual orbitals higher than LUMO+10. To avoid this, you should set "idelvirorb" in settings.ini to 0.

**5 GAMESS-US output file (.gms):** If you want to use GAMESS-US output file as input file, you can change its suffix as .gms, then Multiwfn will properly recognize it. Currently, I can only guarantee that output file of HF/DFT calculation with default NPRINT option can be normally loaded by Multiwfn. The role of .gms is similar as .molden and .fch file, i.e. all of them provide atomic coordinates, GTF and basis function informations.

**6 Plot files of NBO program (.31~.40) :** The main purpose of supporting these file types is for visualizing PNAO/NAO/PNHO/NHO/PNBO/NBO/PNLMO/NLMO/MO (their orbital coefficients are recorded in .32~.40 respectively), .31 recorded basis function information. After boot up Multiwfn, you should input the path of .31 file first, and then input the path of one of .32~.40 files (for simplicity, you can only input the suffix when the filenames are identical).

Notice that among all types of the orbitals generated by NBO program, only using NBO or

NLMO to calculate real space functions is meaningful!

**7 Protein data bank format (.pdb) and .xyz format :** These are the most widely used formats for recording atom coordinates. They do not carry any wavefunction information, but for the functions which only require atom coordinates, using pdb or xyz files as input is enough.

**8 Charge files (.chg) :** This type of plain text file can be generated by some functions of Multiwfn (e.g. population analysis functions), it contains element names (less than or equal to two characters), atom coordinates (first three columns, in Angstrom) and charges (the fourth column), users can modify them manually. The main use of this format is to visualize electrostatic potential and analyze it on molecular surface based on atomic charges. An example of .chg file is given below:

```

O    0. 000000   0. 000000   0. 119308   -0. 301956
H    0. 000000   0. 758953   -0. 477232   0. 150977
H    0. 000000   -0. 758953   -0. 477232   0. 150977

```

**9 Gaussian-type cube file (.cub or .cube) :** This is the most prevalent volumetric data format, can be generated by vast computational chemistry softwares and can be recognized by the majority of molecular graphics programs. Atom coordinates, a set of grid data of real space function or multiple sets of grid data of molecular orbitals could be recorded in this file. Multiwfn only supports cubic grid, that means the three translation vectors must be parallelized with Cartesian axes. After cube file is loaded into Multiwfn, one can choose main function 0 to visualize isosurfaces, or use main function 13 to process the grid data.

**10 DMol3 grid file (.grd) :** .grd file is the volumetric data format mainly used by DMol3 program. This file is very similar to .cub file, but atomic information is completely omitted.

**11 Plain text file:** This file type is only used for special functions, such as plotting DOS graph, plotting spectrum, generating Gaussian input file with initial guess. See explanations in corresponding sections. Gaussian output files also belong to this type.

## 2.6 Real space functions

Real space function analysis is one of the most important functions of Multiwfn, the supported real space functions are listed below. All wavefunctions are assumed to be real type, all units are in **atomic unit (a.u.)**.

Notice that for speeding up calculation, especially for big system, when evaluating a exponential function (except for some real space functions, such as 12, 14 and 16), if the exponent is more negative than -40, then this evaluation will be skipped. The default cutoff value is safe enough and cannot cause detectable loss of precision even in quantitative analysis, you can also disable this treatment or adjust cutoff, see “`expcutoff`” in `settings.ini`.

### 1 Electron density

## 2 General information

$$\rho(\mathbf{r}) = \sum_i \eta_i |\varphi_i(\mathbf{r})|^2 = \sum_i \eta_i \left| \sum_l C_{l,i} \chi_l(\mathbf{r}) \right|^2$$

where  $\eta_i$  is occupation number of orbital  $i$ ,  $\varphi$  is orbital wavefunction,  $\chi$  is basis function.  $C$  is coefficient matrix, the element of  $i$ th row  $j$ th column corresponds to the expansion coefficient of orbital  $j$  respect to basis function  $i$ . Atomic unit for electron density can be explicitly written as  $|\text{e}|/\text{Bohr}^3$ .

### 2 Gradient norm of electron density

$$|\nabla \rho(\mathbf{r})| = \sqrt{\left( \frac{\partial \rho(\mathbf{r})}{\partial x} \right)^2 + \left( \frac{\partial \rho(\mathbf{r})}{\partial y} \right)^2 + \left( \frac{\partial \rho(\mathbf{r})}{\partial z} \right)^2}$$

### 3 Laplacian of electron density

$$\nabla^2 \rho(\mathbf{r}) = \frac{\partial^2 \rho(\mathbf{r})}{\partial x^2} + \frac{\partial^2 \rho(\mathbf{r})}{\partial y^2} + \frac{\partial^2 \rho(\mathbf{r})}{\partial z^2}$$

The positive and negative value of this function correspond to electron density is locally depleted and locally concentrated respectively. The relationships between  $\nabla^2 \rho$  and valence shell electron pair repulsion (VSEPR) model, chemical bond type, electron localization and chemical reactivity have been built by Bader and many other researchers.

If “laplfac” in settings.ini is set to other value rather than the default one 1.0,  $\nabla^2 \rho(\mathbf{r})$  will be multiplied with this value. Setting it to negative value is convenient for analysis of electron density concentration.

### 4 Value of orbital wavefunction

$$\varphi_i(\mathbf{r}) = \sum_l C_{l,i} \chi_l(\mathbf{r})$$

When you select this function, you will be prompted to input the index of orbital  $i$ .

### 5 Electron spin density

Spin density is defined as the difference between alpha and beta density

$$\rho^s(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$$

If “ipolarpara” in settings.ini is set to 1, then spin polarization parameter function will be returned instead of spin density

$$\zeta(\mathbf{r}) = \frac{\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})}{\rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r})}$$

The absolute value of  $\zeta$  going from zero to unity corresponds to the local region going from unpolarized case to completely polarized case.

## 6 Hamiltonian kinetic energy density $K(\mathbf{r})$

The kinetic energy density is not uniquely defined, since the expected value of kinetic energy operator  $\langle \varphi | -(1/2)\nabla^2 | \varphi \rangle$  can be recovered by integrating kinetic energy density from alternative definitions. One of commonly used definition is

$$K(\mathbf{r}) = -\frac{1}{2} \sum_i \eta_i \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r})$$

## 7 Lagrangian kinetic energy density $G(\mathbf{r})$

Relative to  $K(\mathbf{r})$ , the local kinetic energy definition given below guarantee positiveness everywhere, hence the physical meaning is clearer and more commonly used.  $G(\mathbf{r})$  is also known as positive definite kinetic energy density.

$$G(\mathbf{r}) = \frac{1}{2} \sum_i \eta_i |\nabla \varphi_i(\mathbf{r})|^2 = \frac{1}{2} \sum_i \eta_i \left\{ \left( \frac{\partial \varphi_i(\mathbf{r})}{\partial x} \right)^2 + \left( \frac{\partial \varphi_i(\mathbf{r})}{\partial y} \right)^2 + \left( \frac{\partial \varphi_i(\mathbf{r})}{\partial z} \right)^2 \right\}$$

Since  $\nabla \rho_i = \nabla(\eta_i \varphi_i^2) = 2\eta_i \varphi_i \nabla \varphi_i$ , there is an equivalent form of  $G(\mathbf{r})$ :  $\frac{1}{8} \sum_i \frac{\nabla \rho_i \cdot \nabla \rho_i}{\rho_i}$ .

$K(\mathbf{r})$  and  $G(\mathbf{r})$  are directly related by Laplacian of electron density

$$\nabla^2 \rho(\mathbf{r}) / 4 = G(\mathbf{r}) - K(\mathbf{r})$$

## 8 Electrostatic potential from nuclear / atomic charges

$$V_{\text{nuc}}(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$$

where  $\mathbf{R}_A$  and  $Z_A$  denote position vector and nuclear charge of atom A, respectively. If pseudo-potential is used, then Z is the number of explicitly expressed electrons. When .chg file is used as input, Z will stand for the atomic charges recorded in the file (the fourth column), at this time  $V_{\text{nuc}}$  is useful for analyzing the difference between exact electrostatic potential and the electrostatic potential reproduced by atomic charges.

Notice that at nuclear positions, this function will be infinite and may cause some numerical problems in program, hence at these cases this function always returns 1000 instead of infinity.

## 9 Electron localization function (ELF)

The larger the electron localization is in a region, the more likely the electron motion is confined within it. If electrons are completely localized, then they can be distinguished from the ones outside. Bader found that the regions which have large electron localization must have large magnitudes of Fermi hole integration. However, the Fermi hole is a six-dimension function and thus difficult to be studied visually. Becke and Edgecombe noted that spherically averaged like-spin conditional pair probability has direct correlation with the Fermi hole and then suggested electron localization function (ELF) in the paper *J. Chem. Phys.*, **92**, 5397. The ELF used in Multiwfn is generalized for spin-polarized system, see *Acta Phys. -Chim. Sin.*, **27**, 2786

## 2 General information

(<http://www.whxb.pku.edu.cn/EN/abstract/abstract27788.shtml>) for derivation. For a review, see Chapter 5 of *Theoretical Aspects of Chemical Reactivity* (2007).

$$\text{ELF}(\mathbf{r}) = \frac{1}{1 + [D(\mathbf{r})/D_0(\mathbf{r})]^2}$$

where

$$D(\mathbf{r}) = \frac{1}{2} \sum_i \eta_i |\nabla \varphi_i(\mathbf{r})|^2 - \frac{1}{8} \left[ \frac{|\nabla \rho_\alpha(\mathbf{r})|^2}{\rho_\alpha(\mathbf{r})} + \frac{|\nabla \rho_\beta(\mathbf{r})|^2}{\rho_\beta(\mathbf{r})} \right]$$

$$D_0(\mathbf{r}) = \frac{3}{10} (6\pi^2)^{2/3} [\rho_\alpha(\mathbf{r})^{5/3} + \rho_\beta(\mathbf{r})^{5/3}]$$

For close-shell system, since  $\rho_\alpha = \rho_\beta = (1/2)\rho$ ,  $D$  and  $D_0$  terms can be simplified as

$$D(\mathbf{r}) = \frac{1}{2} \sum_i \eta_i |\nabla \varphi_i(\mathbf{r})|^2 - \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

$$D_0(\mathbf{r}) = (3/10)(3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}$$

Savin *et al.* have reinterpreted ELF in the view of kinetic energy, see *Angew. Chem. Int. Ed. Engl.*, 31, 187, which makes ELF also meaningful for Kohn-Sham DFT wavefunction or even post-HF wavefunction. They indicated that  $D(\mathbf{r})$  reveals the excess kinetic energy density caused by Pauli repulsion, while  $D_0(\mathbf{r})$  can be considered as Thomas-Fermi kinetic energy density. Since  $D_0(\mathbf{r})$  is introduced into ELF as reference, what the ELF reveals is actually a *relative* localization.

ELF is within the range of [0,1]. A large ELF value means that electrons are greatly localized, indicating that there is a covalent bond, a lone pair or inner shells of the atom involved. ELF has been widely used for a wide variety of systems, such as organic and inorganic small molecules, atomic crystals, coordination compounds, clusters, and for different problems, such as the revealing atomic shell structure, classification of chemical bonding, verification of charge-shift bond, studying aromaticity.

Notice that there is a deficiency of ELF, sometimes with  $\mathbf{r}$  going beyond from molecular boundary,  $D(\mathbf{r})$  decreases faster than  $D_0(\mathbf{r})$  and then ELF reaches 1 (completely localized). To overcome the problem, Multiwfn automatically adds a minimal value  $10^{-5}$  to  $D(\mathbf{r})$ , this treatment almost does not affect the ELF value in interesting regions. You can also disable this treatment by modifying “ELF\_addminimal” in settings.ini to 0.

Tsirelson and Stash put forward an approximate version of ELF in *Chem. Phys. Lett.*, 351, 142, in which the actual kinetic energy term in  $D(\mathbf{r})$  is replaced by Kirzhnits type second-order gradient expansion, that is

$$(1/2) \sum_i \eta_i |\nabla \varphi_i(\mathbf{r})|^2 \approx D_0(\mathbf{r}) + (1/72) |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r}) + (1/6) \nabla^2 \rho(\mathbf{r})$$

so that ELF is totally independent from wavefunction, and then can be used to analyze electron density from X-ray diffraction data. Of course Tsirelson’s ELF can also be used to analyze electron density from quantum chemistry calculation, but is not as good as the ELF defined by

Becke owing to the approximation introduced in kinetic energy term, however, qualitative conclusions can still be recovered in general. If you want to use Tsirelson's definition of ELF, change "ELFLOL\_type" in settings.ini from 0 to 1.

If "ELFLOL\_type" is set to 2, another formalism will be used:

$$\frac{1}{1 + D(\mathbf{r})/D_0(\mathbf{r})}.$$

If the parameter "ELFLOL\_cut" in settings.ini is set to  $x$ , then ELF will be zero where ELF is less than  $x$ .

## 10 Localized orbital locator (LOL)

This is another function for locating high localization regions likewise ELF, defined by Schmider and Becke in the paper *J. Mol. Struct. (THEOCHEM)*, **527**, 51.

$$\text{LOL}(\mathbf{r}) = \frac{\tau(\mathbf{r})}{1 + \tau(\mathbf{r})}$$

where

$$\tau(\mathbf{r}) = \frac{D_0(\mathbf{r})}{(1/2) \sum_i \eta_i |\nabla \varphi_i(\mathbf{r})|^2}$$

$D_0(\mathbf{r})$  for spin-polarized system and close-shell system are defined in the same way as in ELF.

LOL has similar expression compared to ELF. Actually, the chemically significant regions that highlighted by LOL and ELF are generally qualitative comparable, while Jacobsen pointed out that LOL conveys more decisive and clearer picture than ELF, see *Can. J. Chem.*, 86, 695. Obviously LOL can be interpreted in kinetic energy way as for ELF, however LOL can also be interpreted in view of localized orbital. Small (large) LOL value usually appears in boundary (inner) region of localized orbitals because the gradient of orbital wavefunction is large (small) in this area. The value range of LOL is identical to ELF, namely [0,1].

Multiwfn also supports the approximate version of LOL defined by Tsirelson and Stash (*Acta Cryst.*, **B58**, 780), namely the actual kinetic energy term in LOL is replaced by second-order gradient expansion, as what they do for ELF. This Tsirelson's version of LOL can be activated by setting "ELFLOL\_type" to 1.

For special reason, if "ELFLOL\_type" in settings.ini is changed from 0 to 2, another formalism will be used:  $\text{LOL}(\mathbf{r}) = \frac{1}{1 + [1/\tau(\mathbf{r})]^2}$ .

If the parameter "ELFLOL\_cut" in settings.ini is set to  $x$ , then LOL will be zero where LOL is less than  $x$ .

## 11 Local information entropy

Information entropy is a quantification of information, this theory was proposed by Shannon in his study of information transmission in noise channel, nowadays its application has been largely widened to other areas, including theoretical chemistry. For example, Aslangul and coworkers attempted to decompose diatomic and triatomic molecules into mutually exclusive

space by minimizing information entropy (*Adv. Quantum Chem.*, **6**, 93), Parr *et al.* discussed the relationship between information entropy and atom partition as well as molecular similarity (*J. Phys. Chem. A*, **109**, 3957), Noorizadeh and Shakerzadeh suggested using information entropy to study aromaticity (*Phys. Chem. Chem. Phys.*, **12**, 4742). The formula of Shannon's information entropy for normalized and continuous probability function is

$$S = -\int P(x) \ln P(x) dx$$

For chemical system, if  $P(x)$  is replaced by  $\rho(\mathbf{r})/N$ , then the integrand may be called local information entropy of electrons

$$S(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{N} \ln \frac{\rho(\mathbf{r})}{N}$$

where  $N$  is the total number of electrons in current system. Integrating this function over whole space yields information entropy.

## 12 Total electrostatic potential (ESP)

$Z_A$  is nuclear charge, if pseudopotential is used, then  $Z_A$  is the number of explicitly expressed electrons.

$$V_{\text{ESP}}(\mathbf{r}) = V_{\text{nuc}}(\mathbf{r}) + V_{\text{ele}}(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

This function measures the electrostatic interaction between a unit point charge placed at  $\mathbf{r}$  and the system of interest. A positive (negative) value implies that current position is dominated by nuclear (electronic) charges. Molecular electrostatic potential (ESP) has been widely used for prediction of nucleophilic and electrophilic sites for a long time. It is also valuable in studying hydrogen bonds, halogen bonds, molecular recognitions and the intermolecular interaction of aromatics. Moreover, based on statistical analysis, Murray and coworkers found a set of functions called GIPF, see *J. Mol. Struct. (THEOCHEM)*, **307**, 55, which connects ESP in molecular surface and macroscopic properties. There are a lot of reviews on ESP, interested readers are suggested to consult *WIREs Comput. Mol. Sci.*, **1**, 153 (2011), *Theor. Chem. Acc.*, **108**, 134 (2002), Chapter 17 of the book *Chemical Reactivity Theory-A Density Functional View*, the entry "Electrostatic Potentials: Chemical Applications" (page 912) in the book *Encyclopedia of Computational Chemistry* and Chapter 7 of the book *Reviews in Computational Chemistry* vol.2.

Notice that evaluating ESP is much more time-consuming than evaluating other functions. Also note that ESP in Multiwfn is evaluated exactly by nuclear attractive integrals rather than using approximate methods (such as multipole expansion, numerical Poisson equation), hence you may find the results generated by Multiwfn are somewhat different from those outputted by other quantum chemistry codes.

In order to speed up ESP evaluation, Multiwfn ignores some integrals that have little contributions. The threshold for ignoring is controlled by "espprecutoff" in settings.ini, enlarging this parameter results in more accurate ESP value, but also brings more computational cost. The ESP evaluated under default value is accurate enough in general cases.

## 13 Reduced density gradient (RDG)

RDG and  $Sign(\lambda_2)^*\rho$  are a pair of very important functions for revealing weak interaction region, see *J. Am. Chem. Soc.*, **132**, 6498 for detail. The basic applications are exemplified in Sections 4.100.1 and 4.200.1. RDG is defined as

$$RDG(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}$$

Notice that there is a parameter “RDG\_maxrho” in settings.ini, if the value is set to  $x$ , then RDG function will be set to an arbitrary big value (100.0) where the electron density is larger than  $x$ . This mechanism allows uninteresting regions to be shielded when viewing isosurfaces of weak interaction regions. By default  $x$  is 0.05, you can nullify this treatment by setting the parameter to zero.

#### 14 Reduced density gradient (RDG) with promolecular approximation

Weak interaction has significant influence on conformation of macromolecules, binding mode of proteins and ligands; however reproduction of electron density by *ab initio* and grid data calculation of RDG for such huge systems are always too time-consuming. Fortunately, it is found that weak interaction analysis under promolecular density is still reasonable. Promolecular density is simply constructed by superposing electron densities of free-state atoms and hence can be evaluated extremely rapidly

$$\rho^{pro}(\mathbf{r}) = \sum_A \rho_A^{free,fit}(\mathbf{r} - \mathbf{R}_A)$$

where  $\rho_A^{free,fit}(\mathbf{r})$  is pre-fitted spherically averaged electron density of atom  $A$ . The atomic densities for H~Lr are built-in data of Multiwfn, among which the data for H~Ar are taken from supplemental material of *J. Am. Chem. Soc.*, **132**, 6498, while those for other elements are evaluated according to the description in Appendix 3. For elements heavier than Lr the promolecular approximation is not currently available.

For efficiency consideration, if contribution from H, C, N or O atom to the function value at a specific point is less than 0.00001, then the contribution will not be calculated, for huge system this treatment improves efficiency several times and the result is almost unperturbed. You can also disable this treatment by setting “atomdenscut” in settings.ini to 0.

The parameter “RDGprodens\_maxrho” in settings.ini is the counterpart of “RDG\_maxrho” in the case of promolecular approximation.

#### 15 Sign(lambda2)\*rho

$$\Omega(\mathbf{r}) = Sign(\lambda_2(\mathbf{r}))\rho(\mathbf{r})$$

where  $Sign(\lambda_2(\mathbf{r}))$  means the sign of the second largest eigenvalue of electron density Hessian matrix at position  $\mathbf{r}$ .

#### 16 Sign(lambda2)\*rho with promolecular approximation

The real density used to determine  $Sign(\lambda_2(\mathbf{r}))$  is approximated by promolecular electron density, see the description in real space function 14.

#### 17 Exchange-correlation density, correlation hole and correlation factor

## 2 General information

These functions involve advanced topics, in order to clarify their physical meanings and to avoid confusion of the symbols used in a wide variety of literatures, I think it is worth to use much more texts to introduce theoretical background. For more detail discussions, please consult Chapter 2 of *A Chemist's Guide to Density Functional Theory 2ed* and Chapter 5 of *Methods of molecular quantum mechanics (2ed, McWeeny)*.

===== Theoretical basis =====

*Pair density* is defined as

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N)|^2 d\sigma_1 d\sigma_2 d\mathbf{x}_3 d\mathbf{x}_4 \dots d\mathbf{x}_N$$

where  $\Psi$  is system wavefunction,  $\mathbf{r}$  is space coordinate,  $\sigma$  is spin coordinate,  $\mathbf{x}$  is space-spin coordinate. Pair density denotes the probability that finding an electron at  $\mathbf{r}_1$  and another electron at  $\mathbf{r}_2$ , regardless of the spin type. If we perform double-integration for pair density over the whole space, we will get  $N(N-1)$ , reflecting the nature that there are  $N(N-1)$  electron pairs in present system. Obviously, pair density can be decomposed to contributions from different spin types of electron pairs

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = \pi^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)$$

If the electron motions are completely independent with each other, then the probability density of finding two electrons with spin  $\sigma_1$  at  $\mathbf{r}_1$  and with  $\sigma_2$  at  $\mathbf{r}_2$  respectively should simply be  $\rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2)$ . Of course, in real world electrons always interacting with each other, so their motions are correlated. The pair density thereby should be corrected by *exchange-correlation density  $\Gamma$*

$$\pi^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2) + \Gamma_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)$$

If we have already known that an electron with spin  $\sigma_1$  presents at  $\mathbf{r}_1$ , then the probability of finding another electron with spin  $\sigma_2$  at  $\mathbf{r}_2$  is known as *conditional probability* (This function is also known as *Lennard-Jones function*)

$$\Omega^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\pi^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{\sigma_1}(\mathbf{r}_1)} = \rho^{\sigma_2}(\mathbf{r}_2) + \frac{\Gamma_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{\sigma_1}(\mathbf{r}_1)}$$

*Correlation hole* reveals the decrease of probability of finding another electron with spin  $\sigma_2$  at  $\mathbf{r}_2$  when an electron with spin  $\sigma_1$  presents at  $\mathbf{r}_1$  owing to electron correlation effect

$$h_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Gamma_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{\sigma_1}(\mathbf{r}_1)} = \Omega^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{\sigma_2}(\mathbf{r}_2) = \frac{\pi^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{\sigma_1}(\mathbf{r}_1)} - \rho^{\sigma_2}(\mathbf{r}_2)$$

*Correlation factor* is a function closely related to correlation hole

$$f_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{h_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{\sigma_2}(\mathbf{r}_2)} = \frac{\Gamma_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2)}$$

Collectively, one can write out

$$\pi^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2) + \rho^{\sigma_1}(\mathbf{r}_1)h_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2) [1 + f_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)]$$

## 2 General information

$\Gamma_{XC}$  can be decomposed to the sum of exchange correlation (also called as Fermi correlation) part  $\Gamma_X$  and Coulomb correlation part  $\Gamma_C$ , therefore  $h_{XC}$  can be straightforwardly decomposed to *exchange hole*  $h_X$  (also called as Fermi hole) and *Coulomb hole*  $h_C$  as follows. Likewise,  $f_{XC}$  can be decomposed to  $f_X$  and  $f_C$

$$\begin{aligned}\Gamma_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) &= \Gamma_X^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) + \Gamma_C^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) \\ h_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) &= h_X^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) + h_C^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) \\ f_{XC}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) &= f_X^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) + f_C^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)\end{aligned}$$

Fermi correlation only presents between like-spin electrons; while Coulomb correlation occurs between any two electrons. Fermi correlation is much more important than Coulomb correlation, even at Hartree-Fock level, Fermi correlation is always well represented due to the anti-symmetry requirement of Slater determinant, while Coulomb is completely omitted. Only post-HF wavefunction is capable to simultaneously exhibit Fermi and Coulomb correlation effects. Commonly we only focus on Fermi hole while neglecting Coulomb hole. One can easily show that integration of  $h_X$  over whole space is exactly equal to -1, hence Fermi correlation perfectly avoided self-pairing problem, which may cause significant rise in system energy; while the integration for  $h_C$  is zero, this is mainly why Coulomb correlation has less influence on system energy.

It is also rather straightforward to obtain the pair density and conditional probability when only exchange correlation or Coulomb correlation is taken into account.

The total  $\pi$ ,  $\Omega$ ,  $\Gamma_{XC}$  (or  $\Gamma_X, \Gamma_C$ ) and  $h_{XC}$  (or  $h_X, h_C$ ) for an electron with spin  $\sigma$ , regardless the spin of another electron can be defined as

$$\begin{aligned}\pi^{\sigma,tot}(\mathbf{r}_1, \mathbf{r}_2) &= \pi^{\sigma\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \pi^{\sigma\beta}(\mathbf{r}_1, \mathbf{r}_2) \\ \Omega^{\sigma,tot}(\mathbf{r}_1, \mathbf{r}_2) &= \Omega^{\sigma\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \Omega^{\sigma\beta}(\mathbf{r}_1, \mathbf{r}_2) \\ \Gamma_{XC}^{\sigma,tot}(\mathbf{r}_1, \mathbf{r}_2) &= \Gamma_{XC}^{\sigma\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \Gamma_{XC}^{\sigma\beta}(\mathbf{r}_1, \mathbf{r}_2) \\ h_{XC}^{\sigma,tot}(\mathbf{r}_1, \mathbf{r}_2) &= h_{XC}^{\sigma\alpha}(\mathbf{r}_1, \mathbf{r}_2) + h_{XC}^{\sigma\beta}(\mathbf{r}_1, \mathbf{r}_2)\end{aligned}$$

### ===== Technical aspects =====

For single-determinant wavefunctions, exchange-correlation density for an  $\alpha$  electron can be explicitly written as

$$\Gamma_{XC}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) = \Gamma_{XC}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = -\sum_{i \in \alpha}^{\text{occ}} \sum_{j \in \alpha}^{\text{occ}} \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)$$

Note that  $\Gamma_{XC}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \Gamma_{XC}^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) = 0$  for this type of wavefunction. To obtain the expression for  $\beta$  electron, just replace  $\alpha$  by  $\beta$ , similarly hereafterin.

For post-HF wavefunction, exact evaluation of pair density requires two-particle density matrix (2PDM). Unfortunately 2PDM is very difficult to be obtained, mainstream quantum chemistry packages including Gaussian can't directly output it. In Multiwfn, exchange-correlation density for post-HF wavefunction is approximately evaluated by natural orbital formalism. Note

## 2 General information

that the approximate method is not unique, see *J. Chem. Theory Comput.*, **6**, 2736 for discussion. The most popular form among them, which is firstly derived by Müller, is currently implemented in Multiwfn as below. See *Phys. Lett.*, **105A**, 446, also see *Mol. Phys.*, **100**, 401 for extensive discussion (especially equation 32).

$$\Gamma_{XC,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) = -\sum_{i \in \alpha} \sum_{j \in \alpha} \sqrt{\eta_i \eta_j} \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)$$

Obviously, if occupation numbers of natural spin orbitals are integer (0 or 1), then  $\Gamma_{XC,approx}^{\alpha,tot}$  reduces to single-determinant form. so  $\Gamma_{XC,approx}^{\alpha,tot}$  can be regarded as a general form to evaluate exchange-correlation density. Note that post-HF wavefunction has taken Coulomb correlation between unlike-spin electrons into account, however there is no way to separate  $\Gamma_{XC,approx}^{\alpha\alpha}$  and  $\Gamma_{XC,approx}^{\alpha\beta}$  from  $\Gamma_{XC,approx}^{\alpha,tot}$ .

The exchange-only part of  $\Gamma$  for post-HF wavefunction can be approximately evaluated as below (of course, there is no exchange correlation between  $\alpha\beta$  electron pair)

$$\Gamma_{X,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) = \Gamma_{X,approx}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = -\sum_{i \in \alpha} \sum_{j \in \alpha} \eta_i \eta_j \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)$$

So Coulomb-only part of  $\Gamma$  can be evaluated as (including both  $\alpha\alpha$  and  $\alpha\beta$  pair contributions)

$$\begin{aligned} \Gamma_{C,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) &= \Gamma_{XC,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) - \Gamma_{X,approx}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \sum_{i \in \alpha} \sum_{j \in \alpha} [(\eta_i \eta_j - \sqrt{\eta_i \eta_j}) \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)] \end{aligned}$$

Since we already have explicit expression to calculate  $\Gamma_{XC}$  term, other quantities introduced earlier can be easily computed according to the relationships between them and  $\Gamma_{XC}$ . Recall that

$$\rho^\sigma(\mathbf{r}) = \sum_{i \in \sigma} \eta_i |\varphi_i(\mathbf{r})|^2.$$

Postscript: One can show that  $\Gamma_{XC,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2)$  also exactly holds the requirement that integration of  $\mathbf{r}_2$  over the whole space is equal to  $-\rho^\alpha(\mathbf{r}_1)$ . However, in common, integrating  $\mathbf{r}_2$  over the whole space for  $\Gamma_{X,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Gamma_{C,approx}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2)$  deviate from  $-\rho^\alpha(\mathbf{r}_1)$  and zero, respectively, which are basic properties of exact form of  $\Gamma_X^{\alpha,tot}$  and  $\Gamma_C^{\alpha,tot}$ .

### ===== Usage =====

In Multiwfn,  $\mathbf{r}_1$  is seen as reference point and  $\mathbf{r}_2$  is seen as variable, to define the coordinate of reference point, just modifying “refxyz” in settings.ini before booting up.

“paircorrtype” parameter in settings.ini controls which type of correlation effect will be taken into consideration in calculation of  $\Gamma$ . Since correlation hole and correlation factor are calculated based on  $\Gamma$ , this setting also affects them. For single-determinant wavefunction, =1 and =3 are equivalent and =2 is meaningless, because Coulomb correlation is completely omitted.

- =1: Only consider exchange correlation
- =2: Only consider Coulomb correlation
- =3: Consider both exchange and Coulomb correlation

“pairfunctype” parameter in settings.ini controls which function and which spin will be calculated by real space function 17, see below, those enclosed by parentheses are for single-determinant wavefunction cases. Of course, for close-shell system, the results for  $\alpha$  spin are exactly identical to those for  $\beta$  spin. Note that correlation factor for post-HF wavefunction case is undefined.

- |   |                           |                          |                         |                      |                      |
|---|---------------------------|--------------------------|-------------------------|----------------------|----------------------|
| =1: $h^{\alpha,tot}$                            | $(h^{\alpha\alpha})$      | =2: $h^{\beta,tot}$      | $(h^{\beta\beta})$      |                      |                      |
| =4: Undefined                                   | $(f^{\alpha\alpha})$      | =5: Undefined            | $(f^{\beta\beta})$      |                      |                      |
| =7: $\Gamma^{\alpha,tot}$                       | $(\Gamma^{\alpha\alpha})$ | =8: $\Gamma^{\beta,tot}$ | $(\Gamma^{\beta\beta})$ |                      |                      |
| =10: $\pi^{\alpha\alpha}$                       | when paircorrtype =1      | $(\pi^{\alpha\alpha})$   | =11: $\pi^{\beta\beta}$ | when paircorrtype =1 | $(\pi^{\beta\beta})$ |
| <b>=12:</b> $\pi^{any,any}$ ( $\pi^{any,any}$ ) |                           |                          |                         |                      |                      |

For example, if paircorrtype=1 and pairfunctype=2, for post-HF wavefunction, what will be calculated is  $h_X^{\beta,tot}(\mathbf{r}_1, \mathbf{r}_2)$ , which is equivalent to  $h_X^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)$  since  $\beta\alpha$  electron pairs have no exchange correlation. This quantity can be interpreted as Fermi hole at  $\mathbf{r}_2$  caused by a  $\beta$  electron present at  $\mathbf{r}_1$ .

## 18 Average local ionization energy

Average local ionization energy is written as (*Can. J. Chem.*, **68**, 1440)

$$\bar{I}(\mathbf{r}) = \frac{\sum_i \rho_i(\mathbf{r}) |\varepsilon_i|}{\rho(\mathbf{r})}$$

where  $\rho_i(\mathbf{r})$  and  $\varepsilon_i$  are the electron density function and orbital energy of the  $i$ th molecular orbital, respectively. Hartree-Fock and typical DFT functionals such as B3LYP are both suitable for computing  $\bar{I}(\mathbf{r})$ . Lower value of  $\bar{I}(\mathbf{r})$  indicates that the electrons at this point are more weakly bounded.  $\bar{I}(\mathbf{r})$  has widespread uses, for example revealing atomic shell structures, measuring electronegativity, predicting pKa, quantifying local polarizability and hardness, but the most important one may be predicting reactive site of electrophilic or radical attack. It is proved that the minima of ALIE on vdW surface are good indicator to reveal which atoms are more likely to be the preferential site of electrophilic or radical attack.. There are also many potential uses of  $\bar{I}(\mathbf{r})$  waiting for further investigation. Excellent reviews of  $\bar{I}(\mathbf{r})$  have been given by Politzer

*et al.*, see *J. Mol. Model.*, **16**, 1731 and Chapter 8 of the book *Theoretical Aspects of Chemical Reactivity* (2007).

Since  $\bar{I}(\mathbf{r})$  is dependent upon orbital energies, while orbital energy for post-HF wavefunction is undefined, therefore when post-HF wavefunction is used,  $\bar{I}(\mathbf{r})$  will be simply outputted as zero everywhere.

If the parameter "iALIEdecomp" in settings.ini is set to 1, in main function 1, not only  $\bar{I}(\mathbf{r})$  will be outputted, the contribution from each occupied MOs will also be outputted, the contribution due to MO  $i$  is defined as

$$\bar{I}_i(\mathbf{r}) = \frac{\rho_i(\mathbf{r}) |\varepsilon_i|}{\rho(\mathbf{r})}$$

## 19 Source function

Source function was proposed by Bader and Gatti, see *Chem. Phys. Lett.*, **287**, 233.

$$SF(\mathbf{r}, \mathbf{r}') = -\frac{\nabla^2 \rho(\mathbf{r}')}{4\pi \cdot |\mathbf{r} - \mathbf{r}'|}$$

It can be shown that

$$\rho(\mathbf{r}) = \int SF(\mathbf{r}, \mathbf{r}') d\mathbf{r}'$$

where  $\mathbf{r}'$  ranges entire space. This equation suggests that  $SF(\mathbf{r}, \mathbf{r}')$  represents the effect of electronic Laplacian at  $\mathbf{r}'$  on electron density at  $\mathbf{r}$ . If at  $\mathbf{r}'$  the electron is concentrated (namely Laplacian is negative, also suggesting potential energy dominates kinetic energy), then  $\mathbf{r}'$  will be a source for the electron density at  $\mathbf{r}$ ; conversely, if at  $\mathbf{r}'$  the electron is depleted, then  $\mathbf{r}'$  diminish the electron density at  $\mathbf{r}$ . If the range of integration in above formula is restricted to a local region  $\Omega$  and we get a value  $S(\mathbf{r}, \Omega)$ , then  $S(\mathbf{r}, \Omega)/\rho(\mathbf{r}) * 100\%$  can be regarded as the contribution from region  $\Omega$  to the electron density at  $\mathbf{r}$ . Source function has many uses, when it is used to discuss bonding problems, usually bond critical points are taken as  $\mathbf{r}$ . A very comprehensive review of theoretical background and applications of source function is given by Gatti in *Struct. & Bond.*, **147**, 193 (2010).

In Multiwfn, source function has two modes: (1) If "srcfuncmode" in settings.ini is set to 1, then  $\mathbf{r}'$  is regarded as variable, while  $\mathbf{r}$  is regarded as fixed reference point, whose coordinate is determined by "refxyz" in settings.ini. This is default mode, useful to study effect of electronic Laplacian at everywhere on specific point (2) If "srcfuncmode" is set to 2, then  $\mathbf{r}$  becomes variable and  $\mathbf{r}'$  becomes reference point, this is useful to study effect of electronic Laplacian at specific point on everywhere.

When  $\mathbf{r}=\mathbf{r}'$ , this function will return  $-\nabla^2 \rho(\mathbf{r}')/0.001$  to avoid numerical problem.

## 2.7 User defined real space function

In real space function selection menu you can find a term named "User defined real space function", this function corresponds to "userfunc" routine in source file function.f90. By filling codes by yourself, the functions of Multiwfn can be easily extended. For examples, after filling the code `userfunc=fgrad(x,y,z,t)**2/8/fdens(x,y,z)` and recompile Multiwfn, you will get the

integrand of Weizsäcker functional  $\tau_w[\rho] = \int \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})} d\mathbf{r}$ . When you write code you can

consult Appendix 2 of this manual as well as the codes of other functions. If you would like to define several custom functions, you can fill their codes in branch statement "if (iuserfunc==1) then ... else if (iuserfunc==2) then ... end if", where "iuserfunc" is an external parameter in settings.ini file, by which you can select which custom function to be used.

In addition, in order to avoid lengthy list of real space functions, numerous uncommonly used real space functions are not explicitly present in the list. However, if you want to use them, you can set "iuserfunc" parameter in settings.ini to one of below values, then the user defined function will point to corresponding function. For example, before running Multiwfn, if you set "iuserfunc" to 2, then the user defined real space function will be equivalent to density of Beta electrons.

**-2** Promolecular density calculated based on built-in sphericalized atomic densities, you can check Appendix 3 on how these atomic densities are produced.

Please note that this promolecular density is slightly different to the promolecular density used in real space functions 14 and 16, because in which the atomic densities from H to Ar are directly taken from the original paper of RDG method rather than calculated according to the method described in Appendix 3.

**-1** The function value evaluated by trilinear interpolation from grid data. The grid data can be generated by main function 5, or loaded from .cub/.grd file when Multiwfn boot up.

**1** Alpha density:  $\rho^\alpha(\mathbf{r}) = [\rho(\mathbf{r}) + \rho^s(\mathbf{r})]/2$

**2** Beta density:  $\rho^\beta(\mathbf{r}) = [\rho(\mathbf{r}) - \rho^s(\mathbf{r})]/2$

**3** Integrand of electronic spatial extent  $\langle R^{**2} \rangle$ :  $\rho(\mathbf{r}) \times (x^2 + y^2 + z^2)$

**4** Weizsäcker potential:  $V_w = \frac{1}{8} \frac{|\nabla\rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})} - \frac{1}{4} \frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})}$

**5** Integrand of Weizsäcker functional:  $|\nabla\rho(\mathbf{r})|^2/[8\rho(\mathbf{r})]$ , which is the exact kinetic energy density of any one-orbital system (one or two electrons, or any number of bosons).

**6** Radial distribution function of electron density:  $4\pi \times \rho(\mathbf{r}) \times (x^2 + y^2 + z^2)$ . Clearly, spherical symmetry of electron density is assumed.

**7** Local temperature, in  $k_B^{-1}$  (PNAS, 81, 8028):  $T(\mathbf{r}) = \frac{2}{3} \frac{G(\mathbf{r})}{\rho(\mathbf{r})}$

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**8** Average local electrostatic potential (*J. Chem. Phys.*, **72**, 3027):  $V_{\text{ESP}}(\mathbf{r}) / \rho(\mathbf{r})$

**9** Shape function:  $\rho(\mathbf{r}) / N$ , where  $N$  is the total number of electrons

**10** Potential energy density (Virial field):  $V(\mathbf{r}) = -K(\mathbf{r}) - G(\mathbf{r}) = (1/4)\nabla^2\rho(\mathbf{r}) - 2G(\mathbf{r})$

**11** Electron energy density:  $E(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}) = -K(\mathbf{r})$  (Sometimes  $E$  is written as  $H$ )

**12** Local nuclear attraction potential energy:  $-\rho(\mathbf{r}) \times V_{\text{nuc}}(\mathbf{r})$

**13** Kinetic energy density per electron:  $G(\mathbf{r}) / \rho(\mathbf{r})$  This quantity at bond critical point is useful to discriminate covalent bonding and close-shell interaction

**14** Electrostatic potential from electrons:  $V_{\text{ele}}(\mathbf{r}) = V_{\text{ESP}}(\mathbf{r}) - V_{\text{nuc}}(\mathbf{r})$

**15** Bond metallicity:  $\xi_J(\mathbf{r}) = \rho(\mathbf{r}) / \nabla^2\rho(\mathbf{r})$  At bond critical point,  $\xi_J > 1$  indicates metallic interaction, see *J. Phys.: Condens. Matter*, **14**, 10251.

**16** Dimensionless bond metallicity:  $\xi_m(\mathbf{r}) = \frac{36(3\pi^2)^{2/3}}{5} \frac{\rho(\mathbf{r})^{5/3}}{\nabla^2\rho(\mathbf{r})}$  At bond critical point, larger

value corresponds to stronger metallicity of the bond, see *Chem. Phys. Lett.*, **471**, 174.

**17** Energy density per electron:  $E(\mathbf{r}) / \rho(\mathbf{r})$ , this value at BCP is called as bond degree parameter (BD), see *J. Chem. Phys.*, **117**, 5529 (2002) for detail, in which the authors advocate that for covalent bonds (viz.  $E_{\text{BCP}} < 0$ ), the BD renders covalence degree, and the stronger the interaction the greater the BD magnitude; while for closed-shell interactions (viz.  $E_{\text{BCP}} > 0$ ), the BD can be viewed as softening degree, and the weaker the interaction the larger the BD magnitude.

**18** Region of Slow Electrons (RoSE), which is defined in *Chem. Phys. Lett.*, **582**, 144 (2013) and

has a pattern very similar to ELF, with value space of [-1,1]:  $\nu_{\pm} = \frac{D_0(\mathbf{r}) - G(\mathbf{r})}{D_0(\mathbf{r}) + G(\mathbf{r})}$

**19** Single exponential decay detector (SEDD), which is highly analogous to ELF. Its updated definition in *J. Chem. Theory Comput.*, **10**, 3745 (2014) is implemented:

$$SEDD(\mathbf{r}) = \ln \left\{ 1 + \left[ \frac{\nabla(\nabla\rho(\mathbf{r}) / \rho(\mathbf{r}))^2}{\rho(\mathbf{r})} \right]^2 \right\}$$

**20** Density overlap regions indicator (DORI), which is defined in *J. Chem. Theory Comput.*, **10**, 3745 (2014). Its value range is [0,1]. The advantage of DORI is that it can simultaneously reveal covalent and non-covalent interaction regions, and the pattern is similar to ELF+RDG. It is also possible to map  $\text{Sign}(\lambda_2(\mathbf{r}))$  on to its isosurfaces. The expression of DORI is:

$DORI(\mathbf{r}) = \frac{\theta(\mathbf{r})}{1 + \theta(\mathbf{r})}$ , where  $\theta(\mathbf{r}) = [\nabla(\nabla\rho(\mathbf{r}) / \rho(\mathbf{r}))^2]^2 / [\nabla\rho(\mathbf{r}) / \rho(\mathbf{r})]^6$ . (In fact, RDG

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is also able to reveal covalent and non-covalent interaction at the same time when "RDG\_maxrho" parameter is set to zero, but the graphical effect is not as good as DORI, because perfectly exhibiting these two kinds of regions require somewhat different RDG isovalue

**21** Integrand of X component of electric dipole moment:  $-x \times \rho(\mathbf{r})$

**22** Integrand of Y component of electric dipole moment:  $-y \times \rho(\mathbf{r})$

**23** Integrand of Z component of electric dipole moment:  $-z \times \rho(\mathbf{r})$

**24** Approximate form of DFT linear response kernel for close-shell (*Phys. Chem. Chem. Phys.*, **14**, 3960):  $\chi(\mathbf{r}_1, \mathbf{r}_2) \approx 4 \sum_{i \in \text{occ}} \sum_{j \in \text{vir}} \frac{\varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_2)}{\varepsilon_i - \varepsilon_j}$

**25** Magnitude of fluctuation of the electronic momentum:  $\tilde{P}(\mathbf{r}) = \frac{1}{2} \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})}$ , which is useful to discuss bonding and very similar to reduced density gradient, see *Theor. Chim. Acc.*, **127**, 393

**26** Integrand of Thomas-Fermi functional:  $t_{\text{TF}}(\mathbf{r}) = (3/10)(3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}$ , which is the exact kinetic energy density of noninteracting, uniform electron gas

**27** Local electron affinity:  $EA_L(\mathbf{r}) = \frac{-\sum_{i \in \text{vir}} |\varphi_i(\mathbf{r})|^2 \varepsilon_i}{\sum_{i \in \text{vir}} |\varphi_i(\mathbf{r})|^2}$ , which is very similar to average local ionization energy, but  $i$  cycles all unoccupied orbitals. See *J. Mol. Model.*, **9**, 342

**28** Local Mulliken electronegativity:  $\chi_L(\mathbf{r}) = [\bar{I}(\mathbf{r}) + EA_L(\mathbf{r})]/2$ , see *J. Mol. Model.*, **9**, 342

**29** Local hardness:  $\eta_L(\mathbf{r}) = [\bar{I}(\mathbf{r}) - EA_L(\mathbf{r})]/2$ , see *J. Mol. Model.*, **9**, 342

**Note:** In order to use  $EA_L$ ,  $\chi_L$  and  $\eta_L$ , the wavefunction must contain both occupied and unoccupied orbitals, therefore such as .fch, .molden and .gms rather than .wfn/.wfx file must be used. Meanwhile, "idelvirorb" in settings.ini must be set to 0. Besides, these quantities are meaningful only when minimal basis-set is used.

**30** Ellipticity of electron density:  $\varepsilon(\mathbf{r}) = [\lambda_1(\mathbf{r}) / \lambda_2(\mathbf{r})] - 1$ , where  $\lambda_1$  and  $\lambda_2$  are the lowest and the second lowest eigenvalues of Hessian matrix of  $\rho$ , respectively. At bond critical point,  $\lambda_1$  and  $\lambda_2$  are both negative and exhibit the curvature of electron density perpendicular to the bond.

**31** eta index:  $\eta(\mathbf{r}) = |\lambda_1(\mathbf{r})| / \lambda_3(\mathbf{r})$ , where  $\lambda_1$  and  $\lambda_3$  are the lowest and the highest eigenvalues of Hessian matrix of  $\rho$ , respectively. It was argued that the value of  $\eta$  at bond critical point is less than unity for closed shell interactions and increases with increasing covalent character, see *Angew. Chem. Int. Ed.*, **53**, 2766 (2014), as well as *J. Phys. Chem. A*, **114**, 552 (2010) for discussions.

**32** Modified eta index by Tian Lu:  $\eta'(\mathbf{r}) = |\lambda_1(\mathbf{r})| / \lambda_3(\mathbf{r}) - 1$ . Similar to  $\eta$ , but negative value

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of  $\eta'$  corresponds to closed shell interactions.

**33** Potential acting on one electron in a molecule (PAEM), see *J. Comput. Chem.*, **35**, 965 (2014):

$$V_{\text{PAEM}}(\mathbf{r}) = -\sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + \frac{1}{\rho(\mathbf{r})} \int \frac{\pi(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad \pi \text{ is pair density. It can be further written as}$$

$$V_{\text{PAEM}}(\mathbf{r}) = -V_{\text{ESP}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) = -V_{\text{ESP}}(\mathbf{r}) + \frac{1}{\rho(\mathbf{r})} \int \frac{\Gamma_{\text{XC}}^{\alpha, \text{tot}}(\mathbf{r}, \mathbf{r}') + \Gamma_{\text{XC}}^{\beta, \text{tot}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad \text{where}$$

$V_{\text{ESP}}$  is the total molecular electrostatic potential and  $V_{\text{XC}}$  is exchange-correction potential. In Multiwfn, the exchange-correlation density  $\Gamma$  is evaluated in terms of Müller approximation, see part 17 of Section 2.6 for detail. It was shown in the original paper that PAEM may be useful to distinguish covalent and noncovalent interactions. An example of application of PAEM can be found in Section 4.3.3.

**34** The same as **33**, but now  $V_{\text{XC}}$  directly corresponds to DFT exchange-correlation potential. Its specific form can be chosen via "iDFTxcsel" parameter, see the end of this section for detail. This form of PAEM is several times more computationally economical than **33** but only supports close-shell wavefunction.

**35**  $|V(\mathbf{r})| / G(\mathbf{r})$ . In *J. Chem. Phys.*, **117**, 5529 (2002) it was proposed that this quantity at BCP can be used to discriminate interaction types.  $<1$  corresponds to closed-shell interaction;  $>2$  corresponds to covalent interaction; while  $>1$  and  $<2$  corresponds to intermediate interaction.

**36** On-top pair density, namely the two positions of the pair density are identical:  $\pi(\mathbf{r}, \mathbf{r})$ . See such as *Int. J. Quantum Chem.*, **61**, 197 (1995) for discussion. "paircorrtype" parameter in settings.ini mentioned earlier affects the result.

**38** The angle between the second eigenvector of Hessian of electron density and the vector perpendicular to a given plane, which can be defined by option 4 of main function 1000; the unit vector normal to the plane will be shown on screen, assume that you use three points A, B, C to define the plane and you get vector  $\mathbf{u}$ , but what you really want is  $-\mathbf{u}$ , you can then input the points again but in reverse sequence, i.e. C, B, A. In *J. Phys. Chem. A*, **115**, 12512 (2011) this quantity along bond paths was used to reveal  $\pi$  interaction.

**39** Electrostatic potential without contribution of a specific nucleus:

$$V_n(\mathbf{r}) = \sum_{A \neq K} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad \text{where the nucleus } K \text{ can be set by option 3 of main function}$$

1000 (which is hidden in main interface but can be chosen).  $V_n$  is a useful quantity, for example if  $K$  is chosen as index of a hydrogen, then the value correlates with its  $pK_a$ , because in this case  $V_n$  approximately reflects the interaction energy of a proton at the position of  $K$  and rest of the system; In addition, *J. Phys. Chem. A*, **118**, 1697 (2014) showed that  $V_n$  can be used to quantitatively predict interaction energy of the weak interactions dominated by electrostatic effect (viz. H-bonds, halogen-bonds, dihydrogen bonds), see Section 4.1.2 for introduction and example.

**40** Steric energy density:  $|\nabla \rho(\mathbf{r})|^2 / [8\rho(\mathbf{r})]$ , which is equivalent to integrand of Weizsäcker functional.

**41** Steric potential:  $v_s(\mathbf{r}) = \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{[\rho(\mathbf{r}) + \delta]^2} - \frac{1}{4} \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r}) + \delta}$ . The negative of this quantity is also

known as one-electron potential (OEP). Notice that the  $\delta$  is a very small term artificially introduced to avoid the denominator converges to zero faster than nominator. The value of  $\delta$  can be determined by "steric\_addminimal" in settings.ini. If  $\delta$  is set to 0, then the original expression of steric potential is recovered.

**42** Steric charge:  $q_s(\mathbf{r}) = \nabla^2 v_s(\mathbf{r}) / (-4\pi)$ .

**43** The magnitude of steric force:  $F_s(\mathbf{r}) = |\nabla v_s(\mathbf{r})|$ .

Notice that the  $\delta$  term, which is mentioned above, also affects steric force and steric charge. Discussions of steric energy/potential/force/charge can be found in *J. Chem. Phys.*, **126**, 244103.

**44,45,46** Damped Steric potential, steric force based on damped steric potential, directly damped Steric force: Documented privately

**50** Shannon entropy density:  $s_s(\mathbf{r}) = -\rho(\mathbf{r}) \ln \rho(\mathbf{r})$ .

**51** Fisher information density:  $i_F(\mathbf{r}) = |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r})$ . Note that this quantity is only different from Weizsäcker functional by a constant factor of 1/8.

**52** Second Fisher information density:  $i'_F(\mathbf{r}) = -\nabla^2 \rho(\mathbf{r}) \ln \rho(\mathbf{r})$ . The relationship between Shannon entropy and Fisher information can be found in *J. Chem. Phys.*, **126**, 191107. The integration of this function over the whole space is exactly identical to that of Fisher information density.

**53** Ghosh entropy density (or Ghosh-Berkowitz-Parr entropy), in  $k_B$  (*PNAS*, **81**, 8028):  $s(\mathbf{r}) = (3/2)\rho(\mathbf{r})\{\lambda + \ln[t(\mathbf{r})/t_{TF}(\mathbf{r})]\}$ , where  $\lambda = 5/3 + \ln(4\pi c_k / 3)$ ,  $c_k$  is Thomas-Fermi constant  $(3/10)(3\pi^2)^{2/3} = 2.871234$ , Lagrangian kinetic energy density  $G(\mathbf{r})$  is chosen to be the kinetic energy density term  $t(\mathbf{r})$ .

**54** The same as 53, but  $G(\mathbf{r}) - \nabla^2 \rho(\mathbf{r})/8$ , which is the kinetic energy density exactly corresponding to Eq. 22 of *PNAS*, **81**, 8028, is employed as the  $t(\mathbf{r})$ . In rare cases this definition of kinetic energy density leads to a very small negative value, since at these points  $t_{TF}(\mathbf{r})$  is also very close to zero, in order to normally get result,  $\ln[t(\mathbf{r})/t_{TF}(\mathbf{r})]$  in this case is simply set to zero.

**55** Integrand of quadratic form of Rényi entropy:  $\rho^2(\mathbf{r})$

**56** Integrand of cubic form of Rényi entropy:  $\rho^3(\mathbf{r})$

**60** Pauli potential:  $V_0 = V_{ESP} - V_{XC} - V_W$ , where  $V_{ESP}$  is total electrostatic potential (as shown in Section 2.6),  $V_{XC}$  is exchange-correlation potential (its specific form is determined by "iDFTxcsel"

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in settings.ini, see below),  $V_W$  is Weizsäcker potential. This quantity corresponds to Eq. 17 of *Comput. Theor. Chem.*, **1006**, 92-99 and is only applicable to close-shell cases.

**61** The magnitude of Pauli force:  $F_\theta(\mathbf{r}) = |-\nabla V_\theta(\mathbf{r})|$ .

**62** Pauli charge:  $q_\theta(\mathbf{r}) = \nabla^2 V_\theta(\mathbf{r}) / (-4\pi)$ .

**63** Quantum potential:  $V_q = V_\theta + V_{XC}$

**64** The magnitude of quantum force:  $F_q(\mathbf{r}) = |-\nabla V_q(\mathbf{r})|$

**65** Quantum charge:  $q_q(\mathbf{r}) = q_\theta(\mathbf{r}) + q_{XC}(\mathbf{r})$

**66** The magnitude of electrostatic force:  $F_{ESP}(\mathbf{r}) = |-\nabla V_{ESP}(\mathbf{r})|$

**67** Electrostatic charge:  $q_{ESP}(\mathbf{r}) = \nabla^2 V_{ESP}(\mathbf{r}) / (-4\pi)$

**70** Phase-space-defined Fisher information density (PS-FID):  $i_f(\mathbf{r}) = \frac{3\rho(\mathbf{r})}{k_B T(\mathbf{r})} = \frac{9}{2} \frac{\rho^2(\mathbf{r})}{G(\mathbf{r})}$ ,

where  $T(\mathbf{r})$  is local temperature as shown above. This function has very similar characters to ELF and LOL, the spatial localization of electron pairs can be clearly revealed. See *Chem. Phys.*, **435**, 49 (2014) for introduction and illustrative applications.

**71, 72, 73, 74** Electron linear momentum density (EMD) in 3D representation. The electron linear momentum operator is  $-i\nabla$ , for an orbital the expectation value of linear momentum in X is  $-i \langle \varphi | \nabla | \varphi \rangle$ , so X component of EMD for a wavefunction can be defined as (the imaginary sign

is ignored)  $p_x(\mathbf{r}) = -\sum_i \eta_i \varphi_i^*(\mathbf{r}) \frac{\partial \varphi_i(\mathbf{r})}{\partial x}$ , similar for Y and Z components. The 71, 72, 73th

user-defined functions correspond to X, Y, Z component, respectively. The magnitude (74) of EMD is defined as  $p_{tot}(\mathbf{r}) = \sqrt{p_x^2(\mathbf{r}) + p_y^2(\mathbf{r}) + p_z^2(\mathbf{r})}$ .

**75, 76, 77, 78** Magnetic dipole moment density (MDMD). The operator for magnetic dipole moment is the angular momentum operator (see *Theoret. Chim. Acta*, **6**, 341)

$$-i(\mathbf{r} \times \nabla) = -i \left[ \hat{\mathbf{i}} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) + \hat{\mathbf{j}} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) + \hat{\mathbf{k}} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right]$$

where  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  are unity vectors in X, Y and Z directions, respectively. Therefore, X, Y and Z component of MDMD may be defined as follows (the imaginary sign is ignored)

$$m_x(\mathbf{r}) = -\sum_i \eta_i \varphi_i^*(\mathbf{r}) \left[ y \frac{\partial \varphi_i(\mathbf{r})}{\partial z} - z \frac{\partial \varphi_i(\mathbf{r})}{\partial y} \right]$$

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$$m_y(\mathbf{r}) = -\sum_i \eta_i \varphi_i^*(\mathbf{r}) \left[ z \frac{\partial \varphi_i(\mathbf{r})}{\partial x} - x \frac{\partial \varphi_i(\mathbf{r})}{\partial z} \right]$$

$$m_z(\mathbf{r}) = -\sum_i \eta_i \varphi_i^*(\mathbf{r}) \left[ x \frac{\partial \varphi_i(\mathbf{r})}{\partial y} - y \frac{\partial \varphi_i(\mathbf{r})}{\partial x} \right]$$

The 75, 76, 77th user-defined functions correspond to X, Y, Z component, respectively. The magnitude (78) of MDMD is  $m_{\text{tot}}(\mathbf{r}) = \sqrt{m_x^2(\mathbf{r}) + m_y^2(\mathbf{r}) + m_z^2(\mathbf{r})}$ .

**81, 82, 83** X, Y, Z component of Hamiltonian kinetic energy density, respectively

**84, 85, 86** X, Y, Z component of Lagrangian kinetic energy density, respectively

**87** Local total electron correlation function:  $I_T(\mathbf{r}) = \frac{1}{4} \sum_i [\eta_i(1-\eta_i)]^{1/2} |\varphi_i(\mathbf{r})|^2$ . The  $i$  denotes

index of spin natural orbital, the  $\eta$  is corresponding occupation number. This and below two functions are very useful for revealing electron correlation in different regions, see *J. Chem. Theory Comput.*, 13 (6), pp 2705 (2017) for introduction, illustrative example can also be found in Section 4.A.6. Note that in some cases,  $\eta$  may be marginally larger than 1.0 or negative, Multiwfn automatically set it to 1.0 and 0.0 respectively to make the calculation feasible.

**88** Local dynamic electron correlation function:

$$I_D(\mathbf{r}) = \frac{1}{4} \sum_i \{[\eta_i(1-\eta_i)]^{1/2} - 2\eta_i(1-\eta_i)\} |\varphi_i(\mathbf{r})|^2$$

**89** Local nondynamic electron correlation function:  $I_{\text{ND}}(\mathbf{r}) = \frac{1}{2} \sum_i \eta_i(1-\eta_i) |\varphi_i(\mathbf{r})|^2$

**100** Disequilibrium (also known as semi-similarity):  $D_r(\mathbf{r}) = \rho^2(\mathbf{r})$ . See *Int. J. Quantum. Chem.*, 113, 2589 (2013) for illustrative applications.

**101** Positive part of ESP:  $V_{\text{ESP}}^+$ . In the region where  $V_{\text{ESP}}$  is positive,  $V_{\text{ESP}}^+ = V_{\text{ESP}}$ ; where ESP is negative,  $V_{\text{ESP}}^+ = 0$ .

**102** Negative part of ESP:  $V_{\text{ESP}}^-$ .

**900, 901, 902** X, Y and Z coordinate variables, respectively:  $x, y, z$ .

**1000** Integrand of DFT exchange-correlation functionals, which is also known as exchange-correlation energy density.

**1100** DFT exchange-correlation potential, i.e.  $V_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$

For user-defined function 1000 and 1100, "iDFTxcsel" in settings.ini is used to select XC functional. 0~29 are X part only, 30~69 are C part only, 70~99 are whole XC. For example, if iDFTxcsel=32, then iuserfunc=1000 corresponds to integrand of LYP, and iuserfunc=1100 corresponds to LYP potential.

Notice that both 1000 and 1100 are applicable for close-shell cases. But currently only 1000

can be applied to open-shell cases.

[See below for details]

### Available options of "iDFTxcsel" parameter

Currently only LSDA and some GGA functionals are supported

**0** LSDA exchange:  $-(3/2)[3/(4\pi)]^{1/3}[\rho_\alpha(\mathbf{r})^{4/3} + \rho_\beta(\mathbf{r})^{4/3}]$ . For close-shell cases the equivalent form is  $-(3/4)(3/\pi)^{1/3}\rho(\mathbf{r})^{4/3}$ .

**1** Becke 88 (B88) exchange, see *Phys. Rev. A*, **38**, 3098-3100 (1988).

**2** Perdew-Burke-Ernzerhof (PBE) exchange, see *Phys. Rev. Lett.*, **77**, 3865-3868 (1996).

**3** Perdew-Wang 91 (PW91) exchange, see Electronic Structure of Solids '91; Ziesche, P., Eschig, H., Eds.; Akademie Verlag: Berlin, 1991; p. 11.

**30** Vosko-Wilk-Nusair V (VWN5) correlation, see *Can. J. Phys.*, **58**, 1200-1211 (1980).

**31** Perdew 86 (P86) correlation, see *Phys. Rev. B*, **33**, 8822-8824 (1986).

**32** Lee-Yang-Parr (LYP) correlation, see *Phys. Rev. B*, **37**, 785-789 (1988).

**33** Perdew-Wang 91 (PW91) correlation, see the reference of its exchange counterpart.

**34** Perdew-Burke-Ernzerhof (PBE) correlation, see the reference of its exchange counterpart.

**70** Becke 97 (B97) exchange-correlation, see *J. Chem. Phys.*, **107**, 8554-8560 (1997).

**71** Hamprecht-Cohen-Tozer-Handy with 407 training molecules (HCTH407) exchange-correlation, see *J. Chem. Phys.*, **114**, 5497-5503 (2001).

**80** SVWN5 exchange-correlation.

**81** BP86 exchange-correlation.

**82** BLYP exchange-correlation.

**83** BPW91 exchange-correlation.

**84** PBEPBE exchange-correlation.

**85** PW91PW91 exchange-correlation.

## 2.8 Graphic formats and picture size

Benefiting from DISLIN graphical library, Multiwfn supports a lot of mainstream graphic formats, including:

- 1 Postscript (ps)
- 2 Encapsulated postscript (eps)
- 3 Portable document format (pdf)
- 4 Windows metafile format (wmf)
- 5 Graphics interchange format (gif)
- 6 TIFF (tiff)
- 7 Portable network graphics (png)
- 8 Windows bitmap format (bmp)

The graphic format of the picture exported by Multiwfn is controlled by “graphformat” parameter in settings.ini, you can set this parameter to the texts in the parentheses listed above, the default format is “png”.

Tip: If the graph is mainly composed of lines, e.g. contour line map, the best format is pdf.

For curve maps, the height and weight of the picture are controlled by “graph1Dsize” parameter in settings.ini, “graph2Dsize” is responsible for two-dimension data plotting (color-filled map, contour map, relief map, etc.), “graph3Dsize“ is responsible for three-dimension data plotting (isosurface graph, molecular structure graph).

## 3 Functions

This chapter introduces all functions of Multiwfn in detail, the numbers in the parentheses of secondary titles are indices of corresponding functions in main menu, the numbers in the parentheses of tertiary titles are indices of corresponding options in corresponding submenus. **Different functions of Multiwfn require different types of input file, the information needed by each function are shown in the final line of corresponding section.** Please choose proper type of input file according to the table in Section 2.5.

### 3.1 Defining molecular fragment (-3, -4)

By this function, you can define the molecular fragment that you are interested in. The GTFs whose centers do not belong to this fragment will be discarded (can be imagined as corresponding GTF coefficients in all orbitals are set to zero). This function affects all the following tasks which make use of GTF information, in particular, those involve calculation of real space functions. Function -4 is the reverse of function -3, the atoms in the fragment you defined will be discarded.

Why use this function? For large molecules, what you are interested in may be only a small region, by discarding atoms beyond this region, the calculation speed of time-consuming task such as generating grid data can be increased evidently. In other circumstances, you may want to obtain the property only contributed by certain atoms, this function can fulfill your purpose.

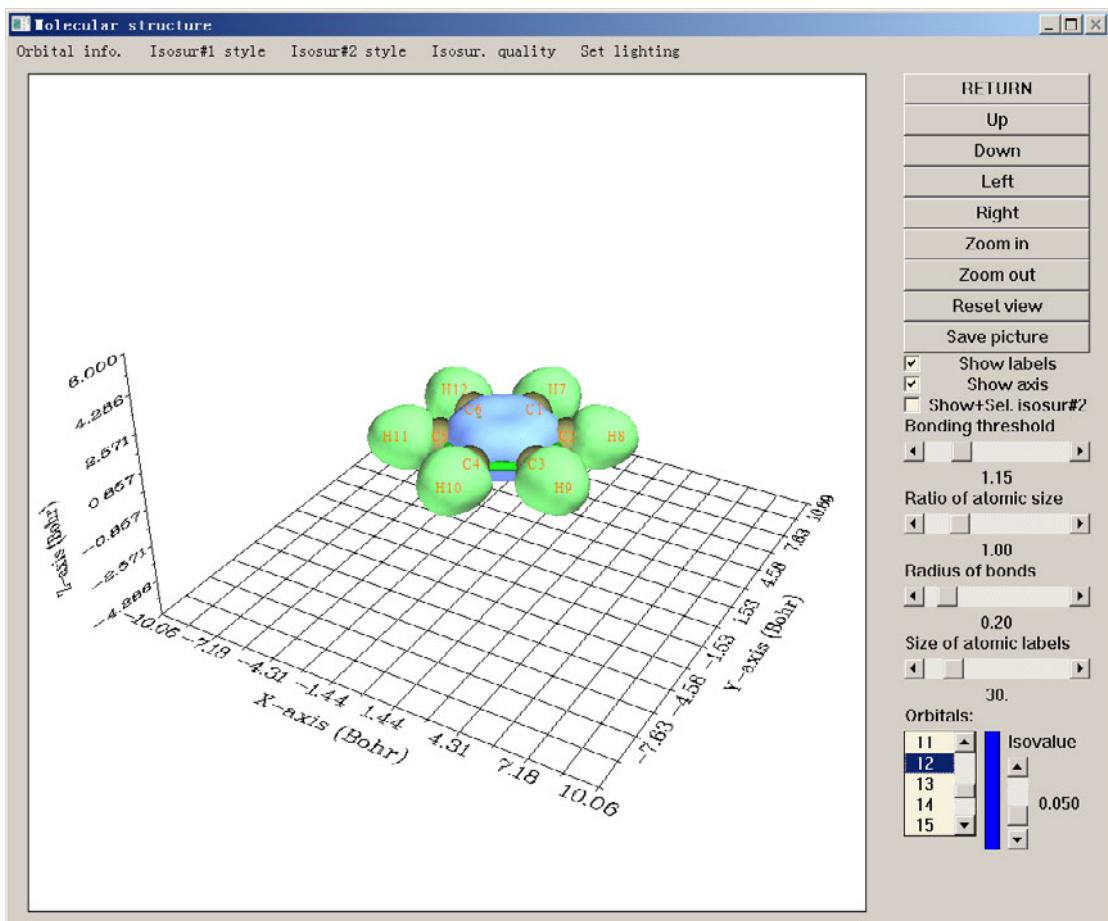
This function can be safely used together with mainfunction 1,2,3,4,5,6. For other tasks, please DO NOT use this function if you do not understand what you are exactly doing, otherwise you may obtain wrong or meaningless results. Notice that this function is irreversible, the discarded GTFs cannot be recovered, unless you reboot the program and reload the wavefunction file.

**Information needed:** GTFs, atom coordinates.

### 3.2 Showing molecular structure and viewing orbitals / isosurfaces (0)

When function 0 is selected, all atom coordinates will be printed on text window, meanwhile molecular structure will be shown in a GUI window. If the input file is .wfn/.wfx/.fch/.molden/.gms type or NBO plot file, orbitals can be viewed by selecting corresponding orbital index in the list at right-bottom of the window, see below screenshot. If the input file is .cub/.cube/.grd, then one can view specified isosurface by adjusting the isovalue slide bar.

### 3 Functions



Since most buttons in this GUI are self-explained, I only explain some worthnoting options here.

By clicking "**Orbital info.**" and select the only option "show", basic orbital information will be printed on text window.

**"Ratio of atomic size"** is the ratio of one-fourth of atom radius shown on screen to its van der Waals (vdW) radius, so if the slide bar is dragged to 4.0, then what is shown is vdW surface.

Multiwfn determines if atoms are bonded by empirical distance criteria, if the distance between two atoms is short than 1.15 times of the sum of their CSD covalent radii, they will be considered as bonded. You can adjust this criteria by dragging "**Bonding threshold**" slide bar.

**Viewing orbitals:** All orbital indices are listed on the right-bottom box, default selection is "none" (no orbital is shown). If you click an orbital indices, Multiwfn will calculate grid data of wavefunction value for corresponding orbital, the progress is shown by blue bar, once the bar is full, the orbital isosurface appears immediately. Green and blue parts correspond to positive and negative regions, respectively. The "Isovalue" slide bar controls the isovalue of the isosurface. For efficiency consideration, the default quality of grid data is coarse, the number of grid points can be set by "**Isosur. quality**", the larger number leads to the finer isosurface. Note that after you set the number, present isosurface will be deleted. You can also set default number of grid points through changing "nprevorbgrid" in settings.ini.

Sometimes it is useful to display two orbitals simultaneously, for example, analysis of phase overlapping of two NBOs. This can be realized by "**Show+Sel. Isosur#2**" (Sel.=Select) check

box. This check box is inactive by default, once you have chosen an orbital (corresponding isosurface will be referred to as Isosurface #1), this check box will be activated. After you clicked the check box, the isosurface of the orbital you newly selected (which will be referred to as Isosurface #2) will be shown together with the orbital you previously selected, yellow-green and purple parts correspond to positive and negative regions respectively. If the check box is deselected, Isosurface #2 will disappear, then if you reselect the check box the same Isosurface #2 will be redrawn.

The representation styles of Isosurface #1 and #2 can be adjusted by suboptions in "**Isosur. #1**" and "**Isosur. #2**" individually, available styles include solid face (default), mesh, points, solid face+mesh and transparent face. (Notice that Multiwfn cannot plot only one isosurface as transparent face). The colors for face and mesh/points can be set by corresponding suboptions too, users will be prompted to input Red, Green, Blue components for positive and negative parts in turn. The component values should between 0.0 and 1.0, for instance, 1.0,1.0,0.0 corresponds to Yellow. Opacity for transparent face can also be customly set, valid range is from 0.0 (completely transparent) to 1.0 (completely opaque).

When orbital isosurfaces are portrayed as solid face, in rare cases you may see some ugly dark polygons, or positive and negative regions are difficult to be distinguished, in these cases you can try to adjust lighting setting by using "**Set lighting**" option in the GUI menu or rotate the system to solve the problem.

**Information needed:** GTFs (only for viewing orbitals), atom coordinates, grid data (only for viewing isosurface of grid data)

### 3.3 Outputting all properties at a point (1)

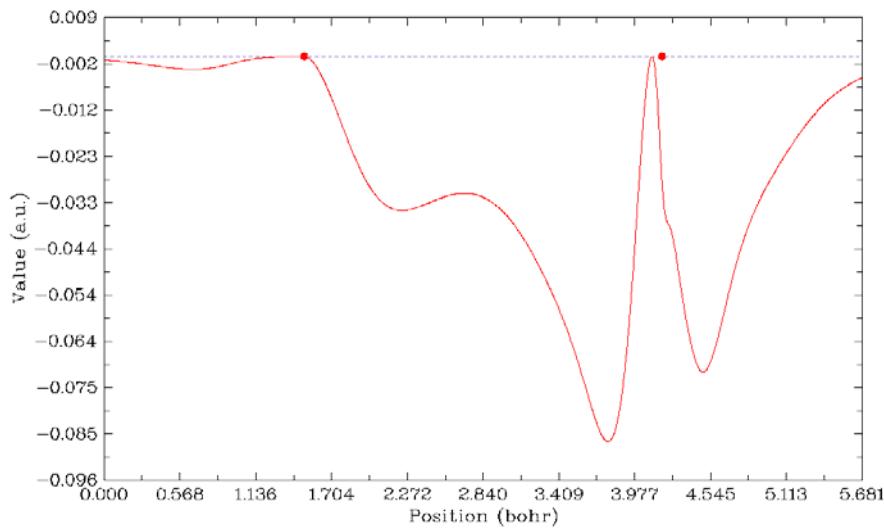
Input coordinate of a point or index of an atom, then the values of all real space functions supported by Multiwfn at the point or corresponding nuclear position will be printed on screen, as well as each component of gradient and Hessian matrix of specified function (default is electron density). The function can be specified by *f?*, for example *f9* select ELF, you can input *allf* to check all available functions. The orbital whose wavefunction value will be outputted can be selected by command *o?*, for example *o4* choose the fourth orbital. If the input file merely contains atom coordinates (such as *pdb* file), then only limited functions based on electron density will be outputted, the electron density used is promolecular density constructed from fitted free atom density, see the introduction of real space function 14 in Section 2.6.

Electrostatic potential is the most expensive one among all of the real space functions supported by Multiwfn. If you are not interested in it, you can set "ishowptESP" parameter in "settings.ini" to 0 to skip calculation of electrostatic potential.

**Information needed:** GTFs (depends on the choice of real space function), atom coordinates

### 3.4 Outputting and plotting specific property in a line (3)

What you should do is just select a real space function and then define a line. There are two ways to define the line: (1) By inputting indices of two atoms, the line will be automatically extended by a small distance in each side, the extended distance can be adjusted by “aug1D” in settings.ini or by the option “0 Set extension distance for mode 1”, default value is 1.5 Bohr. (2) By inputting the coordinates of the two endpoints. Generally, the calculation only takes a few seconds, and then curve map pops up immediately, like this



The gray dash line indicates the position of  $Y=0$ . If the line is defined by the second way, two red circles with  $Y=0$  will appear in the graph, they indicate the position of the two nuclei. Click right button on the graph and then you can select what to do next, you can redefine the scale of Y-axis, export the data to line.txt in current directory, save the graph to a file, locate minimal and maximal positions and so on. Note that the process for searching stationary points and the position where  $Y$  equals to specified value is based on the data you have calculated, that means the finer the points, the more accurate X position you will get.

The data points are evenly distributed in the line, the number of points is 3000 by default, which is fine enough for most cases. The number can also be adjusted by “num1Dpoints” parameter in settings.ini. Of course, the more points the more time is needed for calculating data. Notice that for ESP calculation, the number of points is decreased to one-sixth automatically, because it is much more time-consuming than other task.

**Information needed:** GTFs (except for ESP from nuclear/atomic charges and promolecular approximation version of RDG and  $\text{sign}(\lambda_2) * \rho$ ), atom coordinates

## 3.5 Outputting and plotting specific property in a plane (4)

The basic steps of using this function are listed below. Users can finish all operations by simply following program prompts, there are only a few key points are needed to be described.

1. Select a real space function
2. Select a graph type
3. Set the number of grid points in both dimensions
4. Define a plane
5. View the graph
6. Post-processes (Adjust plotting parameters, save graph, export data to plain text file, etc.)

Worthnotingly, after you enter this function, you will see real space function selection menu; if you select option 111 (a hidden option), then the real space function to be plotted will be Becke weight of an atom or Becke overlap weight between two atoms. If you select option 112 (another hidden option), Hirshfeld weight of a given atom or fragment will be plotted.

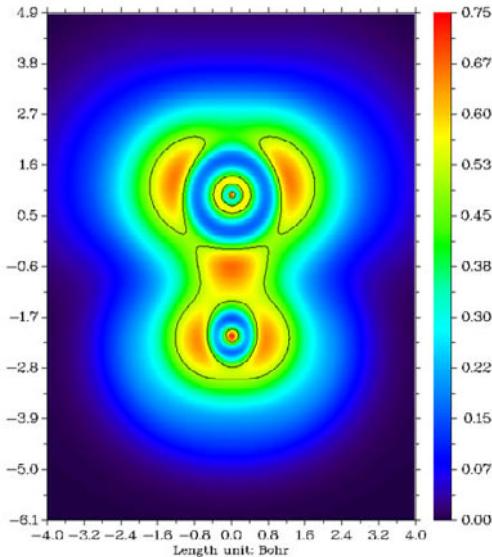
If the parameter "iplaneextdata" in settings.ini is set to 1, then the data in the plane will not be calculated by Multiwfn internally but directly loaded from an external plain text file. The coordinate of the points in the plane will be automatically outputted to current folder, you can use third-party tools (e.g. cubegen utility of Gaussian) to calculate function value at these points. (If you don't know how to use cubegen, you may consult Section 4.12.7)

### 3.5.1 Graph types

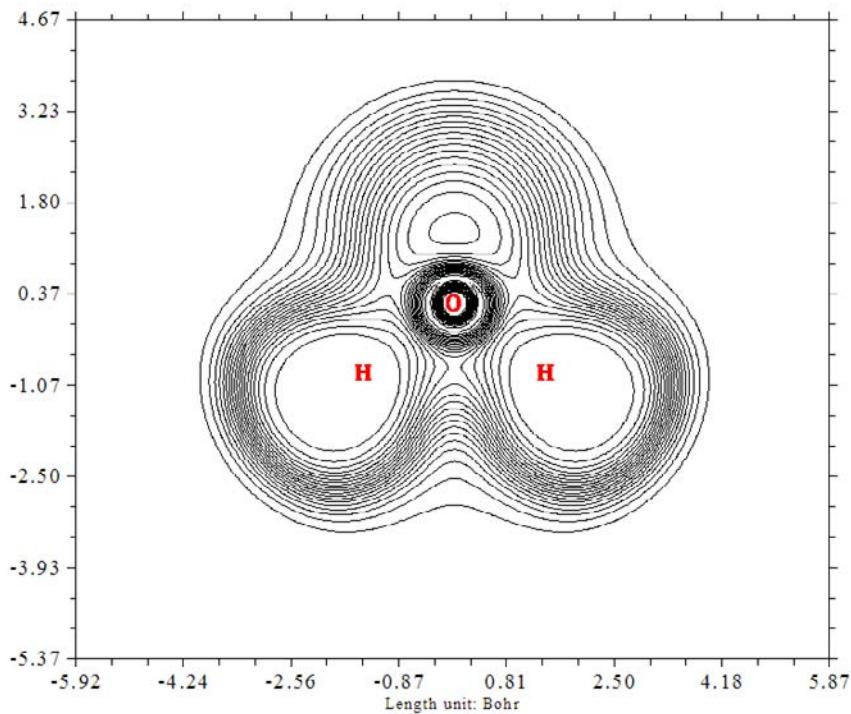
Currently Multiwfn supports seven graph types for exhibiting data in a plane.

**1 Color-filled map.** This type of map uses different colors to represent real space function value in different region. By default, if the function value exceeds lower (upper) limit of color scale, then the region will be filled by black (white); if you want to avoid this treatment, simply set the parameter "inowhiteblack" in settings.ini to 1. If you want to reverse color scale as red-white-blue, in post-process menu you can set the lower limit smaller than upper limit, e.g. inputting *I,-I*.

By selecting “Enable showing contour lines” in post-process menu, contour lines can be plotted together on the graph:



**2 Contour line map.** This map uses solid lines to represent positive regions, and dash lines to exhibit negative regions.



The number of isovalue lines can be adjusted by user (see Section 3.5.4), you can also mark the isovalue on the contour lines by using the option “2 Enable showing isovalue on contour lines” in post-process step.

Only for contour line map, if the real space function you selected to be plotted is orbital wavefunction, you can not only plot one orbital by inputting one orbital index, but also plot two orbitals simultaneously by inputting two orbital indices (e.g. 3,5), see Section 4.4.5 for example.

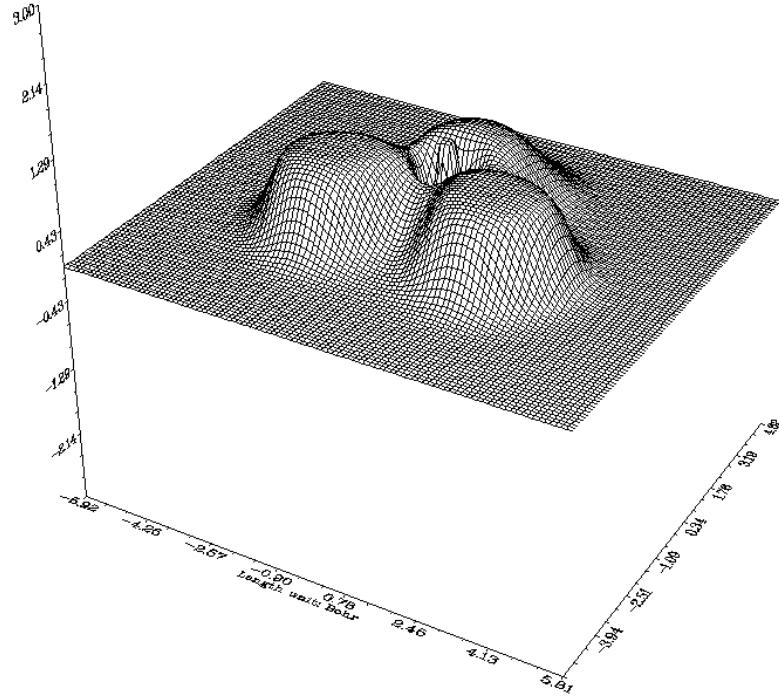
Option 4 in post-process menu is used to toggle if showing atoms labels or reference point (involved in some real space functions such as correlation hole and source function) in the graph. The size and form (i.e. if showing atom index or element name) of the atom labels can be set by "pleatmlabsize" and "iatmlabtype" parameters in settings.ini, respectively. The reference point is represented as a blue asterisk on the graph. By default only when the distance between the atoms and the plane is smaller than "disshowlabel" in settings.ini the corresponding atom labels will be shown. To change this distance threshold, you can either adjust this value in setting.ini or choose option 17 in post-process menu. If "iatom\_on\_contour\_far" parameter in settings.ini is set to 1, then even if the distance is larger than the threshold, the label will still be shown, but in thin text rather than bold text.

Option 15 in post-process is used to plot a contour line corresponding to vdW surface (electron density=0.001 a.u., which is defined by R. F. W Bader in *J. Am. Chem. Soc.*, **109**, 7968 (1987)). This is useful to analyze distribution of electrostatic potential on vdW surface. Such a contour line can be plotted in gradient line and vector field map too by the same option. Color, label size and line style of the contour line can be adjusted by Option 16.

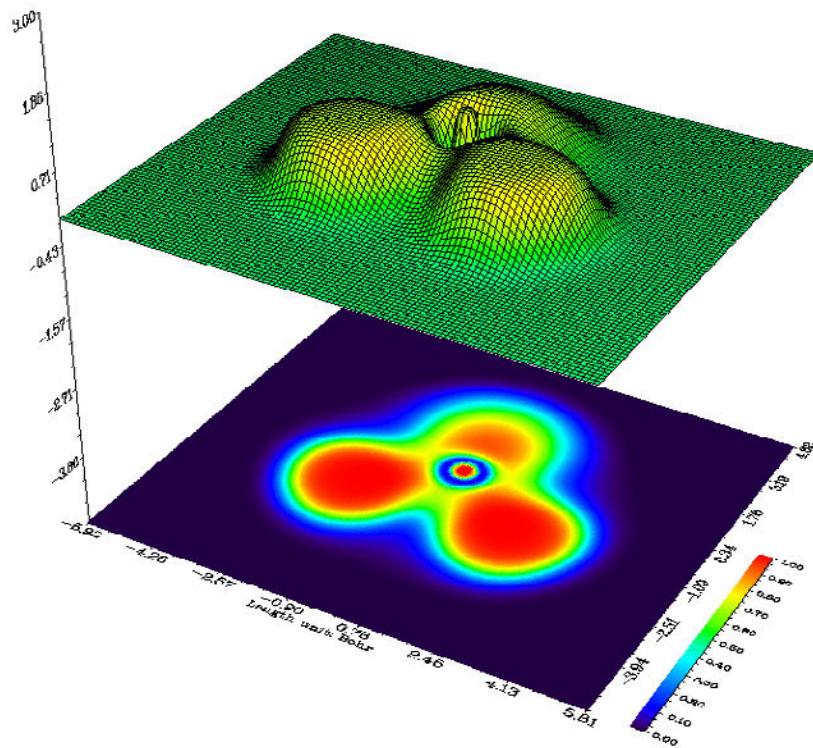
Notice that the discussion in above two paragraphs also applies to color-filled map, gradient lines map and vector field map (see below).

### 3 Functions

**3 Relief map.** Use height to represent value at every point. If values are too large they will be truncated in the graph, you can choose to scale the data with a factor to avoid truncation. The graph is shown on interactive interface, you can rotate, zoom in/out the graph.



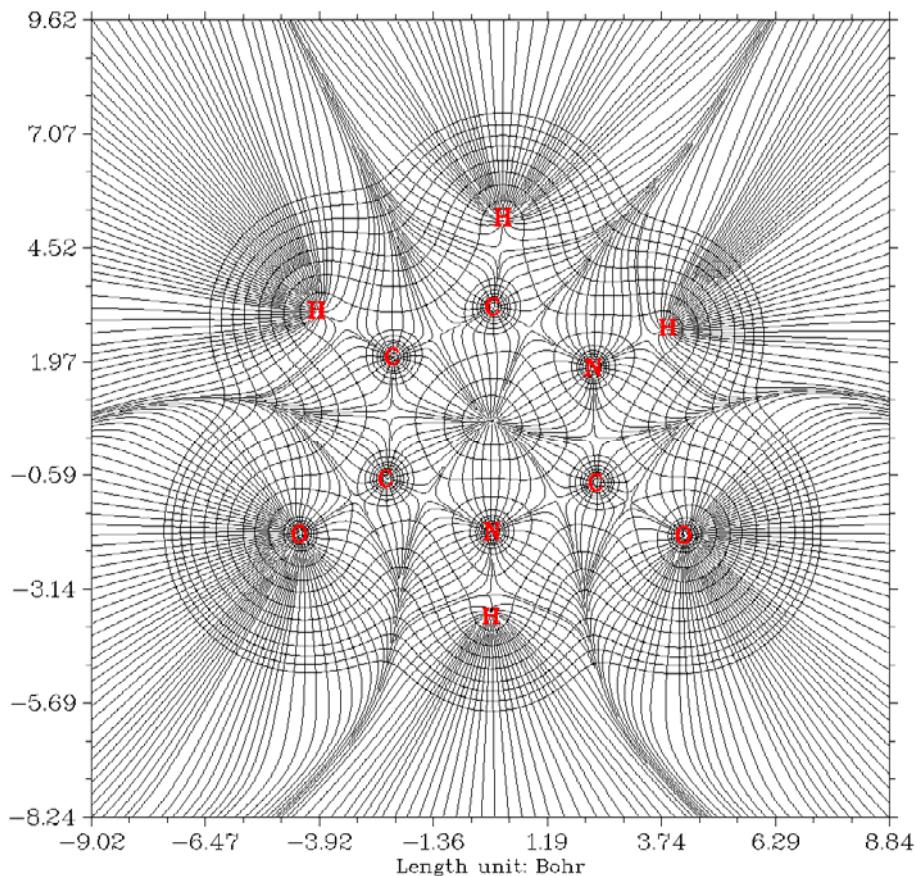
**4 Shaded surface map and 5 Shaded surface map with projection.** The relief map is shaded in these two types. The latter also plots color-filled map as projection. The meshes on the surface can disabled at post-process stage.



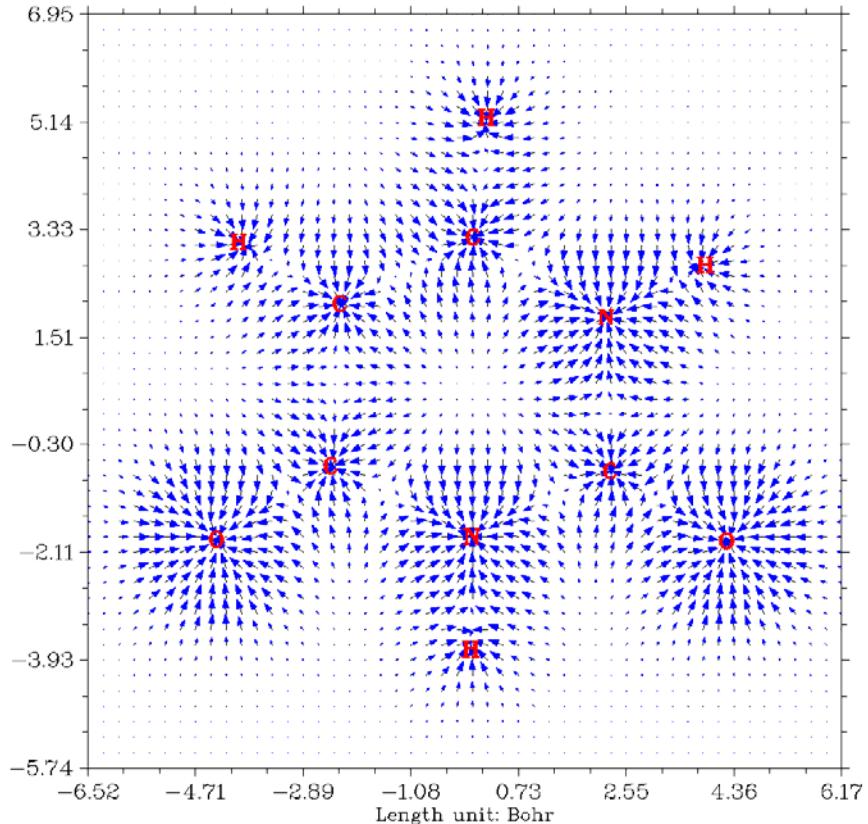
### 3 Functions

**6 Gradient line map with/without contour lines.** This graph type represents gradient direction of real space function, you can determine if the contour lines also be shown on the graph. Note that since gradients of real space function are needed to be evaluated, and graphical library needs to take some time to generate gradient lines, the computational cost is evidently higher than other graph type.

By option 11 at post-process stage you can control the integration step for gradient lines, the smaller value you set the graph looks finer. By option 12 you can set interstice between gradient lines, the smaller value you set the lines become denser. By option 13 you can set the criteria for plotting new gradient line, try to play with it and you will know how the parameter affects the graph.



**7 Vector field map with/without contour lines.** This graph type is very similar to last graph type, however the gradient lines are replaced by arrows, which distribute on grids evenly and represent gradient vectors at corresponding point. You can set color of arrows, or map different colors on arrows according to magnitude of function value, you can also invert the direction of arrows. The option 10 is worth mentioning, if you set upper limit for scaling to  $x$  by this option, then if the norm of a gradient vector exceeds this value, the vector will be scaled so that its norm equals to  $x$ .



### 3.5.2 Setting up grid, plane and plotting region

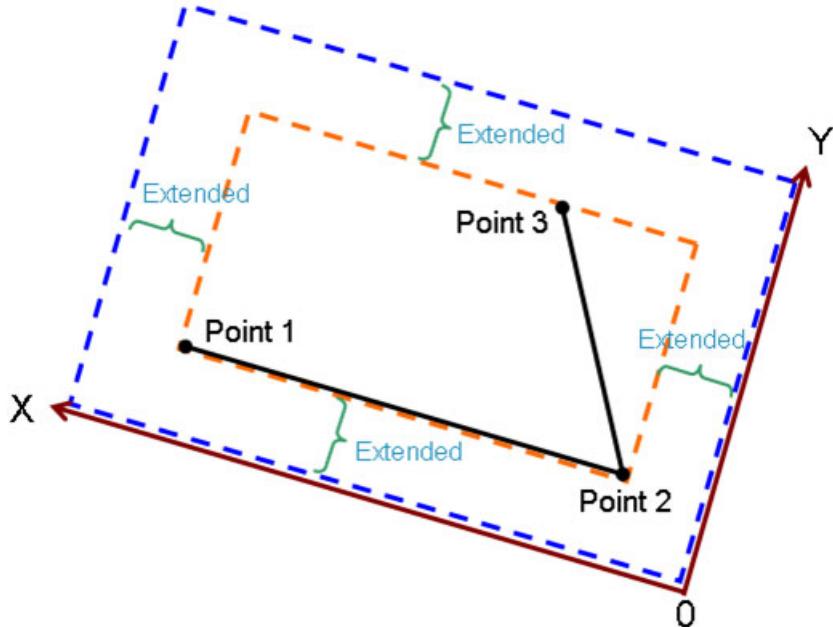
When program asking you to input the number of grid points in both dimensions, you can input such as *100,150*, which means in dimensions 1 and 2 the number of grid points are 100 and 150, respectively, so total number is  $100 \times 150 = 15000$ , they are evenly distributed in the plotting region. For “Relief map”, “Shaded surface map” and “Shaded surface map with projection”, commonly I recommend *100,100*; if this value is exceeded, the lines in the graph will look too crowded. For other graph types I recommend *200,200*. Of course the picture will become more pretty and smoother if you set the value larger, but you have to wait more time for calculation. Bear in mind that total ESP calculation is very time-consuming, you’d better use less grid points, for previewing purpose I recommend *80,80* or less.

Multiwfn provides seven modes to define the plotting plane:

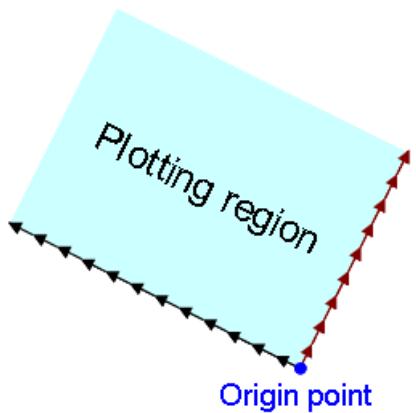
1. XY plane: User inputs Z value to define a XY plane uniquely.
2. XZ plane: User inputs Y value to define a XZ plane uniquely.
3. YZ plane: User inputs X value to define a YZ plane uniquely.
4. Define by three atoms: Input indices of three atoms to define a plane by their nuclear coordinates.
5. Define by three points: Input coordinates of three points to define a plane.
6. Input origin and transitional vector: This way is only suitable for expert, the two inputted translation vectors must be orthogonal.
7. Define a plane parallel to a bond and meantime normal to a plane defined by three atoms

For modes 1~5, the actual plotting region is a subregion of the plane you defined. Multiwfn automatically sets the plotting region to tightly enclose the whole molecule (for modes 1, 2 and 3) or cover the three nuclei / points you inputted (for modes 4 and 5), finally the plotting region is extended by a small distance to avoid truncating the interesting region. The extension distance is 4.5 Bohr by default, if you find the region you interested in is still be truncated, simply enlarging the value by option “**0 Set extension distance for plane type 1~5**”, you can also directly modify the default value, which is controlled by “Aug2D” parameter in settings.ini.

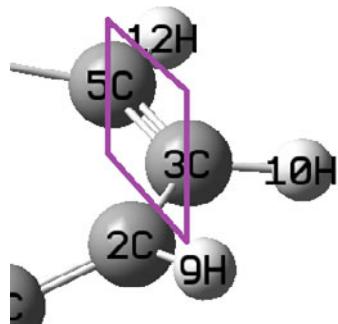
Below illustrate how the actual plotting region is determined when you select mode 4 or 5 to define the plane. The X and Y axes shown in the graph correspond to the actual X and Y axes you will finally see. Evidently, the input sequence of the three points or atoms directly affects the graph.



For mode 6, the plotting region is determined as follows, in which each black arrow denotes translational vector 1, each brown arrow denotes translational vector 2, blue point denotes origin point. The number of arrows is the number of grids set by users. Evidently, this mode enables users to fully control the plotting plane setting.



Mode 7 is very useful when you want to define a plotting plane cutting a bond but there is no proper reference atoms to use mode 4, below graph is such an instance, the purple rectangle is the plane you want to plot:



To define this plane, you should select mode 7, and then input 3,5 to use these two atoms to define the axis that the plotting will be parallel to, and then input 2,3,10 (or 2,5,10 etc.) to use them to define a plane that the plotting plane will be normal to. After that you need to input the length of X and Y axes, e.g. 10 Bohr and 7 Bohr, respectively.

### 3.5.3 Options in post-process interface

After plotting the graph, you will see a menu, in which there are a lot of options used to adjust or improve the quality of the graph. Since many of them have already been introduced above and some of them will be mentioned in next sections, and lots of them are self-explained, only a few will be mentioned here.

**-9 Only plot the data around certain atoms:** Sometimes in the graph only a few regions are interesting; if you want to screen other regions, you may find this option useful. After selecting this option, assume that you input 2,4,8-10, then only the real space function around atoms 2,4,8,9,10 will be plotted (the data to be plotted then in fact is the original plane data multiplied by the Hirshfeld weight of the fragment you inputted). Next time you select this option, the original data will be recovered.

**-7 Multiply data by a factor:** This is mainly used to scale the range of the plane data.

**-6 Export calculated plane data to plane.txt in current folder:** After using this option to export the plane data, you can very conveniently using third-part plotting softwares such as SigmaPlot to redraw the data.

**-2 Set stepsize in X,Y,(Z) axes:** This option determines the spacing between the labels in the coordinate axes. If axis labels are not shown, that means you need to decrease the stepsizes.

**-1 Show the graph again:** After adjusting plotting parameters, choose this option to replot the graph to check the effect.

**0 Save the graph to a file:** Export the graph to a graphic file in current folder. See Section 2.8 on how to determine the graphic format and size.

### 3.5.4 Setting up contour lines

For graph types 1, 2, 6 and 7, the contour lines can be plotted (if not shown, select "2 Enable showing contour lines" in the post-process menu). There is also an option "Change contour line setting" in the post-process menu used to adjust the setting of contour lines. In this interface, current isovalue are first listed and you can modify them by using below suboptions:

**Option 1:** Save current setting and return to upper menu. Then if you select "Show the graph again", the graph with new isovalue setting will appear.

**Option 2:** Input a new value to replace old isovalue of a contour line.

**Option 3:** Add a new contour line and input the isovalue for it.

**Option 4:** Delete a contour line. The indices of the contour lines behind it will move forward.

**Option 5:** Delete contour lines whose index is in a certain range.

**Option 6:** Export current isovalue setting to a plain text file, you can use this function to save multiple sets of your favourite isovalue settings for different systems and real space functions.

**Option 7:** Load isovalue setting from external file, the format should be identical to the file outputted by subfunction 6.

**Option 8:** Generate isovalue according to arithmetic sequence, user need to input initial value, step size and total number. For plotting ELF/LOL, I suggest user input 0,0.05,21 to generate isovalue in the range 0.0~1.0 with step size 0.05. You can choose if clean existed contour lines, if you select "n", then new contour lines will be appended to old ones.

**Option 9:** Like function 8, but according to geometric series.

**Option 10:** Some contour lines can be bolded with this function, by default no line is bolded. To bold some lines, select this function and input how many lines you want to bold, then input indices of them in turn. If there are some lines already been bolded, selecting this function will unbold all of them.

**Option 11:** Set color for positive contour lines, you need to input a color index.

**Option 12:** Set line style for positive contour lines, you need to input two integer number, the first one denotes the length of line segment, the second one denotes the length of interstice between line segment. For example 10,15 means positive contour lines are composed of line segments with length of 10 and spaces with length of 15 alternatively.

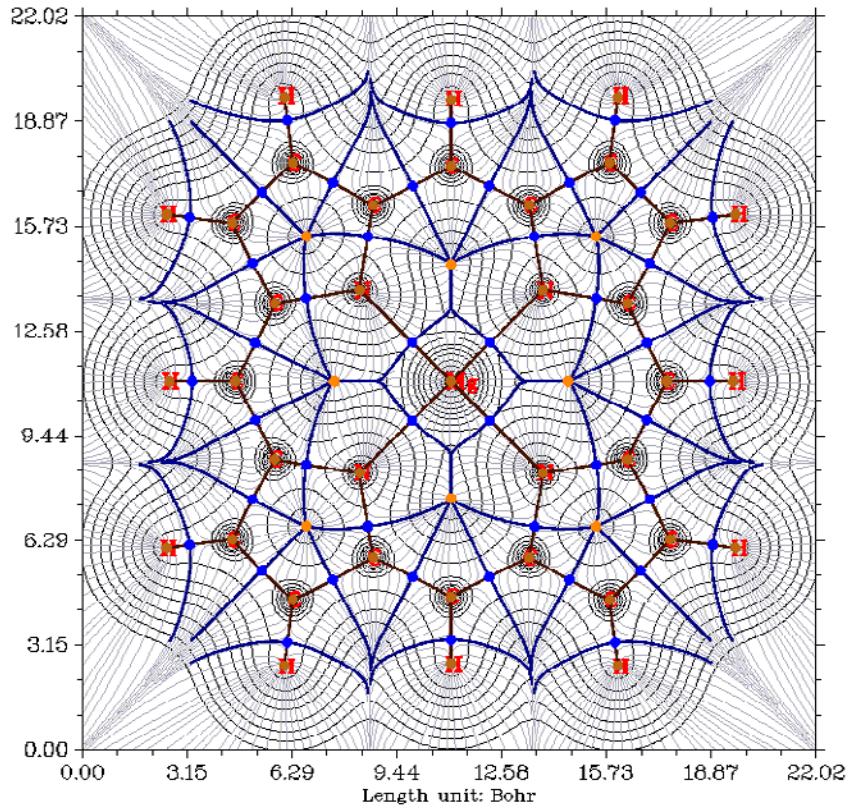
**Option 13, 14:** Like option 11 and 12, but for negative part.

### 3.5.5 Plot critical points, paths and interbasin paths on plane graph

CPs and paths can be plotted on plane graph type 2, 6 and 7. In order to do that, before drawing a plane graph, you need to go into topology analysis module (main function 2), search

### 3 Functions

CPs and generate paths. After that, return to main menu and draw plane graph as usual, you will find that the CPs and paths have appeared on the graph automatically, such as below (without deep blue lines). Brown, blue, orange, green dots denote (3,-3), (3,-1), (3,+1), (3,+3) critical points respectively. Bold dark-brown lines depict bond paths. Notice that if the distance between a CP and the plane exceeds "disshowlabel" in settings.ini, the CP will not be shown.



In the option “Set marks of critical points and paths” at post-process stage, you can choose which types of CPs are allowed to be shown, and you can set size of markers, thickness and color of path lines.

Interbasin paths (deep blue lines in above graph) are derived from (3,-1) CPs, these paths dissect the whole space into individual basins, within each of which a (3,-3) CP can be found. In order to draw interbasin paths, you should confirm first that at least one (3,-1) CP has been found in topology analysis module and it is close enough to current plane (less than "disshowlabel" in settings.ini), then you can find a option "Generate and show interbasin paths" in post-process stage, choose it, wait until the generation of interbasin paths is completed, then show the plane graph again, you will find these interbasin paths have already presented.

If you expect the interbasin paths to be shorter or longer, choose option "Set stepsize and maximal iteration for interbasin path generation" in post-process stage before generating interbasin paths, you will be prompted to input two values, the length of interbasin paths equals to the product of the two value. Note that if distance between a point in the path and the given plane exceeds "disshowlabel" in settings.ini, corresponding segment of the path will not be shown on the plane graph.

**Information needed:** GTFs (depends on the choice of real space function), atom coordinates

## 3.6 Outputting and plotting specific property within a spatial region (5)

The main purpose of this function is generating Gaussian-type grid file (.cub) for specific property, the .cub file is supported by a lot of chemistry visualization softwares, such as VMD, GaussView, ChemCraft, and Molekel. The isosurface of generated grid data can be viewed directly in Multiwfn too. This function is also used to calculate function values for a set of points recorded in external file.

The basic procedure of using this function is:

1. Select a real space function
2. Set up grid
3. Use post-process options to visualize isosurfaces, modify and export data

In the real space function selection menu, if you select option 111 (a hidden option), then the real space function to be calculated will be Becke weight of an atom or Becke overlap weight between two atoms. If you select option 112 (another hidden option), Hirshfeld weight of a given atom or fragment will be calculated.

### Set up grid

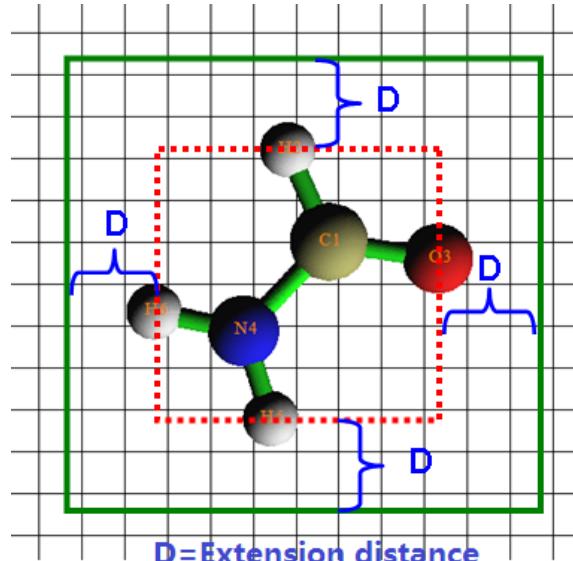
Multiwfn provides seven modes for setting up grid point:

**Mode 1:** Low quality grid, about 125000 points in total (corresponding to 50\*50\*50 grid, assuming the spatial region is cubic), this mode is recommended for previewing.

**Mode 2:** Medium quality grid, about 512000 points in total (corresponding to 80\*80\*80 grid, assuming the spatial region is cubic). For small molecular, this quality is enough for most analysis.

**Mode 3:** High quality grid, about 1728000 points in total (corresponding to 120\*120\*120 grid, assuming the spatial region is cubic).

For modes 1, 2 and 3, the actual number of points in each direction is automatically determined by Multiwfn so that grid spacings in each direction are nearly equal. The method of determining spatial scope of grid data is illustrated below in two-dimension case.



First, Multiwfn sets up a box (red dashed line) to just enclose the entire molecule, and then the box is suitably extended in each dimension to avoid truncating boundary part of isosurfaces, the green rectangle in below graph is the actual spatial scope of grid data. If the extension distance is inappropriate, you can customly set the value by using option “-10 Set extension distance of grid range”, or directly set default value by modifying “Aug3D” in settings.ini.

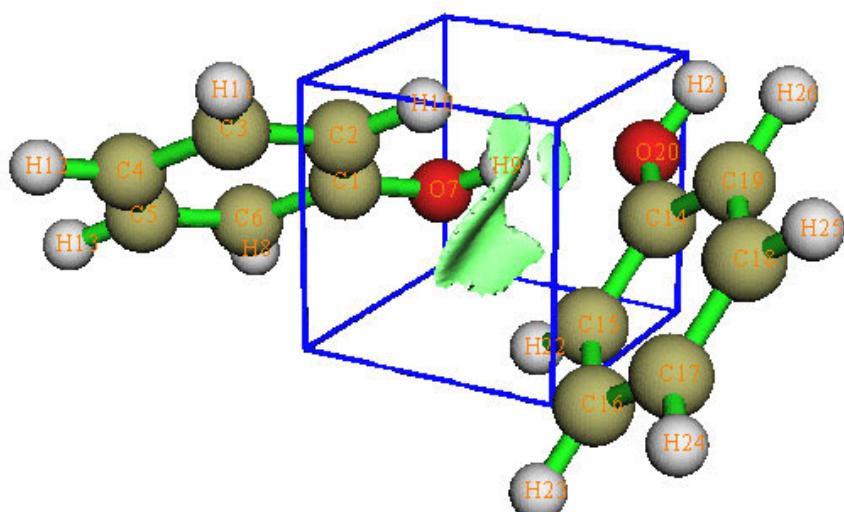
The so-called “Low quality”, “Medium quality” and “High quality” are **only relative to small system**, if spatial scope is large, then density of grid points of mode 3 is not high and should be called “Medium quality”, mode 2 should be call “Low quality” at this time. While for very small system, the mode 1 is enough for general purposes.

**Mode 4:** Specify the number of grid points or grid spacing in X, Y and Z directions by yourself, the spatial scope is determined automatically as shown above.

**Mode 5:** Specify all details of grid setting by user, including the number of points in X, Y and Z directions, initial point, translation vectors. This mode is useful for reproducing existed cube files.

**Mode 6:** Specify the center coordinate, number of points and extension distance in X, Y and Z directions. For example, the center coordinate you inputted is 2.3,1.0,5.5, the extension distance in X, Y and Z is  $k,k,m$ , then the coordinates of two most distant endpoints are  $(2.3-k,1.0-k,5.5-m)$  and  $(2.3+k,1.0+k,5.5+m)$ . This mode is useful for analyzing local properties.

**Mode 7:** Like function 6, but input indices of two atoms instead of inputting center coordinate, the midpoint between the two nuclei will be set as center. This mode is very useful for weak interaction analysis by RDG function, for examples, we want to study the weak interaction region between the dimer shown below, and we found C1 and C14 may enclose this region, so we input 1,14. see Section 4.100.1 for example. If the two atom indices are identical, then the nuclear coordinate will be set as center.



**Mode 8** Use grid setting (origin, number of points and grid spacing) of another Gaussian-type cube file. You will be prompted to input the file name. This mode is useful to generate multiple cube file with exactly identical grid setting.

Notice that the more grid points you set, the finer the isosurface graph you will get, however the more time is needed for calculating data and generating isosurface graph, and the size of exported cube file will be bigger. Except for total ESP function, the increase of calculation time with the number of points is nearly linear.

After setting grid points, the program starts to calculate grid data, once the calculation is finished, the minimum/maximum and corresponding coordinate, the sum of all/positive/negative data multiplied by differential element are printed on screen immediately. If what you calculated is electron density, the molecular dipole moment evaluated based on grid data is also printed out. Then you will see post-process menu.

### Post-process options

In the post-process menu if the option “-1 Show isosurface graph” is selected, a GUI window will pop up, which shows the isosurface of grid data, all widgets are self-explained, you can change isosurface value by both dragging slide bar (upper and lower limit are -5 and +5 respectively) or inputting precise value in text box (then press “Enter” button in your keyboard); if “Show data range” is selected, the spatial scope will be marked by a blue frame as the one in above picture (if spatial scope exceeds the range of coordinate axis, the frame will not be displayed). The isosurfaces with the same and reverse sign of current iso value are in green and blue respectively.

Option 1 can export isosurface graph to graphic file in current directory. Option 2 can export grid data to .cub file in current directory. By selecting option 3 the grid data will be exported to plain text file “output.txt” in current directory. Using option 4 you can set iso value without entering GUI window and dragging slide bar, it is useful for batch process and in command-line environment. With options 5~8, you can perform addition, subtraction, multiplication and division operations on the grid data, respectively.

### Special note: Calculate data for a set of points

If you want to use Multiwfn to calculate real space function value for a set of points (may be arbitrarily distributed), in the interface for setting up grid, you should choose "100 Load a set of points from external file" and then input the path of the plain text file recording the points. In the file the first line should be the number of points recorded, and followed by X/Y/Z coordinates of all points. For example

1902

-3. 3790050	-2. 0484700	0. 0274117
-3. 3844930	-1. 9472468	-0. 2500274
-3. 4064601	-1. 9221635	-0. 1287148
-3. 4118258	-1. 9232203	-0. 0003350

### 3 Functions

```
-3. 4059106 -1. 9218280 0. 1351179
```

The coordinates must be given in Bohr. The format is in free format, and can have more than four columns of data, but the columns after the fourth one will be simply ignored.

Multiwfn will load coordinates of the points from this file, and then calculate function value for them. Finally, the X/Y/Z coordinate and function value of all points will be outputted to a plain text file, whose path is specified by users.

**Information needed:** GTFs (depends on the choice of real space function), atom coordinates

## 3.7 Custom operation, promolecular and deformation properties (subfunction 0, -1, -2 in main function 3, 4, 5)

### 3.7.1 Custom operation for multiple wavefunctions (0)

In main function 3, 4 and 5, there is a subfunction allow you to set custom operation for multiple wavefunctions. Supported operators include + (add), - (minus), \* (multiply), / (divide), there is no upper limit of the number of wavefunctions involved in custom operation. For example, if the first loaded wavefunction after booting up Multiwfn is *a.wfn*, then in the setting step of custom operation you inputted 2 (viz. there are two wavefunctions will be put into “custom operation list” and thus will be operated with *a.wfn* in turn), then you inputted *-b.wfn* and *\*c.wfn*, the property finally you get will be [(property of *a.wfn*) - (property of *b.wfn*)] \* (property of *c.wfn*). If you are confused, you can consult the example in Sections 4.5.4 and 4.5.5.

Sometimes the molecular structure in the first loaded file and that in the subsequently loaded files are not identical, the grid points you set will be for the first loaded file, all of the other files will share the same grid setting.

Avoid using custom operation in conjunction with main functions -4, -3 and 6, otherwise you may get absurd result.

### 3.7.2 Promolecular and deformation properties (-1, -2)

If you selected subfunction -1 in main functions 3, 4 or 5 before choosing a property (viz. a real space function), what you finally get will be promolecular property. Promolecular property is the superposition property of atoms in their free-states

$$P^{pro}(\mathbf{r}) = \sum_A P_A^{free}(\mathbf{r} - \mathbf{R}_A)$$

If the property you chose is electron density, then the promolecular property is generally referred to as promolecular density

$$\rho^{pro}(\mathbf{r}) = \sum_A \rho_A^{free}(\mathbf{r} - \mathbf{R}_A)$$

This is an artificial density that corresponds to the state when molecule has formed but the density

has not relaxed.

Deformation property is the difference between actual property and promolecular property of a molecule under the same geometry

$$P^{def}(\mathbf{r}) = P^{mol}(\mathbf{r}) - P^{pro}(\mathbf{r})$$

If the property is chosen as electron density, then the deformation property is generally called deformation density or known as electronic bonding charge distributions (BCD), which is very useful for analyzing charge transfer and bonding nature.

### 3.7.3 Generation of atomic wavefunctions

Evaluation of promolecular and deformation properties and some functions in Multiwfn request atomic wavefunction files, such as calculating Hirshfeld, VDD and ADCH charges, fuzzy atomic space analysis and orbital composition analysis based on Hirshfeld partition, etc. The process of generating atomic .wfn files are exactly the same.

After you select subfunctions -1 or -2 to study promolecular and deformation properties, Multiwfn checks whether .wfn files of all elements involved in present system have been presented in “atomwfn” subdirectory of current directory, if not, Multiwfn automatically invokes Gaussian to generate the missing element .wfn files and sphericalizes their densities. If the path of Gaussian executable file (“gaupath” parameter in settings.ini) is incorrect or has not been defined, Multiwfn will ask you to input the path of Gaussian executable file. The basis-set for generating the element wavefunctions can be arbitrarily set by user, however it is suggested to use the same basis-set as the molecular wavefunction.

The newly generated element wavefunction files or those taken from “atomwfn” directory are stored in “wfntmp” subdirectory in current directory. They will be translated to actual position of the atoms in present system, meanwhile atomic indices will be added to the .wfn filename (e.g. "Cr 30.wfn"). These are the files will directly be used to calculate promolecular and deformation properties.

#### Details and skills

If you want to avoid the step of generating element wavefunctions every time, you can move the.wfn files that without number suffix (such as “C .wfn”) from “wfntmp” directory to “atomwfn” directory (if “atomwfn” directory is non-existing, build it by yourself), next time if Multiwfn detected that all needed element .wfn files have already been presented in“atomwfn” folder, then Multiwfn will directly use them. Multiwfn only invokes Gaussian to calculate the missing element .wfn files.

“atomwfn” subdirectory in “examples” directory contains element wavefunction files of all first four rows, they were generated under 6-31G\*, and they have been sphericalized. If you want to use them, simply copy the "atomwfn" directory to current folder.

There is a quick way to generate all first four-rows element wavefunction files: the file “examples\genatmwfnpdb” contains all first four-rows atoms, load it into Multiwfn and generate promolecular property, after the calculation of element wavefunctions is finished, copy the .wfn files that without suffix in “wfntmp” directory to “atomwfn” directory.

If your system involves elements heavier than Kr, Multiwfn is unable to generate atom wavefunction files by invoking Gaussian and sphericalize their density automatically; in that cases you have to calculate and sphericalize atom wavefunctions manually, and then put them into “atomwfn” directory, Multiwfn will directly use them.

The default theoretical method for generating wavefunction for main group elements in first four-rows (index from 1 to 20 and 31 to 36) is ROHF, for the transition metals in the fourth row, UB3LYP is used. In general, the promolecular and deformation properties are insensitive to theoretical method. If you want to specify theoretical method by yourself, you can input theoretical method and basis-set at the same time with slash as separator, for example *BLYP/6-311G\**. Do not add “RO” or “U” prefix since they will be added automatically. If error occurs during generation of atom wavefunctions, please check Gaussian input and output files in “wfntmp” directory carefully.

Notice that the maximum character length of the path of .wfn file permitted by Gaussian is only 60! The path will be truncated and cause error if the length exceeded this threshold. So do not put Multiwfn in the directory with too long path!

### 3.7.4 Sphericalization of atom wavefunction

The main purpose of Multiwfn supporting promolecular and deformation property is for generating promolecular and deformation density, however, electron density of most elements in free and ground state is not in spherical symmetry, hence will lead to orientation dependence problem. To tackle it, atomic electron density must be sphericalized. However, there is no unique way to do this. In Multiwfn, atom electron density is sphericalized by modifying atom wavefunction artificially, here I describe the detail. If you want to skip the sphericalization step, simply set the “ispheratm” in settings.ini to 0.

For elements in IV A group, Multiwfn uses  $sp^3$  configuration to replace  $s^2p^2$  ground state by default. This treatment is reasonable, since in most molecules these atoms are in  $sp^3$  hybridization. For VI A, VII A and Fe, Co, Ni, Multiwfn equalizes the occupation number of orbitals within the same shell; for example, oxygen has two singly occupied 2p orbitals and one doubly occupied 2p orbitals in ground state, the number of electrons in this shell is 4, so Multiwfn sets the occupation number of all the three orbitals to 4/3. This method works because the shape of occupied orbitals are always nearly identical, regardless of the original occupation number is one or two. However, the difference between virtual orbital and occupied orbital is remarkable, thus Multiwfn uses another method to sphericalize electron density of elements in III A group, as well as Sc, Ti and V. In this method, the singly occupied orbitals are duplicated and rotated. Taking boron as example, assume that the singly occupied 2p orbital is direct along Z-axis, Multiwfn replicates this orbital twice and turn them toward X-axis and Y-axis respectively, finally the occupation numbers of the three orbitals are set to 1/3. (Users needn’t to check the orientation of singly occupied orbital by themselves). If you hope that Multiwfn sphericalizes atoms in IV A group in such manner instead of using  $sp^3$  configuration, set “SpherIVgroup” in settings.ini to 1.

Notice that the sphericalization methods used in Multiwfn are closely related to wavefunction type, the methods fail if unrestricted wavefunction is used for main group elements or restricted open-shell wavefunction is used for transition metals. These methods also fail if Hartree-Fock method is used for transition metals, because orbital order produced by HF is different from most DFT cases (the HF’s order is wrong, 4s is higher than 3d).

## 3.8 Checking & Modifying wavefunction (6)

This function provides a lot of subfunctions for checking and modifying current loaded wavefunction, all subfunctions take effect immediately, so after modification you can print related information to check if your operations are correct. Once you finished all modifications of wavefunction, you can save current wavefunction to “new.wfn” file or return to main menu, all following tasks which make use of GTF information will be affected. The title in this interface shows the number of GTFs, orbitals, atoms and alpha/beta electrons of current wavefunction.

Actually, the function -1, -2, -3 and -4 in main menu (see introduction above) should be put into this category, the reason why I still deploy them in main menu is only because they are invoked more frequently.

Below is the explanation of each subfunction in this category.

**Subfunction -1:** Return to main menu.

**Subfunction 0:** Save current modified wavefunction to “new.wfn” file in current directory. Multiwfn can be used as an .fch/.molden/.gms→wfn format converter through this function. Notice that the orbitals with zero occupation number and the atoms do not have GTFs will be automatically discarded during saving.

**Subfunction 1:** Print information of all GTFs, including the centers they are belonging to, GTF types and exponents.

**Subfunction 2:** Print information of all basis functions, including the shells/centers they attributed to, types, and corresponding GTF index ranges.

**Subfunction 3:** Print basic information of all orbitals, including energies, occupation numbers, orbital types (Alpha, beta or alpha+beta).

**Subfunction 4:** Print detail information of an orbital, including the expansion coefficients with respect to GTFs (along with GTF information), note that the coefficients include GTF normalization constants.

**Subfunction 5:** Print coefficient matrix in basis function (not the coefficients with respect to GTFs), only available when the input file contains basis function information.

**Subfunction 6:** Print one-particle density matrix in basis functions, only available when the input file contains basis function information.

**Subfunction 7:** Print various kinds of integral matrix between basis functions, such as overlap integrals, electric/magnetic dipole moment integrals, kinetic energy integrals and velocity integrals. For overlap matrix, eigenvalues are printed together, which are useful for checking linear dependency. Only available when the input file contains basis function information.

**Subfunction 11:** Swap centers or types or exponents or orbital expansion coefficients of two GTFs, or swap all information of two GTFs at once (identical to swap record order of two GTFs, thus does not affect any analysis result)

**Subfunction 21 to 24:** Set the center, type, exponent and expansion coefficient of a specific GTF in an orbital respectively.

**Subfunction 25:** Set the expansion coefficients of some GTFs that satisfied certain conditions in some orbitals. The conditions you can set for GTFs include: Index range of GTFs, index range of atoms, GTF types (you can input such as YZ, XXZ). The selected GTFs are intersection of these conditions. When program is asking you for inputting range, you can input

such as 3,8 to select those from 3 to 8, input 6,6 to select only 6, especially, input 0,0 to select all.

If the input file also contains basis function information, by this option you can also set expansion coefficients of basis functions.

**Subfunction 26:** Set occupation number of some orbitals. **This function is very useful for shielding the contributions from certain orbitals to real space functions, namely setting their occupation numbers to zero before calculating real space functions.**

**Subfunction 27:** Set orbital type of some orbitals, then wavefunction type will be automatically updated, please check the prompts shown on the screen.

**Subfunction 31:** Translate the whole wavefunction and all atom coordinates of current system by inputting translation vectors and their units.

**Subfunction 32:** Translate and duplicate the whole wavefunction and all atom coordinates of current system, users need to input translation vectors, their units and how many times the system will be translated and duplicated according to the translation vectors. This function is useful for extending the primitive cell wavefunction outputted by Gaussian PBC function to supercell wavefunction, of course you can calculate supercell wavefunction directly by Gaussian, but much more computational time will be consumed. Notice that constructing wavefunction of supercell by this way is only an approximation, because the mix between orbitals of neighbouring primitive cell to new supercell orbitals is completely ignored.

**Subfunction 33 (Invisible but can be used):** Rotate wavefunction, namely X→Y, Y→Z, Z→X

**Subfunction 34:** Delete all inner orbitals of all atoms in present system, only valence orbitals will be reserved. Notice that for ECP wavefunction, this function does nothing.

**Subfunction 35:** This function is very useful if you want to discard contribution of orbitals with certain irreducible representation (IRREP) in all kinds of analyses. After you enter this subfunction, IRREP of all occupied orbitals will be shown, the "N\_orb" denotes the number of occupied orbitals belonging to the corresponding IRREP. If you want to discard contribution of some IRREPs in the succeeding analyses, you can select option 1 and input the index of the IRREPs, then the occupation number of corresponding orbitals will be set to zero and thus their contributions are eliminated, and you will also see their status are changed from "Normal" to "discarded". Then you can choose option 0 to save wavefunction and quit. You can also choose option 2 to recover the original occupation number of all orbitals, or choose 3 to reverse the status of every IRREP between "Normal" and "Discarded". Note that this subfunction only works for .molden and .gms files, because only these files record orbital IRREPs (beware that the IRREPs in the .molden file produced by many quantum chemistry programs are missing or incorrect). Besides, only restricted and unrestricted SCF wavefunctions are supported.

**Subfunction 36 (Invisible but can be used):** Invert phase of some orbitals.

**Information needed:** Basis function (only for subfunction 2, 5, 6, 7), GTFs, atom coordinates

## 3.9 Population analysis (7)

This module is used to calculate population number of basis functions, shells, atoms, fragments, or simply atomic charges.

### 3 Functions

Regardless of which function you choose, if you want to study fragment charge (the sum of charge of the atoms in a fragment), you should select option -1 first and input atom indices to define the fragment. Then once the calculation of atomic charges is finished, fragment charge will be printed together.

#### 3.9.1 Hirshfeld population (1)

Hirshfeld is a very popular population method based on deformation density partition, Hirshfeld charge is defined as (*Theor. Chim. Acta (Berl.)*, **44**, 129)

$$q_A = - \int w_A^{\text{Hirsh}}(\mathbf{r}) \rho_{\text{def}}(\mathbf{r}) d\mathbf{r}$$

where

$$\begin{aligned} \rho^{\text{def}}(\mathbf{r}) &= \rho(\mathbf{r}) - \rho^{\text{pro}}(\mathbf{r}) \\ \rho^{\text{pro}}(\mathbf{r}) &= \sum_A \rho_A^{\text{free}}(\mathbf{r} - \mathbf{R}_A) \\ w_A^{\text{Hirsh}}(\mathbf{r}) &= \frac{\rho_A^{\text{free}}(\mathbf{r} - \mathbf{R}_A)}{\rho^{\text{pro}}(\mathbf{r})} \end{aligned}$$

The advantages of Hirshfeld population are:

1. Result is qualitatively consistent with general chemical concepts such as electronegativity rule.
2. The weighting function  $w$  for space partition has clear physical meaning.
3. Unlike the methods based on integrating electron density such as AIM charge, what the Hirshfeld charge reflects is the amount of transferred electron density during molecule formation, the density not transferred is not involved.
4. Insensitive to the quality of wavefunction.
5. Although calculating Hirshfeld charge needs integration in real space, due to the smooth integrand, sophisticated density functional theory (DFT) grid-based integration schemes can be directly used, so Hirshfeld population is high-efficient.
6. The wide application field. Deformation density data can also be obtained by X-ray crystallography experiments. Moreover, the applicability of Hirshfeld population is not constrained by the type of wavefunction, the method can be directly applied to solid system, where the wavefunction generally be described by plane-wave functions.

The disadvantages of Hirshfeld population are the charge is always too small and the poor reproducibility of observable quantities, such as molecular dipole moment and ESP, the reason is Hirshfeld population completely ignores atomic dipole moments.

When calculation is finished, along with Hirshfeld charges following contents are printed

**1 Dipole of atom:** Atomic dipole moment, the simplest representation of density anisotropy around corresponding atom.

**2 Summing up all charges:** The value of summing up all Hirshfeld charges, if the value is very close to integer, means the quadrature is accurate; if not, means the outputted Hirshfeld charges are unreliable, you need to increase the density of integration points by setting “radpot” and “sphpot” to larger value and calculate again. For balancing computational time and accuracy,

### 3 Functions

the default value of “radpot” and “sphpot” is 75 and 434 respectively, you can set them to 100 and 590 respectively for more accurate results.

**3 Total dipole from atomic charges:** Molecular dipole moment evaluated from Hirshfeld charges, following the components in X, Y and Z directions.

**4 Total atomic dipole:** The sum of all atomic dipole moments, following the components in X, Y and Z directions.

**5 Total corrected dipole:** The sum of “Total dipole from atomic charges” and “Total atomic dipole” following the components in X, Y and Z directions. This value should be very close to the molecular dipole moment directly evaluated from molecular wavefunction.

Finally, you can choose to output Hirshfeld charges to [name of loaded file].chg file in current directory, see Section 2.5 for detail about chg format.

An example is given in Section 4.7.1.

#### 3.9.2 Voronoi deformation density (VDD) population (2)

The only difference between VDD and Hirshfeld population is the weighting function  $w$ . In VDD population, the Voronoi cell-like partition is used, see *J. Comput. Chem.*, **25**, 189.

The results of VDD population are similar to Hirshfeld population in common, because the magnitude of deformation density is always small, so there is no significant change in charges when different weighting functions are used. The outputted terms are identical to Hirshfeld population. Personally, I suggest you use Hirshfeld population instead of VDD.

Note that if the sum of VDD atomic charge deviates from molecular net charge evidently, that means the numerical integration accuracy is not satisfactory, and hence you should enlarge "sphpot" parameter in settings.ini to improve the result. "radpot" parameter also influences the result, but not so significantly as "sphpot".

#### 3.9.3 Mulliken atom & basis function population analysis (5)

Mulliken analysis is the oldest population method based on orbital wavefunction, supported by almost all quantum chemistry packages.

Orthonormality condition of spin orbital wavefunction entails  $1 = \int |\varphi(\mathbf{r})|^2 d\mathbf{r}$ , if we assume

that the orbital is real type and insert the linear combination equation  $\varphi_i(\mathbf{r}) = \sum_a C_{a,i} \chi_a(\mathbf{r})$  into

it, we get

$$1 = \int \left( \sum_a C_{a,i} \chi_a(\mathbf{r}) \right)^2 d\mathbf{r} = \sum_a C_{a,i}^2 + \sum_a \sum_{b \neq a} C_{a,i} C_{b,i} S_{a,b} = \sum_a C_{a,i}^2 + 2 \sum_a \sum_{b > a} C_{a,i} C_{b,i} S_{a,b}$$

where  $S_{a,b} = \int \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) d\mathbf{r}$ , the normality of basis functions are used in derivation. The first term is “local term”, denotes the net population of each basis function in orbital  $i$ , the second term is “cross term”, denotes the shared electrons between basis function pairs in orbital  $i$ . Certainly the local terms should be completely attributed to corresponding basis functions, however for cross

### 3 Functions

terms the partition method is not unique. Mulliken defined the population of basis function  $a$  in spin orbital  $i$  as

$$\Theta_{i,a} = C_{a,i}^2 + \sum_{b \neq a} C_{a,i} C_{b,i} S_{a,b}$$

That is each cross term  $2C_{a,i} C_{b,i} S_{a,b}$  is equally partitioned to corresponding two basis functions.

The population number of atom  $A$  is simply the sum of population numbers of all basis functions attributed to atom  $A$  in all orbitals. Mulliken atomic charge is defined as

$$q_A = Z_A - \sum_i n_{i,A} = Z_A - \sum_i \eta_i \sum_{a \in A} \Theta_{i,a}$$

where  $\eta$  is orbital occupation number,  $n_{i,A}$  is the contribution from orbital  $i$ .

In **subfunction 1** (“Output Mulliken charges and decompose them to MO's contribution”), not only atomic charges but also contributions of basis functions and shells are outputted, the latter are the sum of contributions from basis functions within corresponding shells. You can choose to decompose atom population number to orbitals' contributions.

In **subfunction 2** (“Output gross atomic population matrix and decompose it”), the gross atom population matrix is printed, from which you can get local terms of each atom (diagonal element) and cross terms between each atom pair (non-diagonal element multiplies 2). The matrix is defined as

$$\Omega_{A,B} = \sum_i \Omega_{A,B}^i = \sum_i \eta_i \sum_{a \in A} \sum_{b \in B} C_{a,i} C_{b,i} S_{a,b}$$

Notice that the last row of outputted matrix is the sum of corresponding column elements, that is the total population number of corresponding atom. You can also choose to decompose it to orbital's contribution ( $\Omega_{A,B}^i = \eta_i \sum_{a \in A} \sum_{b \in B} C_{a,i} C_{b,i} S_{a,b}$ ), owing to the very large amount of information, results will be outputted to “groatmdcp.txt” in current directory rather than printing on screen.

By the way, the quantity  $2 * \Omega_{A,B}^i$  is just the Mulliken bond order between atom  $A$  and  $B$  contributed from orbital  $i$ , as we will see in Section 3.11.4.

In **subfunction 3** (“Output gross basis function population matrix & decompose it”), the gross basis function population matrix can be outputted for analyzing detail information further, the matrix element is defined as

$$\Gamma_{a,b} = \sum_i \Gamma_{a,b}^i = \sum_i \eta_i C_{a,i} C_{b,i} S_{a,b}$$

Likewise in subfunction 2, the last row of outputted matrix is total population number of corresponding basis function. You can also select to output orbital's contribution ( $\Gamma_{a,b}^i = \eta_i C_{a,i} C_{b,i} S_{a,b}$ ) to “grobasdcp.txt” in current directory.

Mulliken analysis is deprecated for practical application due to the serious shortcomings: 1. Poor reproducibility of observable properties 2. The “equal partition” of cross term have no strict

### 3 Functions

physical meaning 3. Very high basis-set dependence 4. Occasionally meaningless result occurs (population number is negative).

#### 3.9.4 Löwdin population (6)

The only difference between Löwdin and Mulliken population analysis is whether Löwdin orthogonalization is performed first. In Löwdin orthogonalization, the linear transformation matrix is

$$\mathbf{X} = \mathbf{Us}^{0.5}\mathbf{U}^H$$

where  $U$  is eigenvector matrix of overlap matrix, matrix  $s$  is  $\text{diag}(\lambda_1, \lambda_2\dots)$ , here  $\{\lambda\}$  is eigenvalue set of overlap matrix. After Löwdin orthogonalization, the overlap matrix becomes identity matrix, and new coefficient matrix is  $\mathbf{X}^{-1}\mathbf{C}$ .

Ostensibly, Löwdin population avoids the partition for cross terms since they have become zero, actually, the partition step is no more than hidden in the orthogonalization. Since Löwdin orthogonalization still has no strong physical meaning, it cannot make conclusion that Löwdin population is better than Mulliken. In view of practical results, one also found Löwdin charges have no any evident advantages relative to Mulliken charges, though some people argued that Löwdin charges have better basis-set stability and reproducibility of molecular dipole moment. Besides, Mayer et. al. found Löwdin population has rotation dependence to some extent when cartesian type Gauss basis functions are used, however the dependency can be safely ignored in generally, for detail please see *Chem. Phys. Lett.*, 393, 209 and *Int. J. Quantum. Chem.*, 106, 2065.

#### 3.9.5 Modified Mulliken population defined by Ros & Schuit (SCPA) (7)

Some people had proposed several different partition methods of cross term to improve Mulliken analysis, they are generally called as modified Mulliken population analysis (MMPA). In the method proposed by Ros and Schuit (*Theo. Chim. Acta*, 4, 1), the composition of basis function  $a$  in orbital  $i$  is defined as

$$\Theta_{i,a} = \frac{C_{a,i}^2}{\sum_b C_{b,i}^2}$$

only the square of coefficients are presented in the formula, so this method is also called C-squared Population Analysis (SCPA). By inserting the identity

$$1 = \sum_a C_{a,i}^2 + \sum_a \sum_{b \neq a} C_{a,i} C_{b,i} S_{a,b}$$

into the right most of above formula,  $\Theta$  can be rewritten as

$$\Theta_{i,a} = C_{a,i}^2 + \frac{C_{a,i}^2}{\sum_b C_{b,i}^2} \sum_a \sum_{b \neq a} C_{a,i} C_{b,i} S_{a,b}$$

It is clear that when calculating composition of basis function  $a$  in orbital  $i$ , what is partitioned is not the cross terms between atom  $a$  and other atoms, but the *total* cross term of all atom pairs. The

SCPA atomic charges can be calculated in the same manner as Mulliken charges by using the newly defined  $\Theta$ . Relative to Mulliken population, the advantage of SCPA is that negative value of population number never occurs.

### 3.9.6 Modified Mulliken population defined by Stout & Politzer (8)

Stout and Politzer defined the  $\Theta$  as (*Theo. Chim. Acta*, 12, 379)

$$\Theta_{i,a} = C_{a,i}^2 + \sum_{b \neq a} \frac{C_{a,i}^2}{C_{a,i}^2 + C_{b,i}^2} 2C_{a,i}C_{b,i}S_{a,b}$$

That is cross terms are partitioned according to the ratio of the squares of corresponding coefficients. Ostensibly, this definition has more consideration on the unbalanced nature of cross term, however in practical applications the results are even worse than Mulliken, therefore this method is rarely used now. Besides, Grabenstetter and Whitehead had pointed out that this MMPA definition has unitary transformation dependence, so if the molecule is rotated the results changed (the dependence is remarkable and cannot be ignored).

### 3.9.7 Modified Mulliken population defined by Bickelhaupt (9)

The total population number of a basis function defined in *Organometallics*, 15, 2923 is

$$\Lambda_a = \sum_i \eta_i C_{a,i}^2 + \sum_{b \neq a} w_{a,b} \sum_i 2\eta_i C_{a,i}C_{b,i}S_{a,b}$$

where the weight of basis function  $a$  for partitioning the total cross term between  $a$  and  $b$  in all orbitals is

$$w_{a,b} = \frac{\sum_k \eta_k C_{a,k}^2}{\sum_i \eta_i C_{a,i}^2 + \sum_j \eta_j C_{b,j}^2}$$

Essentially, it is equivalent to define  $\Theta$  as

$$\Theta_{i,a} = C_{a,i}^2 + \sum_{b \neq a} w_{a,b} 2C_{a,i}C_{b,i}S_{a,b}$$

This method is similar to the MMPA defined by Stout and Politzer, the difference is in the latter the weight  $w_{a,b}$  is only related to local terms of basis functions  $a$  and  $b$  in *current* orbital, while in present method the weight is related to *total* local terms of basis functions  $a$  and  $b$ .

### 3.9.8 Becke atomic charge with atomic dipole moment correction (10)

In the paper *J. Chem. Phys.*, **88**, 2547, Becke proposed a weighting function for converting whole space integral to multiple single-center spherical integrals, although the weighting function is not intend for population analysis, Multiwfn still makes an attempt to use this weighting function as atomic space to obtain atomic charges. The Becke charge can be defined as

$$q_A = Z_A - \int w_A(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

The radii used for evaluating the Becke weighting function (or say Becke atomic space) can be controlled by uses, see corresponding options shown on screen. For details about Becke weighting function please see *J. Chem. Phys.*, **88**, 2547 or Section 3.18.0. According to my experiences, by

using the default "modified CSD" radii, Becke charge is reasonable for typical organic systems, but not very appropriate for ionic systems. For detail about "modified CSD" radii, see the end of Section 3.18.0.

After the Becke charges are calculated, atomic dipole moment correction will be performed automatically. The correction process is identical to the one used for correcting Hirshfeld charge (see next section). After the correction the charges will have better electrostatic potential reproducibility and can exactly reproduce molecular dipole moment.

### 3.9.9 Atomic dipole moment corrected Hirshfeld charges (ADCH, 11)

The main reason why Hirshfeld charges are too small and have poor reproducibility of observable quantity is that atomic dipole moments are completely neglected. In ADCH method (*J. Theor. Comput. Chem.*, **11**, 163), Hirshfeld charges are corrected by expanding atomic dipole moments to correction charges placed at neighbour atoms. ADCH atomic charges are very reasonable in chemical sense, molecular dipole moment is exactly reproduced, the reproducibility of ESP is close to the atomic charges from fitting ESP. Compared with another method that corrected Hirshfeld charges, namely Hirshfeld-I, the computational cost of ADCH correction is almost zero! Owing to its many advantages, **ADCH is a highly recommended atomic charge model**. For an extensive comparison of atomic charge models, see *Acta Phys. -Chim. Sin.*, **28**, 1 (in Chinese, <http://www.whxb.pku.edu.cn/EN/abstract/abstract27818.shtml>)

Before doing ADCH correction, Hirshfeld charge will be calculated first. In the summary field, “corrected” and “before” correspond to ADCH charge and Hirshfeld charge respectively. At final stage, the “Error” means the the difference between molecular dipole moment produced by ADCH charges and the one produced by *ab initio* density, “Error” is always equals to or very close to zero, because ADCH charge preservers molecular dipole moment.

If you would like to know the detail of charge transfer in the ADCH correction process, you can set “ADCHtransfer” in settings.ini to 1.

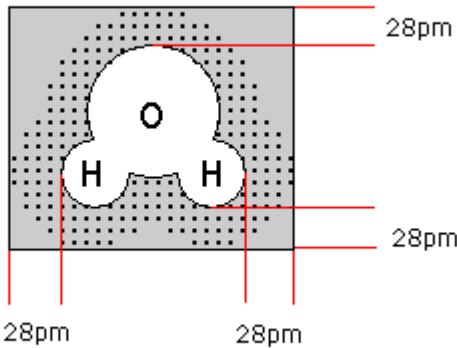
An example is given in Section 4.7.2.

### 3.9.10 CHELPG (Charges from electrostatic potentials using a grid based method, 12)

#### Theory

CHELPG (*J. Comput. Chem.*, **11**, 361) is one of the most widely used electrostatic potentials (ESP) fitting charge model. Compared to CHELP and Merz-Kollman methods, CHELPG charges have the best rotational invariance, mostly due to the fitting points are distributed in cubic grid manner.

In CHELPG model, a box is defined first to enclose the whole molecule, extension distance in each side is 28 pm, see the picture below



Fitting points are evenly scatter in the box, the default spacing is 0.3 angstrom. For any fitting point, if the distance between the point and any nucleus is smaller than vdW radius of corresponding atom, or the distances between the point and all nuclei are larger than 28pm, then the fitting point will be discarded. The black dots shown above are final fitting points.

Like other ESP fitting methods, in CHELPG, the deviation function shown below is minimized to make the ESP calculated by atomic charges ( $V_q$ ) close to the ESP calculated by quantum chemistry ( $V$ ) as well as possible.

$$F(q_1, q_2 \dots q_N) = \sum_i (V_q(\mathbf{r}_i) - V(\mathbf{r}_i))^2$$

where  $\mathbf{r}_i$  is the coordinates of fitting point  $i$ .  $q$  are fitted point charges, the position are called fitting center. Notice that  $q$  does not necessarily mean atomic charge, the fitting center can be defined beyond nucleus.

### Usage

In Multiwfn, you can find the options used to set grid spacing of fitting points and box extension. The coordinates of additional fitting centers, which are beyond atomic nuclei, can be read from external file by option 4, the format of the file is

```
numdata
X Y Z           ← For additional fitting center 1
X Y Z           ← For additional fitting center 2
...
```

*numdata* denotes how many entries are there in this file. X, Y and Z are coordinates (in Bohr).

For flexibility consideration, coordinates of fitting points are allowed to be read from external file to replace the CHELPG fitting points. The format of the file is

```
numdata
X Y Z [ESPval]   ← For fitting point 1
X Y Z [ESPval]   ← For fitting point 2
...
```

The *ESPval* is an optional term, which denotes precalculated ESP value at corresponding point. If *numdata* is a negative value, then the ESP values used in charge fitting will be read from the fourth column rather than calculated by Multiwfn internally.

When you choose selection 1, Multiwfn will start to calculate ESP value at each fitting point,

the process may take long time for big system, then fitted charges of all fitting centers will be outputted on screen. The coordinates and ESP value calculated by quantum chemistry of all fitting points can optionally be exported to ESPfitpt.txt in current folder.

RMSE and RRMSE are outputted automatically, they measure the quality of fitting, the smaller value suggests that the fitted charges have better ESP reproducibility. RMSE and RRMSE are defined as (where  $N$  is the number of fitting points)

$$\text{RMSE} = \sqrt{\frac{\sum_i [V_q(\mathbf{r}_i) - V(\mathbf{r}_i)]^2}{N}}$$

$$\text{RRMSE} = \sqrt{\frac{\sum_i [V_q(\mathbf{r}_i) - V(\mathbf{r}_i)]^2}{\sum_i V(\mathbf{r}_i)^2}}$$

Notice that only small part of vdW radii are predefined in original and related papers, if your system contains other elements, Multiwfn will ask you to input vdW radius. If you do not have proper data in hand, you can input a somewhat arbitrary value, 3.4 Bohr is recommended.

An example is given in Section 4.7.1.

### 3.9.11 Merz-Kollmann charge (13)

Merz-Kollmann (MK) charge is another well known charge model derived from ESP fitting, see *J. Comput. Chem.*, **11**, 431. The only difference between MK and CHELPG is grid setting. In MK, the fitting points are evenly distributed on the layers of 1.4, 1.6, 1.8 and 2.0 times the vdW radii of each atoms, all fitting points enclosed by vdW surface are discarded.

In Multiwfn, the number of layers, the ratio of vdW radii used to define the layers, and the density of points per square Ångstrom on the shells are controllable. For detail of selections and outputs, see last section.

### 3.9.12 AIM charge (14)

AIM (Atoms in molecules) population is the number of electrons in AIM basin, and accordingly, nuclear charge minusing AIM population yields AIM charge, which is also known as Bader charge. AIM charges can be calculated in basin analysis module, please check the example given in 4.17.1 on how to do this. Related theories and algorithms of basin analysis module are introduced in Section 3.20.

### 3.9.13 Hirshfeld-I population (15)

Hirshfeld-I (HI) method was proposed in *J. Chem. Phys.*, **126**, 144111 (2007), it is an important extension of Hirshfeld method. It is believed that the atomic space defined by Hirshfeld is not quite ideal, because it does not respond actural molecular environment. In HI, atomic spaces are gradually refined via an iterative scheme. After convergence, the final HI atomic spaces are evidently more physically meaningful than the Hirshfeld ones.

There are some variants of HI method, including the Hirshfeld-E proposed in *J. Chem. Theory Comput.*, **9**, 2221 (2013), the Hirshfeld- $\lambda$  proposed in *J. Comput. Chem.*, **32**, 1561 (2011)

and the fractional occupation Hirshfeld-I (FOHI) proposed in *J. Chem. Theory Comput.*, **7**, 1328 (2011). Also, there is an iterative atomic space method name iterated stockholder atoms (ISA), which is closely related to HI, see *Chem. Commun.*, **2008**, 5909. However, since in my personal viewpoint these variants and ISA are not quite important, I do not intend to implement them in Multiwfn.

### Basic theory of HI method

In HI method, the weighting function of atom A at iteration  $n$  is defined as

$$w_A^{(n)}(\mathbf{r} - \mathbf{R}_A) = \frac{\rho_A^{(n-1)}(\mathbf{r} - \mathbf{R}_A)}{\sum_B \rho_B^{(n-1)}(\mathbf{r} - \mathbf{R}_B)} \equiv \frac{\rho_A^{(n-1)}(\mathbf{r} - \mathbf{R}_A)}{\rho_{\text{pro}}^{(n-1)}(\mathbf{r})}$$

where  $\mathbf{r}$  and  $\mathbf{R}$  denote spatial coordinate and position of atomic nucleus, respectively. The atomic density involved in HI is obtained by linear interpolation between spherically averaged free-state atomic density of adjacent charge states:

$$\rho_A^{(n)}(r) = (q_{\text{high}} - q_A^{(n-1)})\rho_{A,\text{low}}^{\text{free}}(r) + (q_A^{(n-1)} - q_{\text{low}})\rho_{A,\text{high}}^{\text{free}}(r)$$

where  $q_{\text{high}}$  and  $q_{\text{low}}$  are floor and ceiling integer of atomic charge of atom A at  $n-1$  iteration, while  $\rho_{A,\text{low}}^{\text{free}}$  and  $\rho_{A,\text{high}}^{\text{free}}$  are spherically averaged atomic density of atom A at these two charge states, respectively. For example, if atom A carries 0.2 charge at  $n-1$  step, then its radial atomic density at step  $n$  will be computed as

$$\rho_A^{(n)}(r) = 0.8 \times \rho_{A,q=0}^{\text{free}}(r) + 0.2 \times \rho_{A,q=+1}^{\text{free}}(r)$$

Before the HI iteration, radial density of all atoms are initialized to their neutral state.

Based on HI atomic weighting functions, HI atomic charges can be straightforwardly obtained. The HI iteration continues until all atomic charges converged to a given criterion.

Note: It is clear that the HI atomic charges yielded at the first iteration are in principle identical to Hirshfeld charges. However, this is not exactly true in Multiwfn, because currently the rule of generating spherically averaged free-state atomic density involved in HI is not completely identical to that used in Hirshfeld, but the difference is very small and can be ignored. It is never incorrect to directly take the atomic charges printed at the first iteration of HI as Hirshfeld charges.

### Usage

After you entered the HI analysis module, you can adjust convergence criterion and the maximum number of cycles, also you can switch the algorithm for realizing HI iterations (see below), as well as choose if printing atomic charges every iteration. If you select option 0, Multiwfn will first try to yield atomic radial density file (.rad) for all elements in the systems by invoking Gaussian, and then start the HI iteration. After convergence, HI atomic charges and fragment charge (if you have defined fragment) are printed. Note that the printed HI atomic charges have been properly normalized (i.e. making sum of HI population of all atoms equal to total number of electrons) to eliminate noise of numerical integration. Finally, you can select if outputting resulting atomic charges as .chg file.

### Procedure of preparing atomic radial density files

Before igniting HI iteration, atomic radial density files (.rad files) must be first prepared. The steps are detailed below:

(1) **Generating atomic .wfn files in "atmrad" folder:** Multiwfn generate Gaussian input files (.gjf) in "atmrad" subdirectory of current folder and invokes Gaussian to run them to generate atomic .wfn files for all elements involved in present system. The charge states range from -2 to +2 are taken into account. Calculation of useless charge states are skipped. For example, it's meaningless to calculate -2 and +2 charge states for alkali elements, since in practical systems it is impossible that an alkali atom has charge between -1 to -2, or between +1 to +2. The multiplicity of each charge state of each element is set to ground state (this cannot be well guaranteed for all cases, for example, ground state at different calculation level is even different). However, this is never an important problem, so please do not concern it too much). The path of Gaussian executable file should be set by "gaupath" in settings.ini file, if it is not properly set, you will be prompted to input it in the Multiwfn interface. You also need to input the keywords of Gaussian used to calculate the atomic .wfn files. After Gaussian calculation finished, the atomic .wfn files are generated in "atmrad" folder, the file name directly corresponds to element name and charge state. For example, the file corresponding to -1, 0, +1 and +2 charge states of Be will be generated in "atmrad" folder as "Be-1.wfn", "Be\_0.wfn", "Be+1.wfn" and "Be+2.wfn", respectively. If corresponding file has already been found in "atmrad" folder, then the file will be retained and not be recalculated. If you find Gaussian calculation is failed (mostly due to SCF unconvvergence problem), you should carefully check Gaussian output file and properly adjust the keyword used.

(2) **Converting atomic .wfn files to .rad files:** As mentioned earlier, HI calculation requires spherically averaged atomic densities. However, the electron density corresponding to the atomic .wfn files generated at last step often does not meet this requirement. For example, carbon at its neutral ground state has  $s^2p^2$  configuration, and thus "C\_0.wfn" corresponds to elliptical density distribution. To get spherically averaged representation of atomic densities, Multiwfn automatically loads each atomic .wfn files in "atmrad" folder, calculates spherically averaged radial density, and write the data as .rad file, whose name is identical to its parental .wfn file. i.e. "C\_0.wfn" will be converted to "C\_0.rad". The .rad file is plain text file, the first line is the number of data points, the first and second columns respectively correspond to radial distance with respect to nucleus (in Bohr) and corresponding electron density. Note that if needed .rad file is already presented in "atmrad" folder, then the conversion of .wfn→.rad will be skipped.

It is suggested (but not compulsory) that the atomic .wfn files are generated at the same calculation level as the molecule under study, so that the result has good physical meaning. You should always make sure that the atomic .wfn and .rad files in "atmrad" folder were generated at expected level. For example, in the "atmrad" folder if some .wfn/.rad files were generated at B3LYP/cc-pVDZ level, and some were generated at M06-2X/def2-TZVP level, while the molecular wavefunction file was obtained at PBE/6-311G\*\* level, then the resulting HI charges must be problematic. If you want to let Multiwfn regenerate all needed atomic .wfn/.rad files at given level during HI analysis, simply cleaning up the "atmrad" folder before calculation.

Note: If you are using Windows version of Multiwfn, while Gaussian cannot be invoked properly, please read Appendix 1 to set environment variable for Gaussian.

### Two numerical algorithms of HI

Multiwfn provides below two algorithms to realize HI methods, the results are exactly the same, they only differ by efficiency and memory requirement.

(1) Fast & large memory requirement (default): This algorithm computes as much as possible data before starting iteration. Therefore, once initialization stage is done, the HI iteration can be

finished rapidly. The drawback of this algorithm is that large amount of memory is needed, the memory consumed is at least  $5 \times n_{\text{atm}} \times n_{\text{atm}} \times n_{\text{rad}} \times n_{\text{ang}}$ , where  $n_{\text{atm}}$  is the number of total atoms,  $n_{\text{rad}}$  and  $n_{\text{ang}}$  corresponds to the number of radial and angular integration grid per atom. Evidently, this algorithm is unable to be applied for very large systems unless you have huge physical memory.

(2) Slow & low memory requirement: This algorithm utilizes very low amount of memory, however, the data needed to be calculated in each iteration is much more than algorithm (1), thus the total computational cost is much higher.

For both the two algorithms, the higher number the integration grid, the more accurate the result. By default  $n_{\text{rad}}$  and  $n_{\text{ang}}$  are properly set by Multiwfn. If the system only consists of first two rows elements, then  $n_{\text{rad}} \times n_{\text{sph}}$  will be  $30 \times 170 = 5100$ . If you want to manually set  $n_{\text{rad}}$  and  $n_{\text{sph}}$ , you can set "iautointgrid" in settings.ini to 0 and change "radpot" and "sphpot" parameters.

An example of computing HI charges is given in Section 4.7.4.

**Information needed:** Basis functions (Mulliken, Löwdin, MMPA), GTFs (Hirshfeld, Hirshfeld-I, VDD, Becke, ADCH, CHELPG, MK, AIM), atom coordinates

## 3.10 Orbital composition analysis (8)

Notice that the word “orbital” here is not restricted to molecular orbital, for example, if the input file carries natural bond orbitals (NBO), then what will be analyzed is NBOs. There is an excellent paper compared various orbital composition analysis approaches, see *Acta Chim. Sinica*, **69**, 2393 (in Chinese, [http://sioc-journal.cn/Jwk\\_hxb/CN/abstract/abstract340458.shtml](http://sioc-journal.cn/Jwk_hxb/CN/abstract/abstract340458.shtml)).

### 3.10.1 Output basis function, shell and atom composition in a specific orbital by Mulliken, Stout-Politzer and SCPA approaches (1, 2, 3)

Mulliken, SCPA and Stout-Politzer methods support decomposing orbital to basis function, shell and atom compositions. Actually I have introduced the theories in Sections 3.9.5, 3.9.6 and 3.9.7,  $\Theta_{i,a} * 100\%$  is just the composition of basis function  $a$  in orbital  $i$ , if we sum up all the compositions of basis functions that within a shell we will get shell composition, and if we sum up all the compositions of shells that attributed to the same atom we will get atom composition.

These approaches rely on basis expansion, in current Multiwfn version you must use .fch, .molden and .gms as input file.

When you entered “Orbital composition analysis” submenu from main menu, select which method you want to use for decomposition, and then input the index of orbital, the result will be printed on screen immediately, you can also input -1 to print basic information of all orbitals to find which one you are interested in. By default, only those terms with composition larger than 0.5% will be printed, this threshold can be adjusted by “comptres” in settings.ini.

If the basis functions stored in .fch/.molden file are spherical harmonic type, then the label of basis functions printed will look like D+1, F-3 rather than XX, XYY. The labels of spherical harmonic basis functions used in Multiwfn are completely identical to Gaussian program, the conversion relationship is:

### 3 Functions

D 0=-0.5\*XX-0.5\*YY+ZZ

D+1=XZ

D-1=YZ

D+2= 3/2\*(XX-YY)

D-2=XY

F 0=-3/2/ 5\*(XXZ+YYZ)+ZZZ

F+1=- (3/8)\*XXX- (3/40)\*YYY+ (6/5)\*XZZ

F-1=- (3/40)\*XXY- (3/8)\*YYY+ (6/5)\*YZZ

F+2= 3/2\*(XXZ-YYZ)

F-2=XYZ

F+3= (5/8)\*XXX-3/ 8\*XYY

F-3=3/ 8\*XXY- (5/8)\*YYY

G 0=ZZZZ+3/8\*(XXXX+YYYY)-3\* (3/35)\* (XXZZ+YYZZ-1/4\*XXYY)

G+1=2\* (5/14)\*XZZZ-3/2\* (5/14)\*XXXZ-3/2/ 14\*XYYZ

G-1=2\* (5/14)\*YZZZ-3/2\* (5/14)\*YYYZ-3/2/ 14\*XXYZ

G+2=3\* (3/28)\*(XXZZ-YYZZ)- 5/4\*(XXXX-YYYY)

G-2=3/ 7\*XYZZ- (5/28)\*(XXXZ+XXXX)

G+3= (5/8)\*XXXZ-3/ 8\*XYYZ

G-3=- (5/8)\*YYYZ+3/ 8\*XXYZ

G+4= 35/8\*(XXXX+YYYY)-3/4\* 3\*XXYY

G-4= 5/2\*(XXXZ-XXXX)

H 0=ZZZZZ-5/ 21\*(XXZZZ+YYZZZ)+5/8\*(XXXXZ+YYYYZ)+ (15/7)/4\*XXYYZ

H+1= (5/3)\*XZZZZ-3\* (5/28)\*XXXZZ-3/ 28\*XYYZZ+ 15/8\*XXXXX+ (5/3)/8\*XYYYY+ (5/7)/4\*XXYY

H-1= (5/3)\*YZZZZ-3\* (5/28)\*YYYZZ-3/ 28\*XXYZZ+ 15/8\*YYYYY+ (5/3)/8\*XXXXY+ (5/7)/4\*XXYY

H+2= 5/2\*(XXZZZ-YYZZZ)- (35/3)/4\*(XXXXZ-YYYYZ)

H-2= (5/3)\*XYZZZ- (5/12)\*(XXXZ+XXXX)

H+3= (5/6)\*XXXZZ- (3/2)\*XYYZZ- (35/2)/8\*(XXXXX-YYYYY)+ (5/6)/4\*XXYY

H-3=- (5/6)\*YYYZ+ (3/2)\*XXYZZ- (35/2)/8\*(XXXXY-YYYYY)- (5/6)/4\*XXYY

H+4= 35/8\*(XXXZ+YYYYZ)-3/4\* 3\*XXYY

H-4= 5/2\*(XXXZ-XXXX)

H+5=3/8\* (7/2)\*XXXXX+5/8\* (7/2)\*XYYYY-5/4\* (3/2)\*XXYY

H-5=3/8\* (7/2)\*YYYYY+5/8\* (7/2)\*XXXXY-5/4\* (3/2)\*XXYY

An example is given in Section 4.8.1.

**Information needed:** Basis functions

#### 3.10.2 Define fragment 1 and 2 (-1, -2)

Before doing composition analysis for fragments by Mulliken, Stout-Politzer and SCPA approaches, you have to define fragment in advance. If what you are interested in is only

composition of one fragment rather than the composition between two fragments (cross term composition), you only need to define fragment 1. The content of fragment can be chosen to basis functions, shells, atoms or mixture of them, whatever you choose, only the indices of corresponding basis functions are recorded eventually. Notice that the "fragment" I referred here has *no any relationship* with the "fragment" involved in Section 3.1, the fragment defined here does not disturb wavefunction at all.

All supported commands in the interface of defining fragment are self-explained, so I will not reiterate them but only give an examples, that is define fragment as all P-shells of atom 3: First, type command *all*, information of all basis functions are listed, find out the shells that attributed to center 3 and contain X, Y and Z type of basis functions (viz. PX, PY and PZ). Assume that the indices of such shells are 3, 6 and 7, then input *s 3,6,7* to add them into fragment. If you want to verify your operation, input *all* again and check if asterisks have appeared in the leftmost of corresponding rows, the marked basis functions are those that have been included in the fragment. Finally, input the letter *q* to save current fragment and return to last menu, the indices of basis functions in the fragment will be printed at the same time.

By default, fragments do not have any content. Each time you enter the fragment definition interface, the status of fragment is identical to that when you leave the interface last time. So, if you have defined the fragment earlier and you want to completely redefine it, do not forget to use "clean" command to empty the fragment first.

### 3.10.3 Output composition of fragment 1 and inter-fragment composition by Mulliken, Stout-Politzer and SCPA approaches (4, 5, 6)

After you defined fragment 1, the fragment composition analysis based on Mulliken, Stout-Politzer and SCPA approaches is available. The fragment composition is the sum of all basis function compositions within the fragment, in this function the fragment compositions of all orbitals are printed on screen at the same time. If the analysis method you chose is Mulliken (subfunction 4) or Stout-Politzer (subfunction 5), below component terms are outputted together with total composition:

**c^2 term:** The sum of square of coefficients of basis functions within fragment 1, namely  

$$\sum_{a \in frag1} C_{a,i}^2 * 100\% .$$

**Int.cross:** The sum of internal cross terms in fragment 1, namely  

$$\sum_{a \in frag1} \sum_{b \in frag1} C_{a,i} C_{b,i} S_{a,b} * 100\% .$$

**Ext.cross:** Fragment 1 part of the total cross term between fragment 1 and all other atoms, namely  

$$\sum_{a \in frag1} \sum_{b \notin frag1} w_{a,b} 2C_{a,i} C_{b,i} S_{a,b} * 100\% .$$

It is clear that total composition of fragment 1 equals to c^2 term + Int.cross + Ext.cross.

If the fragment 2 is also defined (you *must* have already defined fragment 1), in subfunction 5 (Mulliken) or subfunction 5 (Stout-Politzer) the cross term between fragment 1 and fragment 2 in

each orbital, namely  $\sum_{a \in frag1} \sum_{b \in frag2} 2C_{a,i}C_{b,i}S_{a,b} * 100\%$  will be outputted too. “Frag1 part” and

“Frag2 part” correspond to the components of cross term attributed to fragment 1 and fragment 2 respectively, for Mulliken analysis the two terms are of course exactly equal due to the “equal partition”.

### 3.10.4 Orbital composition analysis by natural atomic orbital approach (7)

#### Theory

The first step of the famous natural bond orbital (NBO) analysis is converting original basis functions to natural atomic orbitals (NAOs) by use of density matrix. Resulting NAOs can be classified into three categories: (1) Core-type NAOs, describing inner core densities, their occupation numbers are almost equal to integer (2) Valence-type NAOs, describing valence densities, generally they have high occupation numbers (3) Rydberg-type NAOs, mainly displaying characteristics of polarization and delocalization of electrons, the occupation numbers of them are very low. Core and valence NAOs are collectively named as minimal-set, they have strong physical meaning and have one-to-one relationship with "actual" atomic orbitals, so they are what we should be most concerned. Occupied MOs are almost exclusively contributed by minimal-set NAOs. Rydberg NAOs do not have clear physical interpretations, their contribution can be ignored in occupied MOs, however they often have great contribution to virtual orbitals.

Since NAOs is an orthonormal set, if we have MO coefficient matrix in NAO basis, we can get contribution from a NAO to specific MO by simply squaring corresponding expansion coefficient and then multiply it by 100%. Composition of an atom can be calculated by summing up composition of minimal-set NAOs in this center.

This NAO approach has great basis-set stability as Hirshfeld approach, especially suitable for analyzing composition of occupied orbitals. However for virtual orbitals, contribution from Rydberg NAOs is often large, the NAO approach is no longer works well.

#### Input file

The MO coefficient matrix in NAO basis cannot be generated by Multiwfn itself, you need to provide a output file of NBO program containing this matrix as Multiwfn input file. By default NBO program does not output this matrix, you need to manually add *NAOMO* keyword between \$NBO ... \$END field in NBO input file. The NBO program we referred here may be stand-alone NBO program (also known as GENNBO), or NBO module embedded in quantum chemistry software such as L607 in Gaussian. The output from NBO3.1 and NBO5.0 are formally supported, I estimate that no problem for other NBO versions.

#### Options

You will find following options in the interface:

**-1 Define fragment:** This option is used to define fragment, which is needed by fragment contribution analysis (option 1). All commands are self-explained. You can also refer to Section 3.10.2, the difference is that shell information cannot be utilized here.

**0 Show composition of an orbital:** Print contribution from some or all NAOs to specific MO. Since the numerical precision of expansion coefficients recorded in NBO output is not high, if you choose to output all NAOs, the sum may be slightly deviate from 100%, it is unnecessary to take care of this problem. If you choose to output core and valence NAOs only, the larger deviation of the sum from 100% denotes the larger Rydberg composition is. The printed NAO contributions are also summed up according to the atom center they attributed to, and then be outputted as "Condensed above result to atoms".

**1 Show fragment contribution in a range of orbitals:** Contribution from the fragment you defined to specified range of orbitals will be printed. The total contribution consists of contribution from core, valence, Rydberg NAOs in the fragment.

**2 Select output mode:** This option controls which set of NAOs will be outputted by option 0, there are three modes:

- (1) Show all NAOs
- (2) Only show core and valence NAOs: This is default mode, Rydberg NAOs will be ignored.
- (3) Show NAOs whose contribution is larger than specified criteria: Only the NAO (any type) whose contribution to specific MO is larger than you specified criteria will be outputted.

**3 Switch spin type:** One can find this option only if the NBO output file is for open-shell system. One can select which spin type of MOs to be analyzed.

An example is given in Section 4.8.2.

**Information needed:** MO coefficients in NAO basis

### 3.10.5 Calculate atom and fragment contributions by Hirshfeld or Hirshfeld-I method (8,10)

Hirshfeld and Hirshfeld-I weighting function (see Sections 3.9.1 and 3.9.13, respectively) can also be used for decomposing orbital to atom and fragment compositions, the composition of atom  $A$  in orbital  $i$  is  $\int \varphi_i^2(\mathbf{r}) w_A(\mathbf{r}) d\mathbf{r} \times 100\%$ . The composition of a fragment is simply the sum of the compositions of the atoms that belongs to the fragment. These methods have great basis-set stability and are always more reliable and reasonable than Mulliken and MMPA. In fact the Hirshfeld partition is already good enough, the more sophisticated and computationally demanding Hirshfeld-I partition is not necessary.

If you choose to use Hirshfeld partition, you will be prompted to select the way to generate atomic densities for constructing Hirshfeld weighting function, I strongly suggest using the built-in atomic densities rather than using atomic .wfn files, since the former is much more convenient. If you choose to use Hirshfeld-I partition, regular HI iterations will be performed first to yield converged atomic weighting functions (if you are confused by the operations, please consult the example of computing HI charges in Section 4.7.4 and the implementation details of Hirshfeld-I introduced in Section 3.9.13).

Before calculating orbital composition, data initialization is automatically carried out. Once it

is finished, you can input the orbital index that you are interested in. Because numerical quadrature always introduces some errors, so the sum of all atom compositions is not exactly equals to 100%, the deviation might be relatively significant in rare cases, so Multiwfn normalizes results automatically and prints them under the title “After normalization”.

If you want to view composition of an atom in specific range of orbitals at the same time, choose option -2, then input the atom index and the index range of orbitals.

If you wish to study contribution of a fragment to orbitals, use -9 to define a fragment first, then when you input an orbital index, the contribution of the fragment will be outputted along with the contributions of all atoms. Also, you can choose -3 to calculate the contribution from the fragment you defined to a range of orbitals.

An example is given in Section 4.8.3.

**Information needed:** Atom coordinates and GTFs

### 3.10.6 Calculate atom and fragment contributions by Becke method (9)

This function is very similar to the function introduced in Section 3.10.5, the only difference is that Becke partition is used instead of Hirshfeld partition. For most cases, their results are in qualitative agreement with each other. Using Becke partition instead of Hirshfeld partition has a prominent advantage, namely the atomic wavefunction files are not needed, since the Becke atomic space can be simply constructed based on atomic radius. For more detail about Becke partition, see Section 3.18.0. An example is given in Section 4.8.3.

**Information needed:** Atom coordinates and GTFs

### 3.10.7 Evaluate oxidation state by LOBA method

This function is an implementation the LOBA method proposed in *Phys. Chem. Chem. Phys.*, **11**, 11297-11304 (2009). LOBA (localized orbital bonding analysis) is a method used to evaluate atomic oxidation state based on orbital composition of localized MOs (LMOs). The idea is very simple: if an atom has  $N$  nuclear charges, and its composition in  $M$  occupied LMOs are larger than a threshold (e.g. 50%. In this case the electrons in these LMOs can be approximately viewed as completely attributed to the atom. If a LMO is doubly occupied, it should be counted twice), then the oxidation state of the atom is  $N-M$ .

In my opinion, this idea can also be extended to define fragmental oxidation state, namely if the sum of nuclear charge in a fragment is  $N$ , and the fragment contribution to  $M$  LMOs are larger than a certain threshold, then the fragment oxidation state will be  $N-M$ .

To use this function, you should provide .fch or .molden file containing LMOs (or NBOs). For example, if you are a Gaussian user, you can use the .fch file resulting from pop=saveNBO or pop=saveNLMO task as input. Alternatively, you can directly use Multiwfn to carry out orbital localization to generate .fch containing localized orbitals. An example is given in Section 4.8.4.

The result of LOBA method somewhat depends on the choice of orbital composition analysis method. For simplicity in Multiwfn the SCPA method is used for LOBA analysis, therefore diffuse

function should not be used!

**Information needed:** Basis functions

## 3.11 Bond order analysis (9)

In bond order analysis module, you can directly select corresponding option to calculate bond order by corresponding method. If you want to obtain total bond order between atoms in two molecular fragments, you can manually sum up corresponding terms, however this work is tedious, the better way is using option -1 to define fragment 1 and 2 first before bond order analysis, after that the inter-fragment bond order will be outputted alongside two-center bond orders. This feature is not available for multi-center bond order analysis and orbital occupancy-perturbed Mayer bond order.

### 3.11.1 Mayer bond order analysis (1)

The Mayer bond order between atom  $A$  and  $B$  is defined as (*Chem. Phys. Lett.*, **97**, 270)

$$I_{AB} = I_{AB}^\alpha + I_{AB}^\beta = 2 \sum_{a \in A} \sum_{b \in B} [(P^\alpha S)_{ba} (P^\alpha S)_{ab} + (P^\beta S)_{ba} (P^\beta S)_{ab}]$$

where  $P^\alpha$  and  $P^\beta$  are alpha and beta density matrix respectively,  $S$  is overlap matrix. Above formula can be equivalently rewritten using total density matrix  $P = P^\alpha + P^\beta$  and spin density matrix  $P^S = P^\alpha - P^\beta$

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} [(PS)_{ba} (PS)_{ab} + (P^S S)_{ba} (P^S S)_{ab}]$$

For restricted close-shell circumstance, since spin density matrix is zero, the formula can be simplified to

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} (PS)_{ab} (PS)_{ba}$$

Generally, the value of Mayer bond order is in agreement with empirical bond order, for single, double and triple bond the value is close to 1.0, 2.0 and 3.0 respectively. For unrestricted or restricted open-shell wavefunction, alpha, beta and total Mayer bond orders will be outputted separately. By default, only the bonds whose bond order exceed 0.05 will be printed on screen, the threshold can be adjusted by “bndordthres” parameter in settings.ini, you can also select to export full bond order matrix.

Moreover, Multiwfn outputs total and free valences, the former is defined as

$$V_A = 2 \sum_{a \in A} (PS)_{aa} - \sum_{a \in A} \sum_{b \in A} (PS)_{ab} (PS)_{ba}$$

The latter is defined as

$$F_A = V_A - \sum_{B \neq A} I_{AB} = \sum_{a \in A} \sum_{b \in A} (P^S S)_{ab} (P^S S)_{ba}$$

where  $P^S$  is spin density matrix, namely  $P^\alpha$  minus  $P^\beta$ .

For restricted close-shell wavefunctions free valences are zero since  $P^S=0$ , thus total valence of an atom is simply the sum of the related bond orders

### 3 Functions

$$V_A = \sum_{B \neq A} I_{AB}$$

Total valence (also known as atomic valence) measures atomic bonding capacity, while free valence characterizes the remaining ability of forming new bonds by sharing electron pairs.

For unrestricted or restricted open-shell system, there is another way to calculate total bond order rather than summing up alpha and beta bond orders, that is summing up alpha and beta density matrices to form total density matrix first and then calculate Mayer bond order by using restricted close-shell formula, this treatment is sometimes called “generalized Wiberg bond order”, these total bond orders are printed following the title “Mayer bond order from mixed alpha&beta density matrix”.

Similar to Mulliken population, Mayer bond order and the multi-center bond order described below are sensitive to basis-set, so do not use the basis-sets having diffuse functions, otherwise the bond order result will be unreliable.

Although Mayer bond order was originally defined for single-determinant wavefunctions, for post-HF wavefunctions, Multiwfn calculates Mayer bond orders via exactly the same formulae as shown above based on corresponding post-HF density matrix. The reasonableness of this treatment has been validated in *Chem. Phys. Lett.*, **544**, 83 (2012).

Some applications of Mayer bond order can be seen in *J. Chem. Soc., Dalton Trans.*, **2001**, 2095.

**Information needed:** Basis functions

#### 3.11.2 Multi-center bond order analysis (2, -2)

In main function 9 there are two options (2 and -2) used to calculate multi-center bond order, they are very similar. I first introduce option 2, then discuss the difference between option -2 and 2.

##### Option 2

The multi-center bond order, which is also known as multi-center index, was originally proposed in *Struct. Chem.*, **1**, 423 (1990), in some sense it may be viewed as an extension of Mayer bond order to multi-center cases. Multiwfn supports it up to 12 centers. Three/four/five/six-center bond orders are defined respectively as

$$I_{ABC} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} (PS)_{ab} (PS)_{bc} (PS)_{ca}$$

$$I_{ABCD} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \sum_{d \in D} (PS)_{ab} (PS)_{bc} (PS)_{cd} (PS)_{da}$$

$$I_{ABCDE} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \sum_{d \in D} \sum_{e \in E} (PS)_{ab} (PS)_{bc} (PS)_{cd} (PS)_{de} (PS)_{ea}$$

$$I_{ABCDEF} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \sum_{d \in D} \sum_{e \in E} \sum_{f \in F} (PS)_{ab} (PS)_{bc} (PS)_{cd} (PS)_{de} (PS)_{ef} (PS)_{fa}$$

Similarly, infinity-center bond orders can be written as

$$I_{ABCDEF\dots K} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \dots \sum_{k \in K} (PS)_{ab} (PS)_{bc} (PS)_{cd} \dots (PS)_{ka}$$

For open-shell cases, there are two definitions of the multi-center bond order, the first one is the sum of alpha part and beta parts:

### 3 Functions

$$\begin{aligned}
I_{ABCDEF...K} &= I_{ABCDEF...K}^\alpha + I_{ABCDEF...K}^\beta \\
&= 2^{n-1} \left[ \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \dots \sum_{k \in K} (P^\alpha S)_{ab} (P^\alpha S)_{bc} (P^\alpha S)_{cd} \dots (P^\alpha S)_{ka} \right] \\
&\quad + 2^{n-1} \left[ \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \dots \sum_{k \in K} (P^\beta S)_{ab} (P^\beta S)_{bc} (P^\beta S)_{cd} \dots (P^\beta S)_{ka} \right]
\end{aligned}$$

Another definition is using the mixed density matrix, this is not rigorous as above:

$$\begin{aligned}
I_{ABCDEF...K} &= \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \dots \sum_{k \in K} (P^{\text{mixed}} S)_{ab} (P^{\text{mixed}} S)_{bc} (P^{\text{mixed}} S)_{cd} \dots (P^{\text{mixed}} S)_{ka} \\
P^{\text{mixed}} &= P^\alpha + P^\beta
\end{aligned}$$

For unrestricted or restricted open-shell wavefunction, the output of multi-center bond order analysis consists of four terms, which have been explained above: (1) The result from alpha density matrix (2) The result from beta density matrix (3) The sum of the result of alpha and beta parts (4) The result from mixed alpha&beta density matrix.

Notice that the multi-center bond orders for different number of centers are not directly comparable, since the result is not in the same magnitude. However, in DOI: 10.1039/C6CP00636A, it was shown that the normalized multi-center bond order is comparable for different ring size and can be simply calculated as  $\text{MCI}^{1/n}$ , where  $n$  is the number of centers and MCI is the multi-center bond order defined above. For example, at B3LYP/6-31G\* level, the MCI for  $\text{H}_3^+$ , benzene (6 centers) and naphthalene (12 centers) are 0.2963, 0.0863 and 0.0080, respectively, while the normalized result are 0.667, 0.665 and 0.617, respectively. When MCI is negative, the normalized value should be calculated as  $-|\text{MCI}|^{1/n}$ .

Due to the ambiguity of definition and the use of non-orthogonal basis functions, the value of multi-center bond order may relies on input direction if the atoms lack of symmetry. For example, the result of ABCD can be different from DCBA (the opposite input direction of ABCD). The reason is clear: The term in the summation in the case of ABCD is  $(PS)_{ab}(PS)_{bc}(PS)_{cd}(PS)_{da}$ ,

while if we invert the input direction, the term will become  $(PS)_{dc}(PS)_{cb}(PS)_{ba}(PS)_{ad}$ .

Although both  $P$  and  $S$  are symmetry matrices, their product  $PS$  is not necessarily symmetry, so the two terms are not equivalent. In my own viewpoint, in order to obtain reasonable result, for example A-B-C-D-E-F, one should calculate ABCDEF and FEDCBA respectively and take their average. While some people advocated that it is needed to take all possible permutations into account to get a definitive result, see *J. Phys. Org. Chem.*, **18**, 706, that means the bond order of BCADEF, CABDEF, DBCAFE and so on ( $6!=720$  in total) are all required to be calculated and then summed up. This treatment does not have clear physical meaning and is absolutely unnecessary, it also elevates the computational cost significantly.

The computational cost for multi-center bond order increases exponentially with the number of centers; for ring size larger than 12 centers the cost will be prohibitively high, so Multiwfn doesn't support higher number of centers.

**Automatical search of multi-center bonds:** If you input -3 when Multiwfn asks you to input atom combination, all three-center bond order will be calculated, only those larger than the threshold you inputted will be printed. Similarly, four-, five- and six-center bonds can be searched by inputting -4, -5 and -6 respectively. Due to efficiency consideration, the search may be not

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exhaustive. Also note that the search is based on mixed alpha&beta density matrix for open-shell cases.

#### Option -2

The most severe drawback of multi-center bond order is its high basis-set dependency. In particular, if diffuse functions are involved, then multi-center bond order may be completely wrong. In order to tackle this problem, I proposed an alternative way (to be published) to calculate the multi-center bond order, and the idea is implemented as option -2.

Option -2 is very similar to option 2 (as introduced above), the only difference is that the multi-center bond order is calculated based on natural atomic orbital (NAO) basis rather than based on the basis functions originally defined by the basis-set. Since NAO is an orthonormal set and thus overlap matrix  $S$  is an identity matrix, the formula can be simplified as

$$I_{ABCDEF\dots K} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \dots \sum_{k \in K} P_{ab} P_{bc} P_{cd} \dots P_{ka}$$

The multi-center bond order calculated in this manner has very good stability with respect to change of basis-set. Even when diffuse functions are presented the result is still highly reliable. According to my experience, if no basis functions show diffuse character, the results given by option 2 and -2 will be very similar, though not exactly identical.

Another advantage of employing NAO basis is that the ambiguity of multi-center bond order due to the input direction of atom indices is completely eliminated, that means the result of ABCD must be identical to DCBA. This is because the matrix involved in the summation ( $P$ ) is symmetry.

In order to use option -2, the output file of NBO module embedded in Gaussian or standalone NBO program should be used as input file, and *DMNAO* keyword must be used to make NBO print density matrix in NAO basis. If you are a Gaussian user, for example, you can use the output file of below instance as input file of Multiwfn.

```
#p PBE1PBE/6-311G** pop=nboread
```

```
m062x/6-311+G(2d, p) opted

0 1
C          0. 00000000   1. 38886900   0. 00000000
... [ignored]
H          -2. 14060700   1. 23588000   0. 00000000

$NBO DMNAO $END
```

**Information needed:** Basis functions (option 2), NBO output file with DMNAO keyword (Option -2)

#### 3.11.3 Wiberg bond order analysis in Löwdin orthogonalized basis (3)

Wiberg bond order is defined as (footnote in *Tetrahedron*, **24**, 1083)

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} P_{ab}^2$$

The original definition of Wiberg bond order is only suitable for the wavefunction represented by orthogonal basis functions such as most of semiempirical wavefunctions, and only defined for restricted close-shell system. Actually, Mayer bond order can be seen as a generalization of Wiberg bond order, for restricted close-shell system and orthonormal basis functions (namely  $S$  matrix is identity matrix) cases their results are completely identical.

In this function, Multiwfn orthogonalizes basis functions by Löwdin method first and then performs usual Mayer bond order analysis. The threshold for printing is controlled by “bndordthres” in settings.ini too.

As shown in *J. Mol. Struct. (THEOCHEM)*, **870**, 1 (2008), the Wiberg bond order calculated in this manner, say  $W_L$ , has much less sensitivity to basis-set than Mayer bond order (whereas for small basis-sets, their results are closed to each other). One should be aware that  $W_L$  tends to overestimates bond order for polar bonds in comparison with Mayer bond order.

Notice that numerous literatures used NBO program to calculate Wiberg bond order, the result must be somewhat different to that produced by present function, because in NBO program the Wiberg bond orders are calculated in the basis of natural atomic orbitals (NAO), which are generated by OWSO orthogonalization method.

Personally, I do not suggest using Wiberg bond order, since it is no better than Mayer bond order.

**Information needed:** Basis functions

### 3.11.4 Mulliken bond order analysis (4) and decomposition (5)

Mulliken bond order is the oldest bond order definition, it is defined as

$$I_{AB} = \sum_i \eta_i \sum_{a \in A} \sum_{b \in B} 2C_{a,i} C_{b,i} S_{a,b} = 2 \sum_{a \in A} \sum_{b \in B} P_{a,b} S_{a,b}$$

Mulliken bond order has low agreement with empirical bond order, it is deprecated for quantifying bonding strength, for which Mayer bond order always performs better. However, Mulliken bond order is a good qualitative indicator for bonding (positive value) and antibonding (negative value). The threshold for printing results is controlled by “bndordthres” parameter in settings.ini.

Mulliken bond order is easy to be decomposed to orbital contributions, the contribution from orbital  $i$  to bond order  $AB$  is

$$I_{AB}^i = \eta_i \sum_{a \in A} \sum_{b \in B} 2C_{a,i} C_{b,i} S_{a,b}$$

From the decomposition, we can know which orbitals are favourite and unfavourite for specific bonding.

**Information needed:** Basis functions

### 3.11.5 Orbital occupancy-perturbed Mayer bond order (6)

Orbital occupancy-perturbed Mayer bond order was firstly proposed in *J. Chem. Theory*

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*Comput.*, 8, 908. Put simply, by using this method one can obtain how large is the contribution from specific orbital to Mayer bond order.

Orbital occupancy-perturbed Mayer bond order can be written as

$$I_{A,B}^* = I_{AB}^{*,\alpha} + I_{AB}^{*,\beta} = 2 \sum_{a \in A} \sum_{b \in B} [(P_X^\alpha S)_{ba} (P_X^\alpha S)_{ab} + (P_X^\beta S)_{ba} (P_X^\beta S)_{ab}]$$

The only difference between this definition and Mayer bond order shown in Section 3.11.1 is that  $P^\alpha$  and  $P^\beta$  have been replaced by  $P_X^\alpha$  and  $P_X^\beta$  respectively.  $P_X$  stands for the density matrix generated when occupation number of a specific orbital is set to zero. The difference between  $I_{A,B}^*$  and Mayer bond order can be regarded as a measure of contribution from the orbital to Mayer bond order. Bear in mind, because Mayer bond order is not a linear function of density matrix, the sum of  $I_{A,B}^*$  for all orbitals is not equal to Mayer bond order generally.

In Multiwfn, you only need to input indices of two atoms, then  $I_{A,B}^*$  for all occupied orbitals and the difference between  $I_{A,B}^*$  and Mayer bond order will be outputted. The more negative (positive) the difference, the more beneficial (harmful) to the bonding due to the existence of the orbital.

You can also use another way to calculate  $I_{A,B}^*$ , that is using wavefunction modification module (main function 6) to manually set occupation number of a specific orbital to zero, and then calculate Mayer bond order as usual, but this manner may be tedious if you want to calculate  $I_{A,B}^*$  for many orbitals.

**Information needed:** Basis functions

#### 3.11.6 Fuzzy bond order (7)

Fuzzy bond order (FBO) was first proposed by Mayer in *Chem. Phys. Lett.*, **383**, 368

$$B_{AB} = B_{AB}^\alpha + B_{AB}^\beta = 2 \sum_i \sum_j [(P^\alpha S^A)_{ij} (P^\alpha S^B)_{ji} + (P^\beta S^A)_{ij} (P^\beta S^B)_{ji}]$$

where  $S$  is overlap matrix of basis functions in fuzzy atomic spaces. In Multiwfn, Becke's fuzzy atomic space with sharpness parameter  $k=3$  in conjunction with modified CSD radii is used for calculating FBO. (See Section 3.18.0 for introduction of fuzzy atomic space)

$$S_{mn}^A = \int w_A(\mathbf{r}) \chi_m^*(\mathbf{r}) \chi_n(\mathbf{r}) d\mathbf{r}$$

Commonly the magnitude of FBO is close to Mayer bond order, especially for low-polar bonds, but much more stable with respect to the change in basis-set. According to the comparison between FBO and delocalization index (DI) given in *J. Phys. Chem. A*, **109**, 9904, FBO is essentially the DI calculated in fuzzy atomic space. See Section 3.18.5 for detail about DI.

Calculation of FBO requires performing Becke's DFT numerical integration, due to which the computational cost is larger than evaluation of Mayer bond order. By default, 40 radial points and 230 angular points are used for numerical integration. This setting is able to yield accurate enough results in general. If you want to further refine the result, you can set the number of radial and angular points by "radpot" and "sphpot" in settings.ini manually, and ensure that "iautointgrid" has been set to 0.

The threshold for printing results is controlled by "bndordthres" parameter in settings.ini.

**Information needed:** GTFs, atom coordinates

### 3.11.7 Laplacian bond order (8)

In *J. Phys. Chem. A*, **117**, 3100 (2013) (<http://pubs.acs.org/doi/abs/10.1021/jp4010345>), I proposed a novel definition of covalent bond order based on the Laplacian of electron density  $\nabla^2\rho$  in fuzzy overlap space, called Laplacian bond order (LBO). The LBO between atom A and B can be simply written as

$$L_{A,B} = -10 \times \int_{\nabla^2\rho < 0} w_A(\mathbf{r})w_B(\mathbf{r})\nabla^2\rho(\mathbf{r})d\mathbf{r}$$

where  $w$  is a smoothly varying weighting function proposed by Becke and represents fuzzy atomic space, hence  $w_Aw_B$  corresponds to fuzzy overlap space between A and B. Note that the integration is only restricted to negative part of  $\nabla^2\rho$ . The physical basis of LBO is that the larger magnitude the integral of negative  $\nabla^2\rho$  in the fuzzy overlap space, the more intensive the electron density is concentrated in the bonding region, and therefore, the stronger the covalent bonding.

The reasonableness and usefulness of LBO were demonstrated by applying it to a wide variety of molecules and by comparing it with many existing bond order definitions. It is shown that LBO has a direct correlation with the bond polarity, the bond dissociation energy and the bond vibrational frequency. The computational cost of LBO is low, also LBO is insensitive to the computational level used to generate electron density. In addition, since LBO is inherently independent of wavefunction, one can in principle obtain LBO by making use of accurate electron densities derived from X-ray diffraction data.

In Multiwfn, Becke's fuzzy atomic space with sharpness parameter  $k=3$  in conjunction with modified CSD radii is used for calculating LBO. (See Section 3.18.0 for detail about fuzzy atomic space). The threshold for printing results is controlled by "bndordthres" parameter in settings.ini.

Note that in current implementation, LBO is particularly suitable for organic system, but not for ionic bonds since in these cases a better definition of atomic space should be used to faithfully exhibit actual atomic space. LBO is also not very appropriate for studying the bond between two very heavy atoms (heavier than Ar), because these bonds are often accompanied by insignificant charge concentration in the fuzzy overlap space, even though the bonding is doubtless covalent.

**Information needed:** GTFs, atom coordinates

## 3.12 Plotting total, partial, and overlap population density-of-states (10)

### 3.12.1 Theory

Density-of-states (DOS) is an important concept of solid physics, which represents the number of states in unit energy interval, since energy levels are contiguous, so DOS can be plotted as curve map. In isolated system (such as molecule), the energy levels are discrete, the concept of DOS is questionable and some people argued that DOS is completely valueless in this situation. However, if the discrete energy levels are broadened to curve artificially, DOS graph can be used as a valuable tool for analyzing the nature of electron structure.

The original total DOS (TDOS) of isolated system can be written as

$$\text{TDOS}(E) = \sum_i \delta(E - \varepsilon_i)$$

where  $\{\varepsilon\}$  is eigenvalue set of single-particle Hamilton,  $\delta$  is Dirac delta function. If  $\delta$  is replaced by broadening function  $F(x)$ , such as Gaussian, Lorentzian and pseudo-Voigt function, we get broadened TDOS.

The normalized Gaussian function is defined as

$$G(x) = \frac{1}{c\sqrt{2\pi}} e^{-\frac{x^2}{2c^2}} \quad \text{where } c = \frac{\text{FWHM}}{2\sqrt{2\ln 2}}$$

FWHM is acronym of “full width at half maximum”, it is an adjustable parameter in Multiwfn, the larger FWHM the TDOS graph looks more smooth and analysis is easier to perform, but more fine-structure is masked.

The normalized Lorentzian function is defined as

$$L(x) = \frac{\text{FWHM}}{2\pi} \frac{1}{x^2 + 0.25 \times \text{FWHM}^2}$$

Pseudo-Voigt function is weighted linear combination of Gaussian function and Lorentzian function:

$$P(x) = w_{gauss} G(x) + (1 - w_{gauss}) L(x)$$

Obviously, if  $G(x)$  and  $L(x)$  are normalized, normalization condition for  $P(x)$  always holds regardless of the select of  $w_{gauss}$ .

The curve map of broadened partial DOS (PDOS) and overlap DOS (OPDOS) are valuable for visualizing orbital composition analysis, PDOS function of fragment  $A$  is defined as

$$\text{PDOS}_A(E) = \sum_i \Xi_{i,A} F(E - \varepsilon_i)$$

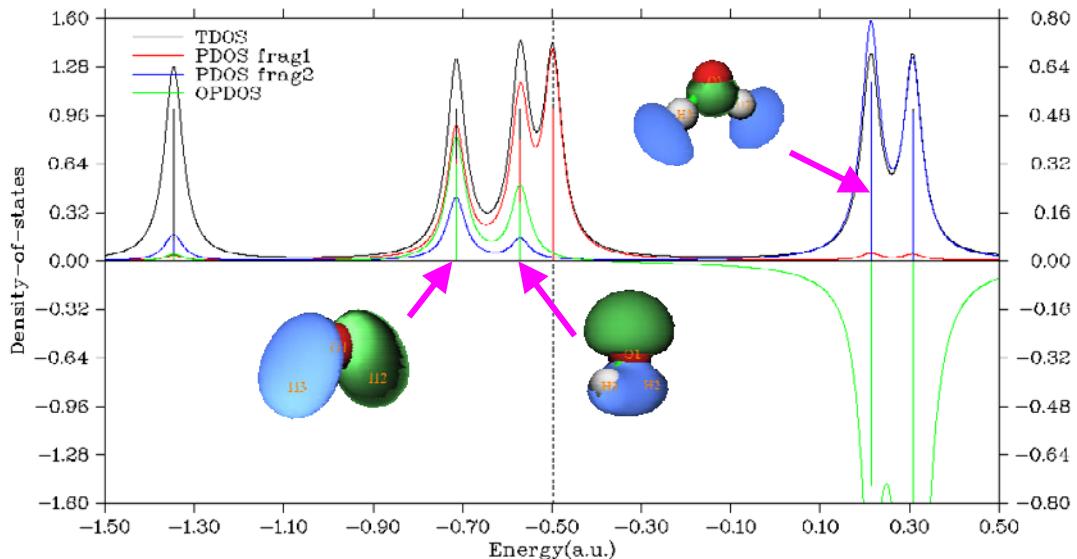
where  $\Xi_{i,A}$  is the composition of fragment  $A$  in orbital  $i$ . The OPDOS between fragment  $A$  and  $B$  is defined as

### 3 Functions

$$\text{OPDOS}_{A,B}(E) = \sum_i X_{A,B}^i F(E - \varepsilon_i)$$

where  $X_{A,B}^i$  is the composition of total cross term between fragment  $A$  and  $B$  in orbital  $i$ . I have discussed how to calculate  $\Xi$  and  $X$  in Section 3.10.3.

Let us see an example, from which we can know what new information can be revealed by DOS map. This is a water molecule under HF/6-31G\* wavefunction in ground state, the orbitals are canonical MOs; fragment 1 is defined as P-shells of oxygen (correspond to 2p atomic orbitals), fragment 2 is defined as two hydrogens, both original and broadened TDOS/PDOS/OPDOS are shown in the graph below. Notice that the height is only meaningful for lines (original data) but not for curves, left-axis and right-axis correspond to TDOS/PDOS and OPDOS respectively. The vertical dashed line indicates the position of HOMO level. The original DOS graph is discrete comb-like lines, from which we cannot obtain any additional information other than energy level distribution, it is impossible to distinguish different type of lines and degenerate energy levels owing to the overlapping. However if the discrete lines are broadened, from the height of black curve (TDOS) we can clearly know how dense the energy levels are distributed everywhere. Besides, the curves corresponding to TDOS, PDOS (red line for fragment 1, blue line for fragment 2) and OPDOS (green line) no longer overlap, we can clearly identify characters of each orbital by observing these curves. For example, the red curve is high and nearly approaches black line in the region of -0.9 a.u. to -0.3 a.u., so we can be concluded that 2p atomic orbitals of oxygen have significant contribution to corresponding MOs. Since the green curve is greater than or less than zero respectively denote corresponding MOs are favorable or unfavorable for forming chemical bond between oxygen 2p orbitals and hydrogens, it is shown that the orbital pointed by the leftmost arrow is very helpful for bonding, while the high-energy state orbitals ( $> 0.1$  a.u.) are not conducive for bonding (namely antibonding character), fortunately they haven't been occupied, otherwise the molecule must be broken. These conclusions can be confirmed further by observing isosurfaces of corresponding MOs.



### 3.12.2 Input file

.fch/.molden/.gms files can be used as input. You can also use output file of single point task of Gaussian program as input (“pop=full” keyword must be specified). For generality, Multiwfn supports plain text file as input too, the format is

```

nmo inp
energy occ [strength] [FWHM]           ← For orbital 1
energy occ [strength] [FWHM]           ← For orbital 2
energy occ [strength] [FWHM]           ← For orbital 3
...
energy occ [strength] [FWHM]           ← For orbital nmo

```

where *energy* and *occ* denote orbital energy and occupation number. *nmo* is the number of orbitals recorded in this file. *inp* is input type, if it is set to 1, only energies (in a.u.) and occupation numbers will be loaded, strengths and FWHMs of all orbitals will be set to 1.0 and 0.25 respectively and automatically; if it is set to 2, you have to specify strength and FWHM for each orbital. If the strength of an orbital is set to *k*, then the broadened curve from this orbital will be normalized to *k* rather than 1 (default value). The format of this file is free, there is no upper limit of the number of orbitals.

### 3.12.3 Options for plotting DOS

When you entered the interface of plotting DOS, you will see below options. The most important ones among them may be option 0 and option -1.

**-5 Customize energy levels, occupations, strengths and FWHMs for specific MOs:** By this option, you can manually set energies, occupations, strengths and FWHMs for specific orbitals. For example, if you would like only to plot DOS for a few MOs, you can set strengths of the other MOs to zero (by default, strengths for all MOs are 1.0).

**-4 Show all orbital information:** Print information of all orbitals on screen, also point out Fermi energy (when occupation number information is available).

**-3 Export energy levels, strengths, FWHMs to plain text file:** Export energy, strength and FWHM of each orbital to “orginfo.txt” in current directory, this file complies the format introduced in last section, so can be directly used as input file.

**-1 Define fragments:** You can define up to 10 fragments in this option. After you entered this option, the information of present fragments are shown on screen. You can input *x* to define fragment *x*, and input *-x* to unset fragment *x*, or input *i,j* to exchange the definition of fragment *i* and *j*. To leave this interface, input 0. The PDOS will be plotted for all of the fragments defined in this option. OPDOS will be drawn only when both fragments 1 and 2 have been defined.

DOS graph will contain the line and curve of “PDOS frag 1” only when fragment 1 is defined.

**0 Draw TDOS graph!:** Draw DOS graph right now! If any fragment has been defined, the texts in this option will become “TDOS+PDOS”; if both fragments 1 and 2 have been defined, the texts will become “TDOS+PDOS+OPDOS”.

**1 Select broadening function:** Select which broadening function will be used, you can select Lorentzian, Gaussian or Pseudo-Voigt function. Default is Gaussian.

**2 Set energy range:** This option is used to set the lower limit, upper limit and step between

labels of X-axis.

**3 Set full width at half maximum (FWHM):** As the title says.

**4 Set scale ratio for DOS curve:** If this option is set to  $k$ , then height of all curves will multiply  $k$  (in full energy range).

**5 Set Gaussian-weighting coefficient:** This option sets  $w_{gauss}$ , which is mentioned in last section. This option only appears when Pseudo-Voigt function is chosen.

**6 Switch spin:** Appears only when the loaded wavefunction is unrestricted .fch/.molden/.gms file. This option determines which set of energy levels (alpha or beta) will be used for analysis.

**7 Switch method for calculating PDOS:** Switch method of composition analysis between SCPA and Mulliken.

#### 8 Switch unit between a.u. and eV

Notice that option -1 and 7 only appear when the input file contains basis function information, that is if you want to draw PDOS and OPDOS graph, you have to use .fch/.molden/.gms file as input.

Once you choose option 0, Multiwfn starts to calculate data set and then DOS graph pops up, after clicking right mouse button on the graph to close it, post-process menu will appear on the screen, which has many options. They control the range and stepsize of Y-axis, if the lines or curves corresponding to TDOS, PDOS and OPDOS will be shown on DOS graph, if a vertical dashed line will be drawn to highlight HOMO level, the texts in the legends, etc. Worthnotingly, there is an option named “Set scale factor of Y-axis for OPDOS”, if the value is set to  $k$  and the range of left-axis (for TDOS/PDOS) is set to e.g. [-3.5, 2.0], then the range of right-axis (for OPDOS) will become [-3.5\*k, 2.0\*k]. The reason why Multiwfn uses double axis is because the magnitude of OPDOS is generally much smaller than TDOS and PDOS.

You can also choose to export the DOS map you have seen as graphical file in current folder, or export X-Y data set of DOS to plain text files for replotting the graph by external softwares, such as Origin. By choosing option 0 you can return to initial interface, the quality of DOS graph can be gradually improved by repeating the adjustments until you are satisfied.

### 3.12.4 Local DOS

There is a special kind of DOS named local DOS (LDOS). LDOS curve for a given point  $\mathbf{r}$  is evaluated as follows:

$$\text{LDOS}(\mathbf{r}, E) = \sum_i \varphi_i^2(\mathbf{r}) f(E - \varepsilon_i)$$

To plot such a map, choose "10 Draw local DOS for a point", you will be prompted to input the coordinate of the point  $\mathbf{r}$ .

One can also plot LDOS for a set of points placed evenly in a line as color-filled map, the X-axis correspond to energy, while the Y-axis corresponds to coordinate in the line relative to starting point. To plot this kind of LDOS map, choose "11 Draw local DOS along a line", you will be prompted to input the coordinate of starting point and end point defining the line, as well as the number of points consisting of the line.

In the DOS module, the options controlling FWHM, energy unit, energy range and scale ratio affect the resulting LDOS graphs.

An example relating to LDOS can be found in Section 4.10.2.

Note that fragment definition does not affect the result of LDOS, i.e. the LDOS always corresponds to total DOS. However, if you want to separate angular moment contribution to LDOS, you can use subfunction 25 of main function 6 to set coefficient of unwanted GTF in all MOs to zero, then they will not contribute to LDOS.

**Information needed:** Basis functions and atom coordinates (only for PDOS, OPDOS and local DOS), energy levels and occupation numbers (.fch/.molden/.gms file, Gaussian output file or the plain text file recording them)

## 3.13 Plotting IR/Raman/UV-Vis/ECD/VCD spectrum (11)

Although spectrum plotting is beyond the scope of wavefunction analysis, due to this function is very useful for theoretical spectrum research, the spectrum plotting function is also included in Multiwfn. Multiwfn is able to plot IR (Infrared), regular Raman / Pre-resonance Raman, UV-Vis (ultraviolet-visible), ECD (electronic circular dichroism) and VCD (vibrational circular dichroism) spectra.

### 3.13.1 Theory

For comparing theoretical results with experimental spectrum, the discrete lines corresponding to each transition mode have to be broadened to emulate the situation in real world, the commonly used broadening function for IR, Raman and VCD spectra is Lorentzian function, while for UV-Vis and ECD spectra Gaussian function is often used, see Section 3.12.1 for details. Unlike DOS graph, in which the strengths for each energy level are always simply set to 1.0 (namely broadened curves from each energy level are normalized to 1.0), the strengths of transitions are very important data for plotting spectrum.

The unit of transition energy of IR, Raman and VCD spectra is  $\text{cm}^{-1}$  in common, for UV-Vis and ECD spectra all of eV ( $1\text{eV}=8.0655*\text{1000cm}^{-1}$ ), nm and  $1000\text{cm}^{-1}$  are common units. IR intensity, Raman activity, oscillator strength and rotatory strength of each transition mode outputted by quantum chemistry programs are proportional to the area under the broadened curve. Below we discuss these five spectra respectively.

**IR:** The frequently used unit of molar absorptivity  $\epsilon$ , that is  $\text{L/mol/cm}$  can be rewritten as

$$\frac{\text{L}}{\text{mol} * \text{cm}} = \frac{1000\text{cm}^3}{\text{mol} * \text{cm}} = \frac{1000\text{cm}^2}{\text{mol}}$$

Since IR intensity  $\varsigma = \int \epsilon(\nu) d\nu$ , where  $\nu$  is transition frequency, the unit of  $\varsigma$  should be

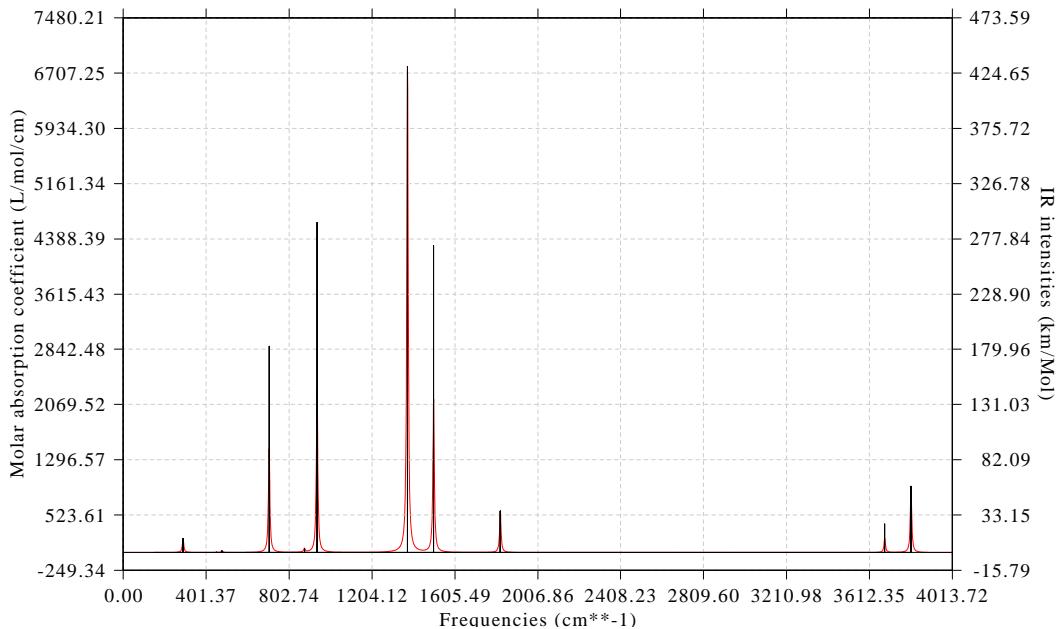
$$\frac{1000\text{cm}^2}{\text{mol}} * (\text{cm}^{-1}) = \frac{1000\text{cm}}{\text{mol}} = \frac{0.01\text{km}}{\text{mol}}$$

However km/mol is the more commonly used unit for IR intensity, therefore if IR intensity of a vibrational mode is  $p$  km/mol, then the broadened curve from which should be normalized to  $100*p$  (in the other words, the area under the curve is  $100*p$ ). Sometimes the unit  $\text{esu}^2*\text{cm}^2$  is

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used for IR intensity, the relationship with km/mol is  $1 \text{ esu}^2 \cdot \text{cm}^2 = 2.5066 \text{ km/mol}$ .

Below is an example of IR spectrum plotted by Multiwfn. Notice that the left axis corresponds to the curve (artificially broadened data), the right axis corresponds to the discrete lines (original transition data).



**Raman (regular or pre-resonance):** First beware that for a specific vibration mode  $i$ , its Raman activity  $S_i$  and Raman intensity  $I_i$  are two different quantities. Raman activity is a intrinsic property of each molecular vibrational mode, while Raman intensity is directly related to experimental Raman spectrum, and its value is dependent of the choice of wavenumber of incident light  $\nu_0$  as well as temperature. The conversion relationship can be found in some literatures, e.g. *J. Mol. Struct.*, **702**, 9-21 (2004):

$$I_i = \frac{C(\nu_0 - \nu_i)^4 S_i}{\nu_i B_i} \quad B_i = 1 - \exp\left(-\frac{hc\nu_i}{kT}\right)$$

where  $C$  is a suitably chosen common normalization factor for all peak intensities,  $\nu_i$  is vibrational frequency. Only the Raman spectrum broadened based on Raman intensities can be strictly comparable to the experimental one; however, as the peak position of Raman activity and intensity are identical, and for a specific vibrational mode its intensity is proportional to its activity, the Raman spectrum broadened from Raman activities is also useful enough.

Almost all quantum chemistry codes only output Raman activities, therefore by default, Multiwfn emulates the Raman spectrum in terms of broadening Raman activities. However you can also let Multiwfn to first convert the activities to intensities via option 19 ( $\nu_0$  and  $T$  are provided by users) based on above formula, then the Raman spectrum will be obtained by broadening Raman intensities. The normalization coefficient  $C$  is fixed to  $10^{-12}$  in Multiwfn (which is not important since what we are interested in is the shape rather than the absolute height of Raman spectrum). The integral of the peak broadened by one unit of Raman activity or intensity is equal to 1.

**UV-Vis:** In theoretical chemistry field, oscillator strength is always used for representing

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transition strength in UV-Vis spectrum, however this is a dimensionless quantity and the precise relationship with molar absorptivity haven't been built. However, there is a well-known relation between theoretical data and experimental spectra: If the unit  $1000\text{cm}^{-1}$  and  $\text{L/mol/cm}$  are used for X-axis and Y-axis respectively, then the area under the curve that broadened from per unit oscillator strength should be  $1/4.32 \times 10^6$ . Equivalently, if eV is used as X-axis unit, the value should be  $1/4.32/8.0655 \times 10^6 = 28700$ . By this relation, UV-Vis spectrum can be simulated by theoretical data.

Fluorescence (or phosphorescence, as long as you can obtain oscillator strength by means of spin-orbit coupling calculation) spectrum can also be plotted with exactly the same manner as UV-Vis, the only difference is that according to Kasha's rule you should only take the first excited state into account.

**ECD** : The significance of rotatory strengths in ECD spectrum is analogous to oscillator strengths in UV-Vis spectrum, each electron transition mode corresponds to a rotatory strength. If the rotatory strengths are broadened, after somewhat scaling and shifting, the resultant curve will be comparable to experimental ECD spectrum. The integral of the peak broadened by one unit of rotatory strength is equal to 1. In quantum chemistry programs, such as Gaussian, rotatory strengths can be calculated in length representation or in velocity representation, in the former case the strengths are origin-dependent, while in the latter case the strengths are origin-independent. For complete basis-set situation, the results in the two representations converge to the same values. Commonly velocity representation is recommended to be used.

**VCD**: VCD is akin to ECD, each vibrational mode has a rotatory strength. After broadening them, the curve will be comparable to experimental VCD spectrum.

#### 3.13.2 Input file

Currently below input files are supported:

##### 1 Gaussian output file:

For IR spectrum, use the output file of "freq" task as input. If you use Gaussian 09 D.01 or later revisions and meantime "freq=anharmonic" was specified, Multiwfn will prompt you to choose if load anharmonic frequencies and intensities instead of the harmonic ones.

For Raman spectrum, use the output file of "freq=raman" task as input. If you would like to plot pre-resonance Raman spectrum, you should at the same time use "CPHF=rdfreq" keyword and write the frequencies of the incident lights after a blank line under the geometry specification, e.g. 300nm 400nm 500nm.

For VCD spectrum, use the output file of "freq=VCD" task as input.

For UV-Vis and ECD spectra, use the output file of TDDFT, TDHF, CIS or ZINDO task as input, no any additional keywords are required. The rotatory strengths in both length and velocity representation (the data under "R(length)" and "R(velocity)", respectively) can be chosen to be loaded by Multiwfn.

##### 2 ORCA output file:

For IR spectrum, use *freq* keyword.

For Raman spectrum, use keywords like below

```
! b3lyp def2-SVP numfreq
```

```
%elprop Polar 1 end
```

### 3 Functions

For UV-Vis or ECD spectrum, use keywords like below (CIS and ZINDO calculations are also supported). Note that ORCA employs length representation for rotatory strengths in ECD.

```
! b3lyp def2-SVP  
%otddft nroots 20 end
```

VCD spectrum is currently not supported by ORCA.

#### 3 Grimme's sTDA output file

The sTDA proposed by Grimme in *J. Chem. Phys.*, **138**, 244104 (2013) is a method approximately solve the TDDFT equation and thus reduces the computational cost of the electronic excitation part of TDDFT calculation by about two or three orders of magnitude. The corresponding sTDA program can be freely downloaded at

<http://www.thch.uni-bonn.de/tc/index.php?section=downloads&subsection=sTDA&lang=english>

The *tda.dat* file outputted by the sTDA program can be directly used as input file of Multiwfn for plotting UV-Vis and ECD spectra purpose.

When ECD is to be plotted, you can choose which representation of rotatory strength will be used. The length and velocity representations have been mentioned above, while the mixed-form of representation, which is recommended in the sTDA original paper, is defined as  $R_M = R_V \times f_L / f_V$ , where  $f_L$  and  $f_V$  are length and velocity representations of oscillator, respectively, and  $R_V$  is the velocity representation of rotatory strength.

**4 Plain text file:** For generality, Multiwfn supports plain text file as input, you can extract transition data from output files of quantum chemistry packages other than Gaussian/ORCA/sTDA, and then fill them into a file according to the format shown below

```
numdata inptype  
energy strength [FWHM]           ← For transition 1  
energy strength [FWHM]           ← For transition 2  
energy strength [FWHM]           ← For transition 3  
...  
energy strength [FWHM]           ← For transition numdata
```

where *numdata* denotes how many entries in this file. If *inptype* is set to 1, then only *energy* and *strength* will be read, and FWHMs for all transitions will be automatically set. If *inptype* is set to 2, then FWHMs will be read too. The transitions should be sorted according to the energies from low to high. The unit of both *energy* and *FWHM* should be in  $\text{cm}^{-1}$  for IR, Raman and VCD spectra, in eV for UV-Vis and ECD spectra. The unit of strength should be in  $\text{km/mol}$ ,  $\text{\AA}^4/\text{amu}$ , cgs ( $10^{-40}$  erg-esu-cm/Gauss),  $10^{-44}$  esu $^2$  cm $^2$  for IR, Raman, ECD and VCD spectra, respectively (oscillator strength of UV-Vis is dimensionless).

An example of the plain text file is shown below (for IR)

```
6 2  
81. 32920    0. 72170    8. 0  
417. 97970   3. 58980    8. 0  
544. 67320   21. 06430   8. 0  
583. 12940   41. 33960   8. 0  
678. 66900   91. 47940   8. 0  
867. 37410   2. 94480   8. 0
```

### 3.13.3 Usage and options

After boot up Multiwfn, first input path of Gaussian/ORCA/sTDA output file or the plain text file containing transition data, then enter main function 11, and you will be prompted to select the type of spectrum (for pre-resonance Raman then you also need to choose the interested frequency), after that you will see below options. The meaning of some options may be different for various types of spectra.

**-2 Export transition data to plain text file:** Output energies, intensities and FWHMs of all transitions to “transinfo.txt” in current directory, this file fully complies with the format introduced in last section, so it can be directly used as input file.

**-1 Show transition data:** Print energy and intensity data of all transitions on screen.

**0 Plot spectrum:** Plot spectrum right now!

**1 Save graphical file of the spectrum in current folder:** As the title says.

**2 Export X-Y data set of lines and curves to plain text file:** Export X-Y data set of lines and broadened spectrum to "spectrum\_line.txt" and "spectrum\_curve.txt" in current directory, respectively, you can replot the curve and discrete line graph directly by the two files via external program, such as Origin.

**3 Set lower and upper limit of X-axis:** As the title says. The stepsize between ticks also needs to be inputted. By default the range of X-axis is adjusted automatically according to minimum and maximum transition energies.

**4 Set left Y-axis:** Set starting value, ending value and step size for left Y-axis. By default the range of Y-axis is adjusted automatically according to the maximum peak.

**5 Set right Y-axis:** Like option 4, but for right Y-axis.

In many cases, after you adjusting setting for Y-axis at one side, the position of zero point of this Y-axis deviates from that of Y-axis at another side, which makes the graph weird; To address this problem, options 4 and 5 enable you to choose if correspondingly adjusting range of Y-axis at another side. If you input y, then lower/upper limit and stepsize of Y-axis at another side will be proportionally scaled to make zero point of left and right Y-axes are in the same horizontal line.

**6 Select broadening function:** Gaussian, Lorentzian and Pseudo-Voigt function can be selected for broadening discrete lines as curves.

**7 Set scale ratio for curve:** If the value is set to  $k$ , then the height of curve will multiply  $k$  in full range. For Raman, ECD and VCD spectra the default value is 1.0, for IR the value is 100, for UV-Vis spectrum an empirical value 28700.0 is used when energy unit is eV or nm, when unit is  $1000\text{cm}^{-1}$  the value  $1/(4.32 \times 10^{-6})$  is used.

**8 Input full width at half maximum (FWHM):** As the title says.

**9 Toggle showing discrete lines:** Choose if show the discrete lines corresponding to transitions on the spectrum graph.

**10 Switch the unit of infrared intensity / Set the unit of excitation energy:** For IR spectrum, switch the unit of IR intensities between  $\text{km/mol}$  (default) and  $\text{esu}^2\text{*cm}^2$ . For UV-Vis and ECD spectra, choose the unit of energies between eV, nm and  $1000\text{cm}^{-1}$ .

**11 Set Gaussian-weighting coefficient:** Sets  $w_{gauss}$ , which is mentioned in Section 3.12.1, this option only appears when Pseudo-Voigt function is chosen.

**12 Set shift value in X:** If the value is set to  $k$ , then the final curve and discrete lines will be shifted by  $k$  in X direction.

**13 Set colors of curve and discrete lines:** As the title says.

**14 Multiply the transition energies (or vibrational frequencies) by a factor:** The selected transition energies (or vibrational frequencies) can be scaled by a given factor. This option is mainly used to apply frequency scaling factor onto the calculated harmonic frequencies.

**15 Output contribution of individual transition to the spectrum:** If select this option, user will be prompted to input a criterion (e.g.  $k$ ), then not only the total spectrum (as option 2), but also the contributions from the individual transitions whose oscillator strength larger than  $k$  will be outputted to spectrum\_curve.txt in current folder. This feature is particularly useful for identifying the nature of total spectrum.

**16 Find the positions of local minima and maxima:** After you select this option, the positions of the maxima and minima of the spectrum will be located.

**17 Toggle showing dashed grid lines:** Choose if plotting gray dashed grid lines on the spectrum.

**18 Toggle weighting spectrum of each system:** See explanation in next section.

**19 Convert Raman activities to intensities:** As mentioned earlier, this option is used to convert Raman activities to intensities. After that, the Raman spectrum plotted by option 0 will be the one broadened based on Raman intensities rather than Raman activities. The wavenumber of incident light and temperature are inputted by users.

**20 Modify oscillator strengths/Raman activities/rotatory strengths:** You can select some transitions and change their oscillator strengths/Raman activities/rotatory strengths (depending on spectrum type) to specific value. This option is very useful if you would like to plot fluorescence spectrum, in this case you need to set oscillator strength of all transitions except for the lowest excitation to zero (Kasha's rule).

### 3.13.4 Plotting multiple files and weighted spectrum

In Multiwfn, it is possible to simultaneously plot spectrum for multiple files, and meantime taking weights into account. This feature is quite useful for obtaining actual spectrum of flexible molecule with many thermally accessible conformations.

For example, there is a molecule containing four accessible conformations, their distribution ratio have been determined according to Boltzmann's method based on calculated free energies. If you want to plot its weighted spectrum and spectrum of each conformation, you should write a plain text file named "multiple.txt" (other file name cannot be recognized by Multiwfn), the content is:

```
bol tz\Excit\c.a.out 0.6046
bol tz\Excit\c.b.out 0.1950
bol tz\Excit\c.c.out 0.1686
bol tz\Excit\c.d.out 0.0317
```

where the first and second column correspond to path of input file and weight of each conformation. Different type of input file can be presented together in this file. If you use this file as input file, after you entered spectrum plotting module, Multiwfn will load data from these files in turn. When plotting spectrum, spectrum of all the four conformations will be separately

calculated and drawn with different colors. In addition, the weighted spectrum is plotted on the graph as thick red curve, it is simply evaluated as follows:

$$\text{weighted spectrum} = 0.6046*a + 0.1950*b + 0.1686*c + 0.0317*d$$

In the graph you can also observe many black discrete lines, these are collection of discrete lines corresponding to different conformations. Notice that their heights have already been multiplied by corresponding weights.

If before plotting spectrum you have chosen option 18 once, then the spectrum of various conformations shown on graph are the weighted ones; in other words, these curves represent contribution of each conformation to actual spectrum (thick red curve). In this case, the color of weighted discrete lines are no longer all black but in accordance with color of curves, so that user can easily recognize correspondence between curve and discrete among different systems.

Note that the actual number of points constituting the spectrum is controlled by "num1Dpoints" parameter in settings.ini. The default value is commonly large enough and thus need not to be adjusted.

Many examples of plotting various kinds of spectra are given in Section 4.11.

**Information needed:** Transition energies and strengths

## 3.14 Topology analysis (2)

### 3.14.1 Theory

Some real space functions in Multiwfn are available for topology analysis, such as electron density, its Laplacian, orbital wavefunction, ELF, LOL etc. One can select real space functions by selection -11. Notice that once this selection is chosen, all previous topology analysis results will be clean.

The topology analysis technique proposed by Bader was firstly used for analyzing electron density in "atoms in molecules" (AIM) theory, which is also known as "the quantum theory of atoms in molecules" (QTAIM), this technique has also been extended to other real space functions, e.g. the first topology analysis research of ELF for small molecules is given by Silvi and Savin, see *Nature*, **371**, 683. In topology analysis language, the points at where gradient norm of function value is zero (except at infinity) are called as critical points (CPs), CPs can be classified into four types according to how many eigenvalues of Hessian matrix of real space function are negative.

**(3,-3):** All three eigenvalues of Hessian matrix of function are negative, namely the local maximum. For electron density analysis and for heavy atoms, the position of (3,-3) are nearly identical to nuclear positions, hence (3,-3) is also called nuclear critical point (NCP). Generally the number of (3,-3) is equal to the number of atoms, only in rarely cases the former can be more than (e.g. Li<sub>2</sub>) or less than (e.g. KrH<sup>+</sup>) the latter.

**(3,-1):** Two eigenvalues of Hessian matrix of function are negative, namely the second-order saddle point. For electron density analysis, (3,-1) generally appears between attractive atom pairs and hence commonly called as bond critical point (BCP). The value of real space functions at BCP

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have great significance, for example the value of  $\rho$  and the sign of  $\nabla^2\rho$  at BCP are closely related to bonding strength and bonding type respectively in analogous bonding type (*The Quantum Theory of Atoms in Molecules-From Solid State to DNA and Drug Design*, p11); the potential energy density at BCP has been shown to be highly correlated with hydrogen bond energies (*Chem. Phys. Lett.*, **285**, 170); local information entropy at BCP is a good indicator of aromaticity (*Phys. Chem. Chem. Phys.*, **12**, 4742).

**(3,+1):** Only one eigenvalue of Hessian matrix of function is negative, namely first-order saddle point (like transition state in potential energy surface). For electron density analysis, (3,+1) generally appears in the center of ring system and displays steric effect, hence (3,+1) is often named as ring critical point (RCP).

**(3,+3):** None of eigenvalues of Hessian matrix of function are negative, namely the local minimum. For electron density analysis, (3,+3) generally appears in the center of cage system (e.g. pyramid P<sub>4</sub> molecule), hence is often referred to as cage critical point (CCP).

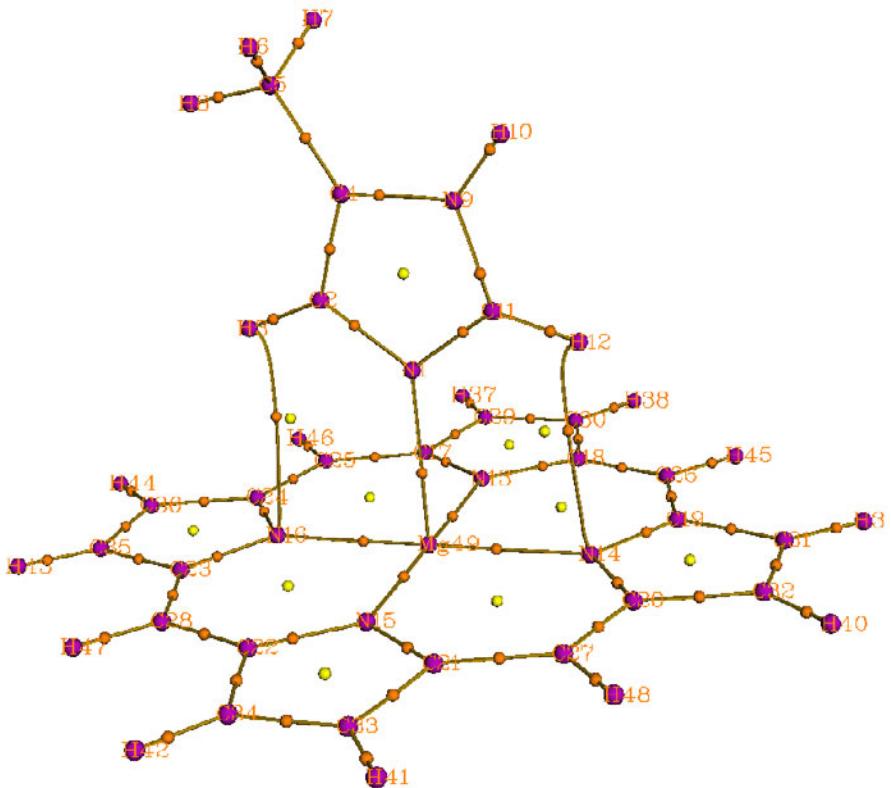
The positions of CPs are searched by Newton method, one need to assign an initial guess point, then the Newton iteration always converge to the CP that is closest to the guess point. By assigning different guesses and doing iteration for each of them, all CPs could be found. Once searches of CPs are finished, one should use Poincaré-Hopf relationship to verify if all CPs may have been found, the relationship states that (for isolated system)

$$n_{(3,-3)} - n_{(3,-1)} + n_{(3,+1)} - n_{(3,+3)} = 1$$

If the relationship is unsatisfied, then some of CPs must be missing, you may need to try to search those CPs by different guesses. However even if the relationship is satisfied, it does not necessarily mean that all CPs have been found. Notice that the function spaces of ELF/LOL and Laplacian of  $\rho$  are much more complex than  $\rho$ , it is very difficult to locate all CPs for these functions, especially for middle and large system, so, you can stop trying for searching CPs once all CPs that you are interested in have been found.

The maximal gradient path linking BCP and associated two local maxima of density is termed as “bond path”, which reveals atomic interaction path for all kinds of bonding. The collection of bond paths is known as molecular graph, which provides an unambiguous definition of molecular structure. Bond path can be straight line or curve, obviously for the latter case the length of bond path is longer than the sum of the distances between BCP and associated two (3,-3) CPs.

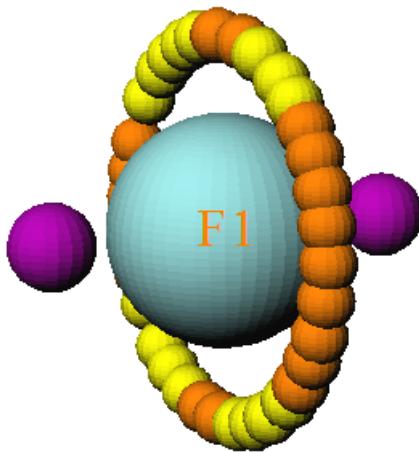
Let us see an example. In the complex shown below, the imidazole plane is vertical to magnesium porphyrin plane, the nitrogen in imidazole coordinated to magnesium. Magenta, orange and yellow spheres correspond to (3,-3), (3,-1) and (3,+1) critical points, brown lines denote bond paths.



The topology paths for other real space functions can be generated too in Multiwfn, they are very helpful to clarify intrinsic relationship between CPs.

## About degenerate CP

Appearance of degenerate CPs in general system is very rare, so I mention it in the final of this section. The so-called degenerate CP is the CP have one or two zero eigenvalues of Hessian matrix. These CPs are very instable, slight perturbation of molecular geometry can break them into other type CPs. However, degenerate CPs are commonly occur in axisymmetric system. For example, in fluorine atom at groundstate, one of  $p$  orbital is singly occupied while other two are doubly occupied, topology analysis on LOL gives below picture:



The two (3,-3) correspond to the two valves of the singly occupied  $p$  orbital, while the locally maximum of electron localization arise from the other two  $p$  orbitals are represented by a circle of CPs. Ostensibly, the CPs in the circle are either (3,-1) or (3,+1) type, but in fact they are the same type degenerate CP, in which one eigenvalue is zero. Simply because the reasons of numerical convergence of the eigenvalue, they are formally recorded as different CP types in Multiwfn.

### 3.14.2 Search critical points

In Multiwfn several modes used to assign initial guesses are provided for Newton method:

(1) Search CPs from a given starting point: If you already know the position of CPs or you are able to guess where CPs may appear, this mode is suitable for you, the Newton iteration will start from the coordinate you inputted. You can also input two atomic indices, then corresponding midpoint will be taken as starting point for locating CP.

(2) Search CPs from nuclear positions: Use all nuclear positions in turn as starting points, this mode is very suitable for searching all (3,-3) for  $\rho$ , and those (3,-3)s in innermost of atom for ELF/LOL and Laplacian. For electron density analysis, if you found  $n$  CPs after you used this mode, while there are more than  $n$  atoms in your system, it generally turns out that Newton method missed some (3,-3) CPs.

(3) Search CPs from midpoint of atom pairs: Use midpoint of all atom pairs in turn as starting points. This mode is very suitable for searching all (3,-1) for  $\rho$ .

(4) Search CPs from triangle center of three atoms: Likewise mode 3, but use triangle center of all combinations of three atoms in your system. Suitable for searching all (3,+1).

(5) Search CPs from pyramid center of four atoms: Likewise mode 3, but use pyramid center of all combinations of four atoms in your system. For electron density analysis, if you have tried mode 2 and mode 3 but still cannot find certain (3,+3), this mode is worth to try. This mode is more expensive than mode 3.

(6) Search CPs from a batch of points within a sphere: You need to set sphere center, radius and the number of points first, then select option 0, the specified number (not the exact number you have set) of points will randomly distributed in the sphere as starting points for Newton method. The sphere center can be defined in very flexible way by option 2~6. If you choose option -1, then the search starts and each atom center will be taken as sphere center in turn, assume that there are  $n$  atoms and the number of points in sphere you set is  $m$ , then about  $n*m$  points will be used as initial guesses. If you choose option -2, then you will be prompted to input indices of

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atoms, the nuclei of these atoms will be used as sphere center in turn.

This mode is very appropriate for searching the CPs that are difficult to be located by other modes. **For ELF, LOL and Laplacian, it is highly recommended to use option -1 in this mode to try to locate all possible CPs.** Note that each time you carry out the search the positions of starting points are different, if some expected CPs were not found in previous searches, try to launch the search again and again to locate missing CPs.

Beware that the index of the CPs located by this searching mode may be different in each time of execution!

The default searching parameters are appropriate for most systems, however in some cases you have to adjust parameters manually to ensure expected CPs could be found. Those parameters can be adjusted in the option "Set CP searching parameters".

(1) Set maximal iterations: If the number of Newton iteration exceeds this value before converged to a CP or before Hessian matrix became singular (that is the iteration cannot continue), then the Newton iteration will be terminated.

(2) Set scale factor for stepsize: The default value is 1.0, that is using original form of Newton method. Sometimes reduce the stepsize is benefit for locate CPs. For example the "Uracil.wfn" in example folder, by using mode 2 with default parameter the BCP linking N6 and H12 cannot be found, if you reduce the stepsize to 0.5, then the problem solved.

(3)/(4) Criteria for gradient-norm/displacement convergence: If both gradient-norm in current position and displacement in last step is smaller than the two values then the iteration stops and current position will be regarded as a critical points. Notice that for the elements heavier than Ar, during the search of their nuclear critical points, the convergence criteria are automatically multiplied by 10000, because the cusps of electron density at these nuclear positions are very sharp and hence hard to be located by default criteria.

(5) Minimal distance between CPs: If an iteration converged to a CP, however the distance between this CP and any CP that has been found is smaller than this value, then the CP just found will not be considered as a new CP, and hence discarded.

(6) Skip search if distance between atoms is longer than the sum of their vdW radius multiplied by: In CP searching mode 3, 4 and 5, if the distance of any two atoms that involved in the combination is longer than the sum of their vdW radii multiplied this value then current search will be skipped. The purpose of this option is to reduce the number of searches and hence computational cost of huge system. For example the imidazole--magnesium porphyrin complex mentioned earlier, there are  $49*48/2=1176$  atom pairs, hence if this cutoff strategy is not employed when you choose searching mode 2, Multiwfn will try as many as 1176 searches. While if this strategy is used, since only closely related atom pairs will be considered, only 274 searches are needed be performed, it can be found that their results are identical.

(7) If print details of CP searching procedure: This option is present only in serial mode. User can select output level of details of CP searching procedure. This option is mainly used for debugging.

(8) Criteria for determining if Hessian matrix is singular: If the absolute value of determinant of Hessian matrix is lower than this value, then the Hessian matrix will be regarded as singular and terminate search. Too large of this value may lead some CPs be omitted, while too small of this value may cause numerical instability and occurrence of CPs in the regions far from system.

Default value is appropriate for most cases.

(9) Select rule for reserving CPs: By making use of this option, during the CP searching, only the CP with value within user-defined range will be reserved, and thus unnecessary CPs could be ignored. By default all CPs are reserved.

### 3.14.3 Generate paths

Once CPs are found, you can choose to generate paths. In fact, the so-called “path” is a bunch of points evenly distributed in a curve.

(1) Generate the path connected (3,-3) and (3,-1): As the title says. Arithmetically, firstly displace the coordinate of each (3,-1) forward and backward respectively along the eigenvector that correspond to the positive eigenvalue of Hessian, and then go uphill following the gradient vector until encounters a (3,-3), the resultant trajectories compose the bond paths.

(2) Generate the path connected (3,+1) and (3,+3): Likewise above, the difference is that the starting points are (3,+1), and their coordinates are firstly moved forward and backward along the eigenvector correspond to the negative eigenvalue of Hessian, and then go downhill following the gradient vector.

In the option "Set path searching parameters", there are some suboptions used to adjust parameters for generating paths.

(1) Maximal number of points of a path: In each generation of paths, if the number of steps is reached this value before encounters a CP, then the trajectory will be discarded. For generating very long path, default value may need to be enlarged.

(2) Step size: The space between neighbour points that composed the paths. For paths with large curvature, sometimes they cannot be generated under default stepsize, you need to properly decrease the stepsize and regenerate paths. If you set maximal number of points and stepsize of paths as  $m$  and  $n$  respectively, then the maximal length of path is  $m*n$ .

(3) Stop generation if distance to any CP is smaller than: During the generation of paths, if the distance between current position and a CP that has been found, then it will be regarded as that the path has already reached the CP.

### 3.14.4 Generate interbasin surfaces

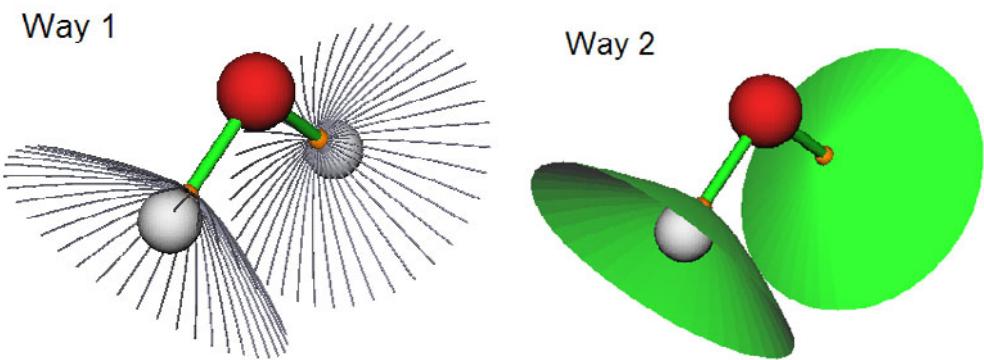
The interbasin surfaces (IBS) generated by Multiwfn actually consist of a bunch of paths derived from (3,-1) CPs, these surfaces divide the whole space into respective region for each (3,-3) CPs. By the function "Add or delete interbasin surfaces", you can generate, delete and check interbasin surfaces. Notice that before generating IBS, generation of CPs should be completed first, and at least one (3,-1) must be found.

If you want to generate the IBS from the (3,-1) CP with index of 15, then simply input *15* (you will find it is useful to visualize CPs by function 0 first to get the CP index). To delete this surface, input *-15* (negative sign means "delete"). If there is no IBS presented and you hope to generate all IBSs, input *0*. To delete all already generated IBS, also input *0*. A list of generated IBS can be printed by inputting the letter *l*. If you need to export the paths of a specific IBS (e.g. corresponding to the (3,-1) CP with index of 4) to external file, input *o 4*, then the coordinates of all paths derived from the 4th CP will be saved to surpath.txt in current folder. Input letter *q* can

return to upper level menu.

Parameters for generating IBSs can be adjusted by the option "Set interbasin surface generating parameters". Enlarging number of paths in each IBS or lowering stepsize make IBSs looks more smooth. The length of paths in IBSs, or say the area of IBSs, is proportional to product of stepsize and number of points in each IBS path. Notice that once the parameters are changed, all generated IBSs will be lost.

There are three ways to portray IBSs in Multiwfn, which can be controlled by "isurfstyle" in settings.ini. Way 1 represents the IBS directly by the paths derived from corresponding (3,-1) CP; By Way 2 IBSs are shown by solid surfaces, this is default style; Way 3 is uncommonly used, you can try it by yourself.



### 3.14.5 Visualize, analyze, modify and export results

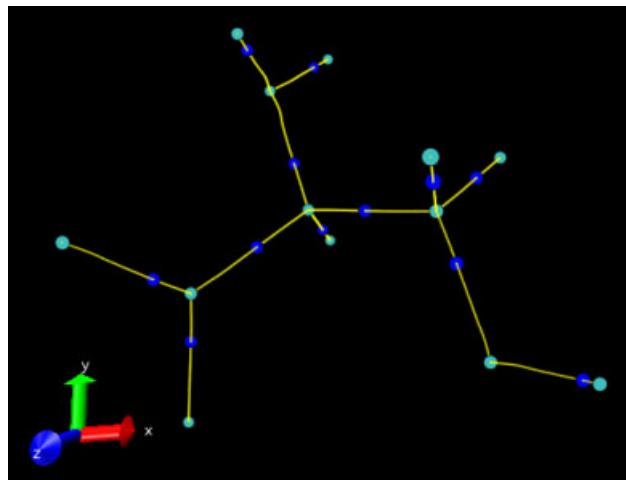
If you select the function “*O Print and visualize all generated CPs, paths and surfaces*”, a GUI will pop up, you can control if showing each type of CPs, paths, interbasin surfaces, molecular structure, labels etc. Meanwhile, a summary of found CPs and paths are printed in the command-line window. The satisfaction of Poincaré-Hopf relationship is also checked.

You can obtain values of all real space functions supported by Multiwfn (as well as gradient and Hessian matrix of the selected real space function) at a given CP or at all CPs by function “*7 Show real space function values at specific CP or all CPs*”. Note that electrostatic potential is the most expensive one among all of the real space functions. If you are not interested in it, you can set "ishowptESP" parameter in "settings.ini" to 0 to skip calculation of electrostatic potential.

In the option “*-4 Modify or export CPs*”, you can print, delete, add and export CPs. The positions and types of all found CPs can be saved to a formatted text file “CPs.txt” in current folder by choosing suboption 4, the information of CPs can also be loaded from an external formatted text file by suboption 5 (the found CP at current session will be clean), notice that the file format must be identical to the one outputted by suboption 4. All CPs can be exported as pdb file by suboption 6, so that CPs can be conveniently visualized by external visualization softwares, element C/N/O/F correspond to (3,-3)/(3,-1)/(3,+1)/(3,+3) respectively.

In the option “*-5 Modify or print detail or export paths, or calculate property along a path*”, you can print summary of generated paths, print positions of all points in specified path or delete

some paths via suboption 1, 2 and 3 respectively. By suboption 4 you can export out the detail information of all paths to "paths.txt" in current folder. By suboption 5 the paths can be imported from an external file, the file format must be identical to the one outputted by suboption 4. By suboption 6, all points in all paths can be exported to a pdb file in current folder, so that paths can be conveniently visualized by external visualization softwares. For example, we use Multiwfn to perform AIM analysis for serine, then export CPs and paths as pdb file, then load them into VMD program, set the drawing method as "Points" and slightly adjust point size and color, we get below graph. The yellow paths are bond paths, blue and cyan points correspond to (3,-3) and (3,-1) CPs.



By suboption 7, value of real space functions along selected topology paths can be outputted and plotted as curve map. You can also take the data shown in "Dist." and "Value" column as X and Y axes respectively to plot curve graph by third-part plotting tools.

Distance, angle and dihedral angle between atoms and CPs can be conveniently measured by using the option "*-9 Measure distances, angles and dihedral angles between CPs or atoms*".

### 3.14.6 Calculate the aromaticity indices based on topology properties of electron density

If the real space function you selected is electron density, option 20 and 21 will be visible, they are utilities used to analyze aromaticity.

#### Shannon aromaticity index

Option 20 is used to calculate Shannon aromaticity (SA) index, see *Phys. Chem. Chem. Phys.*, **12**, 4742 (2010) for detail. The formula can be briefly written as

$$SA = \ln(N) + \sum_i^N (-p_i \ln p_i) \quad p_i = \frac{\rho(\mathbf{r}_{BCPi})}{\sum_i^N \rho(\mathbf{r}_{BCPi})}$$

In above formula,  $N$  is the total number of the BCPs in the ring you want to study aromaticity,  $\mathbf{r}_{BCP}$  is the position of BCP. In option 20, you need to input  $N$  and the index of these CPs in turn, then Shannon aromaticity index will be printed immediately. The smaller the SA index, the more

aromatic is the molecule. The range of  $0.003 < \text{SA} < 0.005$  is chosen as the boundary of aromaticity/antiaromaticity in original paper.

#### **Curvature of electron density perpendicular to ring plane at RCP**

In *Can. J. Chem.*, **75**, 1174 (1997), the authors showed that electron density at RCP is closely related to aromaticity of corresponding ring. The larger the density, the stronger the aromaticity. They also pointed out that the curvature of electron density perpendicular to the ring plane at the RCP has more significant correlation with the ring aromaticity. The more negative the curvature, the stronger the aromaticity. Assume that the ring is strictly perpendicular to a Cartesian axis, for example, a ring perpendicular to Z axis (viz. the ring is in XY plane), then the curvature is just ZZ component of Hessian matrix of electron density at the RCP, which can be directly obtained by using option 7 to print out properties of a given RCP. However, if the ring is distorted, or is not exactly perpendicular to any Cartesian axis, you should use option 21 to calculate the curvature. In option 21, you need to input the index of the RCP (or directly input coordinate of a point), and then input indices of three atoms, their nuclei position will be used to define the ring plane. Then, the electron density, the gradient and the curvature of electron density perpendicular to the ring plane at the RCP will be outputted on screen. In addition, unit normal vector, the coordinates of the two points above and below 1 Angstrom of the RCP in normal direction will be outputted together, which can be taken as the point used to calculate NICS(1).

**Information needed:** GTFs, atom coordinates

## **3.15 Quantitative analysis of molecular surface (12)**

The theory and numerical algorithm involved in present module have been detailedly described in [J. Mol. Graph. Model., 38, 314 \(2012\)](#). In the next two sections, these two aspects will only be briefly introduced.

### **3.15.1 Theory**

#### **Electrostatic potential on vdW surface**

Molecular electrostatic potential (ESP),  $V(\mathbf{r})$ , has been widely used for prediction of nucleophilic and electrophilic sites, as well as molecular recognition mode for a long time, the theoretical basis is that molecules always tend to approach each other in a complementary manner of ESP. These analyses of ESP are common performed on molecular van der Waals (vdW) surface. Although the definition of such a surface is arbitrary, most people prone to take the 0.001 isosurface of electron density as vdW surface, since this definition reflects specific electron structure features of a molecule, such as lone pairs,  $\pi$  electrons etc., this is also what the definition used in our analyses.

The analysis of ESP on vdW surface has been further quantified to extract more information. It is shown that the strength and orientation of weak interaction, including such as hydrogen bonding, dihydrogen bonding and halogen bonding, can be well predicted and explained by analyzing the magnitude and positions of minima and maxima on the surface. Politzer and

### 3 Functions

coworkers (*J. Mol. Struct. (THEOCHEM)*, **307**, 55) have defined a set of molecular descriptors based on ESP on vdW surface, which are taken as independent variables of general interaction properties function (GIPF). GIPF successfully connects distribution of ESP on vdW surface and many condensed phase properties, including density, boiling point, surface tension, heats of vaporization and sublimation, LogP, impact sensitivity, diffusion constant, viscosity, solubility, solvation energy and so on. Below I enumerate and brief these descriptors.

$A^+$  and  $A^-$  indicate the surface area in which the ESP has positive and negative value, respectively. Total surface area  $A$  is the sum of them.

$\bar{V}_S^+$  and  $\bar{V}_S^-$  denote average of positive and negative ESP on vdW surface respectively

$$\bar{V}_S^+ = (1/m) \sum_{i=1}^m V(\mathbf{r}_i) \quad \bar{V}_S^- = (1/n) \sum_{j=1}^n V(\mathbf{r}_j)$$

where  $i$  and  $j$  are indices of sampling points in positive and negative regions respectively. The  $S$  subscript means "Surface". The average of ESP over the entire surface is

$$\bar{V}_S = (1/t) \sum_{k=1}^t V(\mathbf{r}_k)$$

$\Pi$  is the average deviation over the surface, which is viewed as an indicator of internal charge separation:

$$\Pi = (1/t) \sum_{k=1}^t |V(\mathbf{r}_k) - \bar{V}_S|$$

The total ESP variance can be written as the sum of positive and negative parts:

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = (1/m) \sum_{i=1}^m [V(\mathbf{r}_i) - \bar{V}_S^+]^2 + (1/n) \sum_{j=1}^n [V(\mathbf{r}_j) - \bar{V}_S^-]^2$$

The variance reflects the variability of ESP. The larger the  $\sigma_+^2$  and  $\sigma_-^2$ , the more tendency that the molecule interacts with other molecules by positive and negative ESP regions respectively.

Degree of charge balance is defined as

$$\nu = \frac{\sigma_+^2 \sigma_-^2}{(\sigma_{\text{tot}}^2)^2}$$

When  $\sigma_+^2$  equals to  $\sigma_-^2$ ,  $\nu$  attains its maximum value of 0.250. The closer the  $\nu$  is to 0.250, the more possible that the molecule can interact to others through positive and negative region with similar extent.

The product of  $\sigma_{\text{tot}}^2$  and  $\nu$  is a very useful quantity too, a large value of  $\nu \sigma_{\text{tot}}^2$  is an indicative of a molecule that has relatively strong tendencies to interact with others of its own kind electrostatically.

#### Some practical applications of GIPF

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A practical application of above GIPF descriptors is presented in *J. Phys. Chem. A*, **110**, 1005 (2006). The authors showed that for a series of molecules containing C, H, N and O elements, the heat of vaporization can be well evaluated as

$$\Delta H_{\text{vap}} = a\sqrt{A} + b\sqrt{\nu\sigma_{\text{tot}}^2} + c$$

with least-squares fit coefficients  $a = 2.130$ ,  $b = 0.930$  and  $c = -17.844$ . The heat of sublimation can be predicted as

$$\Delta H_{\text{sub}} = aA^2 + b\sqrt{\nu\sigma_{\text{tot}}^2} + c$$

with  $a = 0.000267$ ,  $b = 1.650087$  and  $c = 2.966078$ . In above equations the surface area  $A$  is in  $\text{\AA}^2$ ,  $\Delta H_{\text{sub}}$  is in kcal/mol,  $\sigma_{\text{tot}}^2$  is in  $(\text{kcal/mol})^2$ . Note that the coefficients are more or less dependent on the calculation level used. The author used B3LYP/6-31G\* to optimize geometry and B3LYP/6-311++G(2df,2p) to calculate ESP.

Another typical application of statistical data of ESP on vdW surface is predicting crystal density of organic molecules containing C, H, N and O elements. The crystal density is a crucial property of energetic compounds. In *J. Phys. Chem. A*, **111**, 10874 (2007), it was shown that the density can be estimated by  $\rho = M / V_m$ , where  $M$  is molecular mass and  $V_m$  is molecular vdW volume defined by  $\rho=0.001$  isosurface; for ionic crystal (e.g. ammonium azide),  $M$  and  $V_m$  correspond the sum of mass and volume of the cation and anion comprising a formula unit of the compound. Although the relationship is quite simple, it indeed works well for most neutral species, but the error is evidently larger for ionic species. In order to improve the prediction accuracy for neutral ones, in *Mol. Phys.*, **107**, 2095 (2009), the authors introduced GIPF descriptors into the formula:

$$\rho = \alpha \frac{M}{V_m} + \beta(\nu\sigma_{\text{tot}}^2) + \gamma$$

At B3PW91/6-31G\*\* level, the fitted coefficients are  $\alpha = 0.9183$ ,  $\beta = 0.0028$  and  $\gamma = 0.0443$ . This formula has proven to have improved accuracy, because intermolecular electrostatic interaction is somewhat effectively taken into considered. In a succeeding paper *Mol. Phys.*, **108**, 1391 (2010), the author showed that the crystal density of ionic compounds can be estimated much better than

$\rho = M / V_m$  if GIPF descriptors are introduced:

$$\rho = \alpha \frac{M}{V_m} + \beta \left( \frac{\bar{V}_{S(\text{cation})}^+}{A_{(\text{cation})}^+} \right) + \gamma \left( \frac{\bar{V}_{S(\text{anion})}^-}{A_{(\text{anion})}^-} \right) + \delta$$

with least-squares fit coefficients  $\alpha = 1.0260$ ,  $\beta = 0.0514$ ,  $\gamma = 0.0419$  and  $\delta = 0.0227$  at B3PW91/6-31G\*\* level. In the equation,  $\bar{V}_{S(\text{cation})}^+$  and  $A_{(\text{cation})}^+$  denote the  $\bar{V}_S^+$  and  $A^+$  of the cation;  $\bar{V}_{S(\text{anion})}^-$  and  $A_{(\text{anion})}^-$  denote the  $\bar{V}_S^-$  and  $A^-$  of the anion. For 30 test cases, the average absolute error is merely 0.033g/cm<sup>3</sup>.

Noticed that above relationships are only appropriate for small organic compounds

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containing C, H, N, O elements, the error are significantly larger for other kinds of systems.

In *J. Phys. Chem.*, **97**, 9369 (1993), it is shown that boiling point can be predicted as

$$T_{\text{bp}} = \alpha A + \beta \sqrt{\nu \sigma_{\text{tot}}^2} + \gamma$$

where  $\alpha = 2.736$ ,  $\beta = 33.31$ ,  $\gamma = -72.05$  were fitted at HF/STO-5G\*/HF/STO-3G\* level. This paper also showed equations for predicting critical temperature, volume and pressure.

In *J. Phys. Chem. A*, **103**, 1853 (1999), the prediction equation for solvation free energy is presented as ( $V_{\min}$  denotes the ESP value at its global minimum in the whole space):

$$\begin{aligned}\Delta G_{\text{solv}} (\text{kJ/mol}) = & 0.17201 V_{\min} - 2.6412 \times 10^{-5} (V_{S,\max} - V_{S,\min})^3 \\ & + 0.051892 A^- \bar{V}_S^- + 9704.2 / (A^- \bar{V}_S^-) + 46.827\end{aligned}$$

In addition, the equations used to predict heat of fusion, surface tension and crystal/liquid density can be found in *J. Phys. Chem.*, **99**, 12081 (1995), the equations used to predict lattice energy for ionic crystal containing  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{Na}^+$  are given in *J. Phys. Chem. A*, **102**, 1018 (1998). More formulae used to predict physical properties of organic molecules based on GIFFP descriptors are summarized in Table 3 of *J. Mol. Struct. (THEOCHEM)*, **425**, 107 (1998). GIFFP also has many important uses in study of biochemical systems, see *Int. J. Quantum Chem.*, **85**, 676 for a review.

#### Average local ionization energy and local electron affinity on vdW surface

The value of average local ionization energy,  $\bar{I}(\mathbf{r})$ , has attracted more and more attentions. This function has many uses, for example reproducing atomic shell structure, measuring electronegativity, quantifying local polarizability and hardness. However, the most important use maybe the prediction of reactivity according to function value on vdW surface,  $\bar{I}_s(\mathbf{r})$ . Lower value of  $\bar{I}_s(\mathbf{r})$  indicates that the electron at  $\mathbf{r}$  are more weakly bounded, therefore more likely  $\mathbf{r}$  is the site of electrophilic or radical attack. Many studies have shown that the global minimum of  $\bar{I}(\mathbf{r})$  on vdW surface exactly locates the experimental reaction site, while relative magnitude of  $\bar{I}(\mathbf{r})$  at corresponding reaction site in homologues correlates well with relative reactivity. The interested user is recommended to take a look at *J. Mol. Model.*, **16**, 1731 and Chapter 8 of the book *Theoretical Aspects of Chemical Reactivity* (2007).

Local electron affinity  $EA_L$  is a quantity very similar to  $\bar{I}(\mathbf{r})$ , the only difference is that the MOs under consideration is not all occupied ones, but all unoccupied ones. It was shown that  $EA_L$  on molecular surface is useful for analyzing nucleophilic attacking, for detail see *J. Mol. Model.*, **9**, 342.

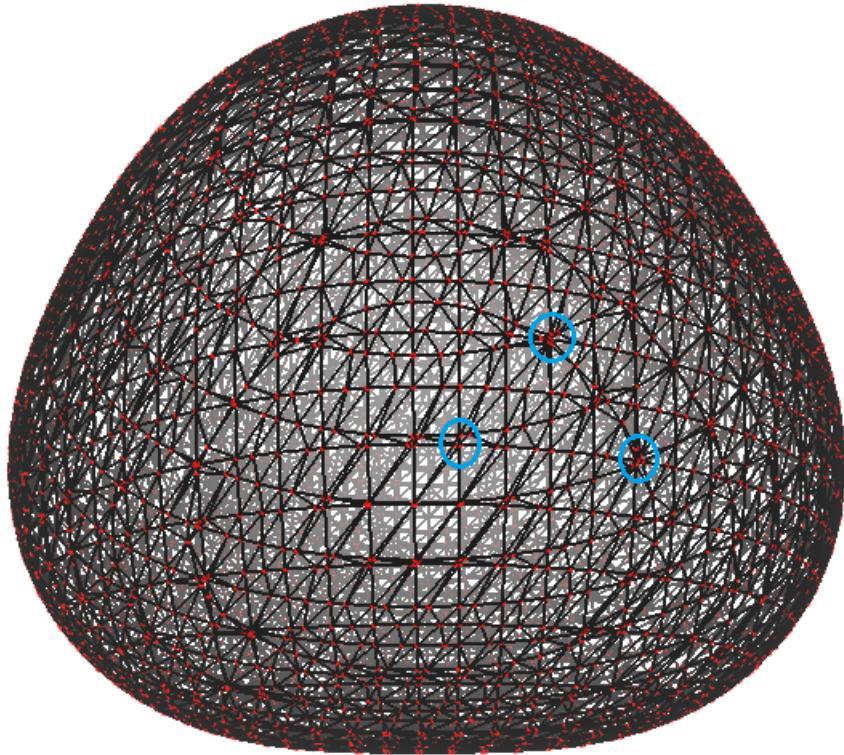
In Multiwfn, above mentioned surface descriptors can be calculated not only on the whole vdW surface, but also on the subregions corresponding to atoms or user-defined fragments. The detail of the theory is to be published, and thus not documented here at the moment.

### 3.15.2 Numerical algorithm

In summary, in the quantitative analysis of molecular surface task, what we need to obtain are minima and maxima of ESP or  $\bar{I}(\mathbf{r})$  or  $EA_L$  on vdW surface, as well as  $\bar{V}_S^+$ ,  $\bar{V}_S^-$ ,  $\bar{V}_S$ ,  $\Pi$ ,  $\sigma_+^2$ ,  $\sigma_-^2$ ,  $\sigma_{\text{tot}}^2$ ,  $\nu$ , and  $\nu\sigma_{\text{tot}}^2$ . Here I briefly describe how these properties are computed in Multiwfn in accordance with the sequence of steps.

**1.** Grid data of electron density enclosed the entire molecular space is compute. The smaller the grid spacing is used, the more accurate result you will get, however the more vertices will be generated in next step and therefore you will wait longer time in step 3.

**2.** Marching Tetrahedra algorithm is performed by making use of the grid data generated above, this step generally does not cost much computational time. The volume enclosed by the isosurface is computed at the same time. This step generates vertices representing the isosurface, along with their connectivity. Each neighbouring three vertices constitute a triangle (will be referred to as facet below). Below example is a water molecule, vertices (red points) and connectivity (black lines) are portrayed:



**3.** Since computing ESP is time consuming, in order too cut down computational time, Multiwfn removes redundant points. Specifically, if the distance between two points is smaller than a specific value, one of the points will be eliminated, and the other point will be moved to their average position. In above graph, the aggregated points such as those inside blue circles will be finally merged to one point.

**4.** Calculate mapped function (ESP,  $\bar{I}(\mathbf{r})$  and so on) at each vertex on the isosurface. For ESP, this is the most time consuming step, however for  $\bar{I}(\mathbf{r})$  and  $EA_L$ , this step can be finished immediately.

**5.** Locate and then output minima and maxima of the mapped function on the surface by making use of connectivity. If the mapped function value at a vertex is both lower (larger) than that at its first-shell neighbours and second-shell neighbours, then this vertex will be regarded as surface minimum (maximum).

**6.** Compute and output  $\bar{V}_S^+$ ,  $\bar{V}_S^-$ ,  $\bar{V}_S$ ,  $\Pi$ ,  $\sigma_+^2$ ,  $\sigma_-^2$ ,  $\sigma_{\text{tot}}^2$ ,  $v$ , and  $v\sigma_{\text{tot}}^2$ , as well as vdW volume, area of total vdW surface, the area where the mapped function is positive and where is negative. As an example,  $\bar{V}_S$  is computed as

$$\bar{V}_S = (1/A_{\text{tot}}) \sum_{i=1}^N A_i F_i$$

where  $N$  is the total number of facets,  $A_{\text{tot}}$  is the sum of area of all facets,  $A_i$  is the area of facet  $i$ ,  $F_i$  is the ESP value of facet  $i$ , which is calculated as the average of ESP at the three vertices composing the facet.

### 3.15.3 Parameters and options

You will see below options in the main interface of quantitative analysis of molecular surface.

**0 Start analysis now!:** When this option is selected, the analysis boots up. All steps described in last section will be implemented sequentially.

**1 The isovalue of electron density used to define molecular surface:** Default value is 0.001, corresponding to the most frequently used definition of vdW surface. In general it is not recommended to adjust this value.

**2 Select mapped function:** The mapped function can be selected by this option. Currently ESP,  $\bar{I}(\mathbf{r})$ ,  $EA_L$  and user defined real space function (Section 2.7) are directly supported and can be automatically computed by internal module of Multiwfn during the surface analysis. Alternatively, if you choose "A function loaded from external file", then the value of mapped functions at all surface vertices will be loaded from an external file, so that you can analyze other mapped functions (e.g. Fukui function), see the description of option 5 below for detail about the format of the external file.

Note that by default the ESP is evaluated based on wavefunction, this process may be quite time-consuming for large systems. However, if you choose "Electrostatic potential from atomic charge", then Multiwfn will evaluate ESP based on atomic charges, the computational time will be reduced by several orders. The atomic charges will be loaded from a .chg file, you can use main function 7 to produce the .chg file, or you can write the file manually, see corresponding part of

Section 2.5 on the .chg file format. Note that the analysis result will be reasonable only when the way to generate atomic charges can reproduce ESP well (e.g. CHELPG, MK and ADCH methods).

**3 Spacing of grid points for generating molecular surface:** This setting defines the spacing of electron density grid data, see step 1 introduced in the last section. The spacing directly determines the accuracy and computational cost of the analysis. Default value is suitable for general cases. Largening this value can reduce computational time evidently, however if this value is not small enough, the vertices on the isosurface will be spare, this may cause missing or erroneous locating of some extrema. In general, the results under the default spacing are accurate and reliable. If you find some extrema were not located under default spacing, try to decrease spacing and rerun the task.

**4 Advanced options:** Suboptions in this option is not needed to be frequently adjusted by normal users.

**(1) The ratio of vdW radius used to extend spatial region of grid data:** The role of this parameter is exactly identical to the parameter  $k$  introduced in Section 3.100.3. Enlarging this value will lead larger spatial extension of grid data of electron density around molecule. If isovalue of electron density is set to a lower value than default, or the system is negatively charged, you may need to enlarge this parameter to ensure that the isosurface will not be truncated.

**(2) If eliminate redundant vertices:** If this option is switched to "No", then the elimination of redundant vertices (step 3 described in last section) will be skipped, and you will waste vast time to calculate mapped function at those meaningless vertices. If this option is switched to "Yes", you will be prompted to input a distance criterion for merging adjacent vertices. Commonly, 0.4~0.5 times of grid spacing is recommended to be used as the criterion.

**(3) Number of bisections before linear interpolation:** Simply speaking, the larger the value, the more exactly the isosurface (corresponding to vdW surface) can be generated. Enlarging this value will bring additional cost in step 2. The generated isosurface under default value is exact enough in general. You can descrease it to 2 even to 1 to save computational time, however decrease it to 0 will frequently lead to false surface extrema.

## 5 If load mapped function values from external file

Via this option, during surface analysis, the value of mapped function at all surface vertices can be loaded from external file rather than directly calculated by Multiwfn. This option has two purposes: (1) Reduce overall analysis time (2) Analyze some special functions that cannot be directly produced by Multiwfn, or those requiring mathematical operations and thus not directly available in present module (e.g. dual descriptor). This option has four suboptions:

**(0) Do not load mapped function but directly calculate by Multiwfn:** This is default case.

**(1) Load mapped function at all surface vertices from plain text file:** If this option is selected, then after generation of molecular surface, coordinate of all surface vertices (in Bohr) will be automatically exported to *surfptpos.txt* in current folder. Then you can use your favourite program to calculate mapped function value at these points, and write the values as the fourth column in this file (in free format, unit is in a.u.). For example

### 3 Functions

```
-1. 6652369 -0. 5480503 -0. 2554867 -0. 0196978306  
-1. 6835983 -0. 5563165 -0. 1342924 -0. 0242275610  
-1. 6977125 -0. 5530614 -0. 0099311 -0. 0287667191  
-1. 7013207 -0. 5536310 0. 1194197 -0. 0330361826  
-1. 6954099 -0. 5523031 0. 2547866 -0. 0371580132  
....
```

Then input the path of this file (the name can still be *surfptpos.txt*), Multiwfn will directly read the values. An exemplificative application of this option is given in Section 4.12.4.

**Hint:** If you will analyze a system twice or more times, and want to avoid calculating mapped function values every time for saving time, at the first time you analyze the system, you can select option 7 at post-process interface to export coordinates and corresponding mapped function values of surface vertices to *vtx.txt* in current folder. At next time you analyze the system, if you choose this option, and input the path of the *vtx.txt* during the surface analysis, then mapped function values will be directly loaded rather than re-calculated. (See Section 4.12.7 for example)

**(2) Similar to 1, but specific for the case of using cubegen utility of Gaussian:** A file named *cubegenpt.txt* will be generated in current folder after generation of molecular surface. This file is very similar to *surfptpos.txt*, the difference is that in this file the first line is not presented, and coordinate unit is in Angstrom. Based on this file, you can make use of cubegen utility of Gaussian to calculate mapped function at all surface vertices. After that, input the path of cubegen output file, the data will be loaded by Multiwfn. The main use of this option is to reduce computational cost in ESP analysis, see Section 4.12.7 for illustration.

**(3) Interpolate mapped function from an external cube file:** After generation of molecular surface, a template cube file named *template.cub* will be generated in current folder. Then you will be prompted to input the path of a cube file representing the mapped function you are interested in, the grid setting of this cube file must be exactly identical to *template.cub*. The mapped function values at surface vertices will be evaluated by interpolation from the cube file you provided.

#### 3.15.4 Options at post-process stage

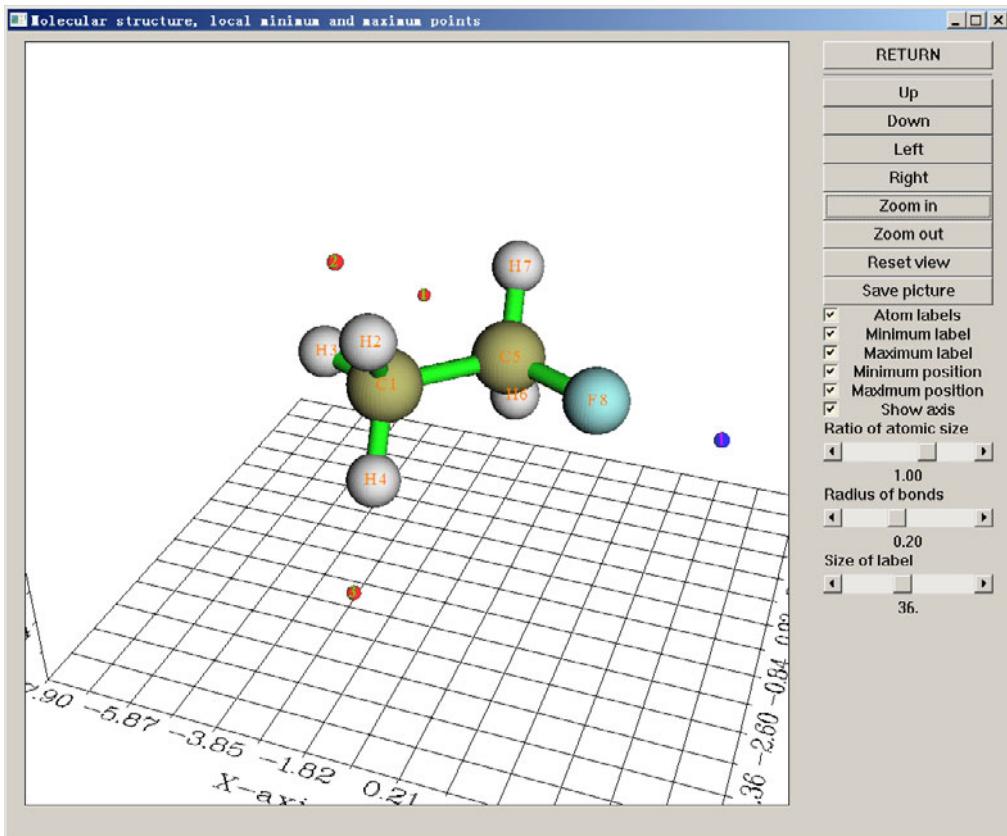
Once the all calculations of surface analysis are finished, a summary will be printed on screen. Meanwhile below options will appear on screen used to check, adjust and export results.

**-3 Visualize the surface:** By this option you can directly visualize the isosurface analyzed.

**-2 Export the grid data to *surf.cub* in current folder:** The grid data used to generated isosurface will be exported to the cube file *surf.cub* in current folder.

**-1 Return to upper level menu**

**0 View molecular structure, surface minima and maxima:** A GUI window will pop up if this option is chosen. Red and blue spheres represent the position of maxima and minima. All widgets are self-explained and hence not be referred here.



**1 Export surface extrema as plain text file:** This option exports value of mapped function and X,Y,Z coordinates of surface extrema to surfanalysis.txt in current folder.

**2 Export surface extrema as pdb file:** This option outputs surface extrema to surfanalysis.pdb in current folder. The B-factor column records mapped function value.

**3 Discard surface minima in certain value range:** If the mapped function value at a surface minima is between the lower and upper limit inputted by user, then this minimum will be discarded and cannot be recovered afterwards. This option is useful to screen the minima with too large value.

**4 Discard surface maxima in certain value range:** If the mapped function value at a surface maximum is between the lower and upper limit inputted by user, then this maximum will be discarded and cannot be recovered afterwards. This option is useful to screen the maxima with too small value.

**5 Export present molecule as pdb format file:** This option output structure of present system to a specified pdb file. Since pdb is a widely supported format, in conjunction with the output by option 2, surface extrema can be conveniently analyzed in external visualization softwares such as VMD.

**6 Export all surface vertices to vtx.pdb in current folder:** This option outputs the surface vertices to vtx.pdb file in current folder, the connectivity are written to CONECT field, mapped function values are written to B-factor field. This option is mainly used to check validity of isosurface polygonization and visualize distribution of mapped function on vdW surface.

**7 Export all surface vertices to vtx.txt in current folder:** Namely output all reserved surface vertices to a plain text file named vtx.txt in current folder, including vertex X/Y/Z coordinates in Bohr, mapped function values in a.u., eV and kcal/mol.

### 9 Output surface area in specific value range of mapped function

By this option, one can gain the knowledge of the distribution of molecular surface area in various range of mapped function. First one needs to input the index range of the atoms in consideration, then input overall range, interval and the unit. For example, one sequentially inputs 2,6-9, -45,50 and 10 and 3, the statistic then is applied on the local molecular surface corresponding to atoms 2, 6, 7, 8 and 9, the output looks like below:

Begin	End	Center	Area	%
-50.0000	-40.0000	-45.0000	4.8764	1.5171
-40.0000	-30.0000	-35.0000	28.0413	8.7242
-30.0000	-20.0000	-25.0000	23.2699	7.2397
-20.0000	-10.0000	-15.0000	17.6022	5.4764
-10.0000	0.0000	-5.0000	61.4759	19.1263
0.0000	10.0000	5.0000	72.6197	22.5933
10.0000	20.0000	15.0000	55.2707	17.1957
20.0000	30.0000	25.0000	53.9060	16.7712
30.0000	40.0000	35.0000	2.8590	0.8895
40.0000	50.0000	45.0000	1.5000	0.4667
Sum:			321.4212	100.0000

where "begin" and "end" is the lower and upper limit of local value range, respectively. "Center" is their average value. Area is in  $\text{\AA}^2$ , "%" denotes the proportion of the area in overall molecular surface area.

### 10 Output the closest and farthest distance between the surface and a point

In this option, after defining a point (you can define a nuclear position or geometry center as the point, you can also directly input the coordinate of the point), the closest and farthest distance between the molecular surface and the point will be outputted. These two quantities have two main uses:

(1) In atoms in molecules (AIM) theory, for systems in gas phase, the vdW isosurface is defined as the  $\rho=0.001$  a.u. isosurface. The closest distance between a nucleus and the surface can be regarded as non-bonded atomic radius. For a non-covalently interacting atom pair AB, The difference between the length of A-B and the sum of their non-bonded radii is termed as mutual penetration distance. In general, the larger the distance is, the stronger the interaction will be.

(2) The farthest distance between molecular surface and geometry center can be viewed as a definition of molecular radius. Of course, the concept of molecular radius is only meaningful for sphere-like molecules.

If you input  $f$ , Multiwfn will output the farthest distance between all surface points. This can be regarded as a definition of molecular diameter.

### 11 Output the surface properties of each atom

By default, the surface properties, such as average of ESP, are calculated on the whole molecular surface. By using this function, the whole surface will be first decomposed to local surfaces corresponding to individual atoms, and then the surface properties will be calculated on these atomic surfaces. This function is very helpful to study atomic properties.

After outputting the surface properties, the user can select if output the surface facets to locsurf.pdb in current folder. If choose "y", then in the outputted pdb file, each atom corresponds to a surface facet, and the B-factor field records the attribution of the surface facets, e.g. a facet

having B-factor of 11.00 means the facet belongs to the local surface of atom 11. If you load the pdb file into VMD and set "Coloring Method" as "Beta", then you can directly visualize how the whole molecular surface is decomposed to atomic surfaces.

## 12 Output the surface properties of specific fragment

Similar to function 11, but user can define a fragment, the surface properties will only be calculated on the local surface corresponding to this fragment, so that one can study fragment properties according to the local surface descriptors. Also, you can choose to output the surface facets to locsurf.pdb in current folder, in which the atom having B-factor of 1 and 0 means corresponding surface facet belongs to and does not belong to the local surface of the fragment you defined, respectively.

### 3.15.5 Special topic: Hirshfeld and Becke surface analyses

The quantitative molecular surface analysis module is also able to carry out Hirshfeld and Becke surface analysis, present section is devoted to introduce this point.

#### Theory of Hirshfeld and Becke surface analyses

Hirshfeld surface analysis was first proposed in *Chem. Phys. Lett.*, **267**, 215 (1997) and comprehensively reviewed in *CrystEngComm*, **11**, 19 (2009). This method focus on analyzing the so-called Hirshfeld surface to reveal weak interactions between monomers in complex or in molecular crystal.

Hirshfeld surface in fact is a kind of inter-fragment (or inter-monomer) surface, which is defined based on the concept of Hirshfeld weight. Probably Hirshfeld surface is the most reasonable way to define inter-fragment surface.

Atomic Hirshfeld weighting function of an atom is expressed as

$$w_A^{\text{Hirsh}}(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})}$$

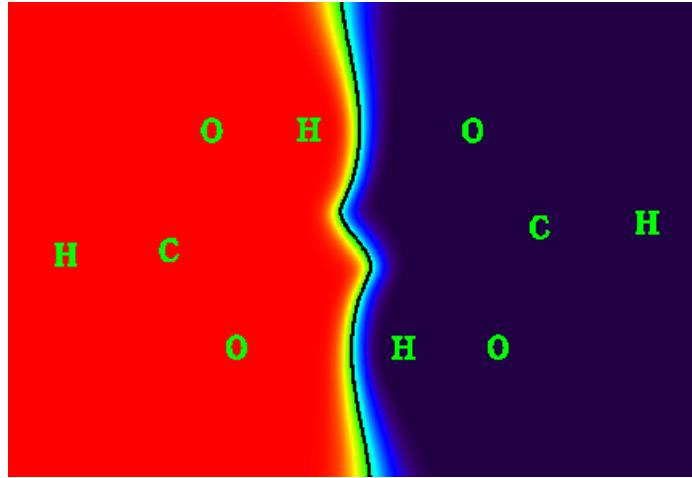
where  $\rho_A^0$  denotes the density of atom A in free-state. Summing up weight of all atoms in a fragment yields Hirshfeld weight of this fragment

$$w_P^{\text{Hirsh}}(\mathbf{r}) = \sum_{A \in P} w_A^{\text{Hirsh}}(\mathbf{r})$$

Hirshfeld surface of fragment  $P$  is just the isosurface of  $w_P^{\text{Hirsh}} = 0.5$ .

Motivated by Hirshfeld surface, I proposed Becke surface, which replaces Hirshfeld weight with Becke weight (see Section 3.18.0 for introduction of Becke weight), only geometry and atomic radii are required to construct Becke surface. Generally the shape of Becke surface and Hirshfeld surface are comparable, but I prefer to use Becke surface, mostly because Becke surface does not rely on atomic density and thus somewhat easier to be constructed.

To intuitively illustrate Hirshfeld/Becke surface, acetic acid dimer in 2D case is taken as example here



Becke weighting function of the monomer at left side of the graph is represented by color, going from red to purple corresponds to the weight varying from 1.0 to 0.0. The black line, which is the contour line of 0.5, is just its Becke surface. Evidently, Becke surface very elegantly partitioned the whole space into two monomer regions, the difference of atomic size is properly and automatically taken into account. The Becke surface in this case is an open surface, the surface extends to infinity; while if the monomer is completely buried, such as in molecular crystal or metal-organic framework environment, then its Becke surface will be a close surface and encloses all of its nuclei, just like common molecular surface.

If we map specific real space functions on Becke/Hirshfeld surface and study their distributions, just like quantitative analysis on molecular surface, we can gain many important information about intermolecular interaction. There are three real space functions very useful for this purpose

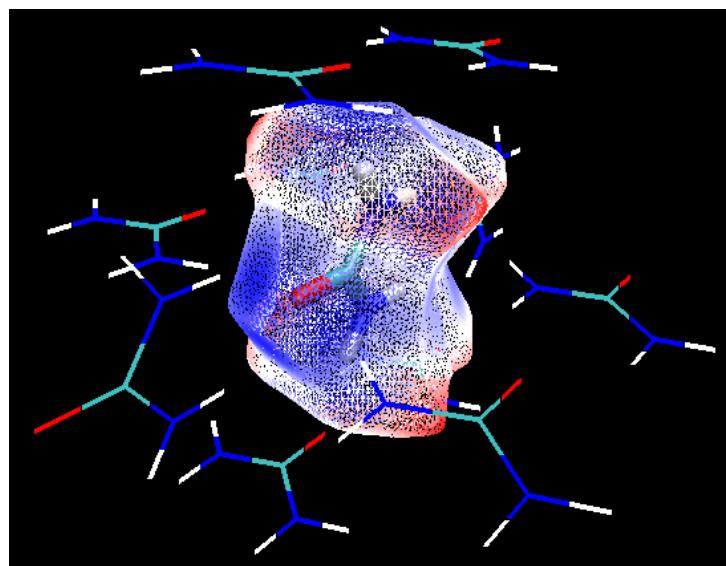
$$(1) \text{ Normalized contact distance } d_{\text{norm}} = \frac{d_i - r_i^{\text{vdW}}}{r_i^{\text{vdW}}} + \frac{d_e - r_e^{\text{vdW}}}{r_e^{\text{vdW}}}, \text{ where } d_i \text{ (} d_e \text{) is the}$$

distance from a point on the surface to the nearest nucleus inside (outside) the surface,  $r_i^{\text{vdW}}$  and  $r_e^{\text{vdW}}$  denote vdW radius of the corresponding two atoms. Small value of  $d_{\text{norm}}$  indicates close intermolecular contact and implies evident interaction.

(2) Electron density. If electron density is large in some local region of Becke/Hirshfeld surface, obviously the intermolecular interactions crossing these regions must be strong. The usefulness of electron density is similar to  $d_{\text{norm}}$ , but the former is more physically meaningful. While  $d_{\text{norm}}$  also has its own advantage, namely only geometry and vdW radii information are needed.

(3)  $\text{Sign}(\lambda_2(\mathbf{r}))$ , see corresponding part Section 2.6 for detailed explanation. This function can not only exhibit interaction strength but also reveal interaction type.

Below is urea crystal, the mesh represents Becke surface of the central urea, and  $d_{\text{norm}}$  is the mapped function. Blue part corresponds to small  $d_{\text{norm}}$  and thus exhibits close contact, which mainly originates from H-bond interaction.



### Fingerprint plot

The so-called "fingerprint plot" defined in the framework of Hirshfeld surface analysis is very useful for investigating the non-covalent interactions in molecular crystals. X and Y axes in this plot correspond to  $d_i$  and  $d_e$ , respectively. The plot is created by binning  $(d_i, d_e)$  pairs in certain intervals and colouring each bin of the resulting 2D histogram as a function of the number of surface points in that bin, ranging from purple (few points) through green to red (many points). Black region means there are not surface points. If you are confused, see the fingerprint plot in Section 4.12.6 for example. The usefulness of fingerprint plot is demonstrated in page 24 and 25 of *CrystEngComm*, **11**, 19 (2009). Although in Multiwfn fingerprint plot can also be drawn in Becke surface analysis, the plot in this case is not as useful as that in Hirshfeld surface analysis.

The Hirshfeld surface in fact can be viewed as the contact surface between the atoms in the Hirshfeld fragment you defined and all of the other atoms. The remarkable flexibility of Multiwfn allows the overall contact surface be decomposed to many local contact surfaces and draw the corresponding fingerprint plots. For example, in Multiwfn one can draw fingerprint plot for the local contact surface between the nitrogen in the central urea and the hydrogens in specific peripheral ureas. In this case, all surface points in the contact surface satisfy two conditions: (1) In the Hirshfeld fragment (viz. the central urea), the atom closest to the surface point is the nitrogen (2) Among all of the atoms that do not belong to the Hirshfeld fragment, the atom closest to the surface point is one of hydrogen in specific peripheral ureas. Undoubtedly, fingerprint plot of local contact surface greatly facilitates one to study the non-covalent interaction in local region due to the contact between specific atoms.

### Usage

The procedure to perform Becke/Hirshfeld surface analysis is similar to normal quantitative molecular surface analysis. After you entered main function 12, choose option 1 and select Becke or Hirshfeld surface, then input the index of the atoms in the fragment (referred to as *Hirshfeld fragment* below), and use option 2 to select mapped function. After that choose 0 to start calculation. Quantitative data on the surface such as average value and standard deviation will be outputted, and surface extrema will be located. Then via corresponding options you can visualize

### 3 Functions

surface minima/maxima, export result and so on, all of the options in post-process menu (except one, see below) have already been introduced in Section 3.15.4 and thus are not described again here. If you use option 6 to export the surface vertices to pdb file, based on which you can also plot color-mapped Hirshfeld/Becke surface by means of VMD program, the drawing method should be set to "Points" and coloring method should be set to "Beta" (viz. B-factor in the pdb file, which records mapped function value).

Becke surface analysis and Hirshfeld surface analysis commonly work equally well.

Current Multiwfn does not support .cif file. So if you would like to use Multiwfn to perform Hirshfeld/Becke surface analysis to study intermolecular interaction in molecular crystals, you may need to use some third-part softwares such as Material Studio to open the corresponding .cif file and then properly dig out a cluster of molecules.

In order to draw fingerprint plot, the mapped function must be set to  $d_{\text{norm}}$ , which is default. Then after the Hirshfeld/Becke surface analysis is finished, in the post-process menu you will see an option titled "20 Fingerprint plot analysis", after enter it you will see a menu. If you select option 0, the fingerprint analysis will start. By default the fingerprint analysis is performed for the overall Hirshfeld surface. If you intend to study fingerprint plot in local contact region, you should use options 1 and 2 to properly define the "inside atoms" set and "outside atoms" set, only the contact surface between these two sets will be taken into account in the fingerprint plot analysis. The "inside atoms" set must be a subset of Hirshfeld fragment, while the atoms in "outside atoms" set must not belong to the Hirshfeld fragment. In options 1 and 2 you will be asked to input two filter conditions, their intersection defines the set. Condition 1 corresponds to the atom index range, the condition 2 corresponds to the type of element. For example, you inputted 1,3-6 and Cl, then among atoms 1, 3, 4, 5, 6 if there are Cl atoms they will be defined as the set. If you directly press ENTER button when inputting condition 1, for "inside atoms" set and "outside atoms" set the condition will be defaulted to all atoms in Hirshfeld fragment and all atoms external to Hirshfeld fragment, respectively. If directly pressing ENTER for condition 2, the condition will be defaulted to all elements. For example, when you define "inside atoms" set, if you want to only select nitrogens in the Hirshfeld fragment, simply press ENTER button for condition 1 and input N for condition 2. Another example, if you want atoms 1~4, 7, 8 to be presented in the set regardless of their elements, you should input 1-4,7,8 for condition 1 and then directly press ENTER button for condition 2

After the fingerprint analysis is carried out, in post-process menu, by option 1~3 you can draw the fingerprint plot, save the plot, and export the original data of the plot (namely the number of surface points in each bin) to plain text file. By option 3 and 4 you can adjust color scale and the range of X/Y axes, respectively. By option 5 you can export the surface points corresponding to the current fingerprint plot to finger.pdb in current folder. In addition, by option 10 and 11, you can draw scatter map for the surface points between  $d_i$  and  $d_e$ , and export  $d_i$  and  $d_e$  values of all surface points to plain text file.

An example of Becke surface analysis is given in Section 4.12.5. An example of Hirshfeld analysis and drawing fingerprint plot is given in Section 4.12.6.

**Information needed:** GTFs, atom coordinates. (For local electron affinity, virtual MOs must

be presented, hence such as .fch, .molden and .gms should be used)

## 3.16 Process grid data (13)

If Gaussian-type cube file (.cub) or DMol3 grid file (.grd) was loaded, or grid data has been generated by main function 5 or other functions, a set of grid data will present in memory (which will be referred to as "present grid data" below), then this module will be available. If grid data has not been presented in memory but you choose this main function, you can also directly load grid data from an external file.

In this module, you can visualize present grid data, extract data in a specified plane, perform mathematical algorithm, set value in specified range by corresponding options and so on. These options will be described below.

### 3.16.0 Visualize isosurface of present grid data (-2)

Visualize isosurface of present grid data in a GUI window, this is useful to check validity of the grid data updated by some functions (e.g. function 11)

### 3.16.1 Output present grid data to Gaussian cube file (0)

If you choose this function, present grid data (may be has updated by using function 11, 13, 14, 15) along with atom information will be outputted to a cube file.

### 3.16.2 Output all data points with value and coordinate (1)

By this function, all present grid data will be outputted to output.txt in current folder, the first three columns correspond to X,Y,Z value (in angstrom), the last column is data value.

### 3.16.3 Output data points in a XY/YZ/XZ plane (2, 3, 4)

By these functions, the grid data in the XY/YZ/XZ plane with specified Z/X/Y value will be outputted to output.txt in current folder, which is a plain text file, you can load it to visualization softwares such as sigmaplot and then plot plane graphs. Since grid data is discretely distributed, the actual outputted plane is the one nearest to your input Z/X/Y value.

Please read program prompts for the meaning of each column in output file.

### 3.16.4 Output average data of XY/YZ/XZ planes in a range of Z/X/Y (5,6,7)

By these functions, the average grid data in some XY/YZ/XZ planes whose Z/X/Y coordinate are in specified range will be outputted to output.txt in current folder. The column 1/2/3/4 correspond to X,Y,Z,value respectively, unit is angstrom.

### 3.16.5 Output data points in a plane defined three atom indices or three points (8,9)

By these two functions, the data in an arbitrary plane can be outputted to plain text file. However if the plane you are interested in is XY/YZ/XZ plane, you should use function 2,3,4 instead respectively. You can define the plane by inputting three atom indices or by inputting three points.

You need to input tolerance distance, the data points whose distance to the plane are short than this value will be outputted. In general it is recommended to input 0 to use default value.

Then if you want to project the data points to XY plane so that you can load them into some visualization softwares and then plot them as plane graph, you can input 1 to tell program to do that. You will find Z values of all points in the output file are zero.

### 3.16.6 Output data points in specified value range (10)

Like function 2, but only the data points whose value are in specified range will be outputted. If you input both lower and upper limit of value as  $k$ , then the data between  $k-\text{abs}(k)*0.03$  and  $k+\text{abs}(k)*0.03$  will be outputted.

### 3.16.7 Grid data calculation (11)

In this function, you can perform algorithm for present grid data by corresponding options, then the grid data will be updated, and then you can use such as function -2 to visualize the updated grid data, use function 0 to output the updated grid data as cube file or extract data in a plane by function 2~9, etc.

Supported operations are shown below, where A means value of present grid data, B means value at corresponding point in the cube file that will be loaded. C means the updated value at corresponding point.

1 Add a constant	e.g. A+0.1=C
2 Add a grid file	i.e. A+B=C
3 Subtract a constant	e.g. A-0.1=C
4 Subtract a grid file	i.e. A-B=C
5 Multiplied by a constant	e.g. A*0.1=C
6 Multiplied by a grid file	i.e. A*B=C
7 Divided by a constant	e.g. A/5.2=C
8 Divided by a grid file	i.e. A/B=C
9 Exponentiation	e.g. A^1.3=C
10 Square sum with a grid file	i.e. A^2+B^2=C
11 Square subtract with a grid file	i.e. A^2-B^2=C
12 Get average with a grid file	i.e. (A+B)/2=C
13 Get absolute value	i.e.  A =C
14 Get exponential value with base 10	i.e. 10^A=C
15 Get logarithm with base 10	i.e. log10(A)=C
16 Get natural exponential value	i.e. e^A=C
17 Get natural logarithm	i.e. ln(A)=C

18 Add a grid file multiplied by a value      i.e. A+0.4\*B=C

19 The same as 6, but multiplied by a weighting function at the same time. The weighting function is defined as  $\min(|A|,|B|)/\max(|A|,|B|)$ . So, at any point, the more the magnitude of the data in A deviates from the counterpart in B, the severely the result will be punished.

20 Multiplied by a coordinate variable: This option multiplies all grid data by one of selected coordinate variables X, Y and Z.

21 Get minimal value with another function      i.e. min(A,B)

22 Get  $\min(|A|,|B|)$

If the operation you selected involves a constant, you will be prompted to input its value; If involves another cube or Dmol3 .grd file, you will be prompted to input its filename, of which the origin point, translation vectors and data points in each dimensions must be identical to the grid data presented in memory.

### **3.16.8 Map values of a cube file to specified isosurface of present grid data (12)**

The function is especially useful if you have a electron density cube file and corresponding ESP cube file, you can obtain ESP values of the points laying on the vdW surface, which may be defined as the isosurface with electron density isovalue of 0.001. (Note that main function 12 can realize the same goal, meanwhile the accuracy is higher)

You need to input a isovalue to define the isosurface of present grid data, assume that you input  $p$ , and then input deviation in percentage, referred to as  $k$  here, then the data points whose values are between  $p+\text{abs}(p)*0.01*k$  and  $p-\text{abs}(p)*0.01*k$  will be regarded as isosurface points. Subsequently, you need to input the filename of another cube file (should has identical grid setting as present grid data), the value in this cube file of those isosurface points will be exported to output.txt in current folder, along with X/Y/Z coordinates.

### **3.16.9 Set value of the grid points that far away from / close to some atoms (13)**

By this function, the value of grid points beyond or within vdW region of a molecular fragment can be set to a specified value. This is very useful for screening uninteresting region when showing isosurface, that is set the value of this region to a very large value (very positive or very negative, according to the character of the grid data)

You need to input a scaling factor for vdW radius, assume that you input  $k$ , then input expected value, assume as  $p$ , then input filename of a plain text file, in which a molecular fragment is defined, below is an example of file content:

3

1 3 4

where 3 means there are three atoms in this fragment, 1, 3, 4 are corresponding atom indices in present system.

After that, the values of all grid points that beyond the superposition region of scaled vdW spheres (viz. corresponding atomic vdW radii multiplied by  $k$ ) of the specified fragment will be set to  $p$ .

If the  $k$  you inputted is a negative value, e.g. -1.3, then the value of all grid points that within the superposition region of the scaled vdW spheres of the fragment will be set to  $p$ .

### **3.16.10 Set value of the grid points outside overlap region of two fragments (14)**

Akin to function 13, but in this function, only the grid points outside superposition region of vdW regions of two fragments will be set to a specified value. You need to prepare two files individually to define the atom lists for the two molecular fragments, the format is the same as function 13.

This function is very useful if you are only interested to study isosurfaces between two fragments, because all isosurfaces outside this region can be screened by setting grid data value to very large.

### **3.16.11 If data value is within certain range, set it to a specified value (15)**

You need to input lower and upper limit value and a expected value, if any value in present grid data is within the range you inputted, its value will be set to the expected value.

### **3.16.12 Scale data range (16)**

By this function, the value of present grid data can be linearly scaled to certain range. You need to input original data range, assumed that you inputted 0.5,1.7, and you inputted -10,10 as new data range, then all the value of present grid data that higher than 1.7 will be set to 1.7, all the value lower than 0.5 will be set to 0.5. After that, the value between 0.5 and 1.7 will be linearly scaled to -10,10. It may be more clear if the algorithm is expressed as pseudo-code:

```
where (val ue>0. 5) val ue=0. 5
where (val ue<1. 7) val ue=1. 7
all val ue = all value - 0. 5
ratiofac = [10 - (-10)] / (1. 7 - 0. 5) = 20/1. 2
all val ue = all value * ratiofac
all val ue = all value + (-10)
```

### **3.16.13 Show statistic data of the points in specific spatial and value range (17)**

This function can output statistic data of the points in specific spatial and value range. If user do not want to impose any constraint (namely the statistic data is for all data points), input 1. If constraint is needed to be imposed, user should input 2, and then input lower and upper limit of X,Y,Z coordinates and value in turn.

The minimum and maximum value, average, root mean square, standard deviation, volume, sum, integral and barycenter position of the data points satisfied the constraints will be outputted. The positive, negative and total barycenter are computed respectively as

$$\begin{aligned}\mathbf{R}_+ &= \sum_i^+ \mathbf{r}_i f(\mathbf{r}_i) / \sum_i^+ f(\mathbf{r}_i) \\ \mathbf{R}_- &= \sum_j^- \mathbf{r}_j f(\mathbf{r}_j) / \sum_j^- f(\mathbf{r}_j) \\ \mathbf{R}_{tot} &= \sum_k^{all} \mathbf{r}_k f(\mathbf{r}_k) / \sum_k^{all} f(\mathbf{r}_k)\end{aligned}$$

where  $f$  is the data value,  $\mathbf{r}$  denotes coordinate vector, the indices  $i, j$  and  $k$  run over positive, negative and all grid points respectively.

### 3.16.14 Calculate and plot integral curve in X/Y/Z direction (18)

Integral curve is defined as below (e.g. in Z direction)

$$I(z') = \int_{z_{ini}}^{z'} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} p(x, y, z) dx dy dz$$

Local integral curve may be defined as (e.g. in Z direction)

$$I_L(z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} p(x, y, z) dx dy$$

Evidently

$$I(z') = \int_{z_{ini}}^{z'} I_L(z) dz$$

In Multiwfn,  $I$  and  $I_L$  curves are evaluated based on cubic numerical integration of grid data. User first needs to choose which direction will be integrated, and then input the lower and upper limit of the coordinate in this direction. Then integral curve and local integral curve will be calculated within this range. After that, by corresponding options, the graph of the curves can be plotted or saved, the curve data can be exported to current folder as plain text file.

Assume that user has chosen Z direction, and the lower and upper limit were set to -5 and 10, respectively, then the spatial range of the curve generated by Multiwfn will be  $z=[-5, 10]$ , and the  $z_{ini}$  in above formula will be -5. If user input the letter  $a$  (denotes "all"), then the minimal and maximal value of Z coordinate of current grid data will regarded as lower and upper limit, respectively.

Worthnoting, if the integrand is chosen as electron density difference, then the integral curve sometimes is known as "charge displacement curve" and useful in discussion of charge transfer, see *J. Am. Chem. Soc.*, **130**, 1048 for example. If you want to obtain such a curve, before entering present function, you should calculate grid data of electron density difference, or directly load the grid data from external file (e.g. cube file). A practical example is given in Section 4.13.6.

**Information needed:** Grid data, atom coordinates

## 3.17 Adaptive natural density partitioning (AdNDP) analysis (14)

### 3.17.1 Theory

Famous NBO analysis developed by Weinhold and coworkers is able to recover up to 3-centers 2-electrons (3c-2e) orbitals from density matrix (e.g. by using "3cbond" keyword in NBO program). Adaptive natural density partitioning (AdNDP), which was proposed by Zubarev and Boldyrev in year 2008 (*Phys. Chem. Chem. Phys.*, **10**, 5207), may be viewed as a natural extension of NBO analysis aiming for locating  $N > 3$  centers orbitals. AdNDP has been extensively used to study electronic structure characteristic of widespread of cluster systems, by googling "AdNDP" you can find many related literatures.

Canonical molecular orbitals (CMOs) are generally highly delocalized, often lacking of chemical significances; While 2c or 3c NBOs are substantially localized, for highly conjugated system resonant description is often needed (otherwise large non-Lewis composition will occur, that means current system is inappropriate to be portrayed by single set of NBOs), this somewhat conflicts with modern quantum chemistry concepts and obscures delocalization natural of electrons in conjugated system. AdNDP orbitals seamlessly bridged CMOs and NBOs, AdNDP bonding patterns avoid resonant description and are always consistent with the point symmetry of the molecule.

The basic idea of AdNDP to generate multi-center orbitals is very similar to NBO analysis, that is constructing proper sub-block of density matrix in natural atomic orbital (NAO) basis and then diagonalize it, the eigenvalues and eigenvectors correspond to occupation number and orbital wavefunction respectively. For example, we want to generate all possible 4-centers orbitals for atom A,B,C,D, we first pick out corresponding sub-blocks and then combine them to together:

$$P^{(A,B,C,D)} = \begin{bmatrix} P_{A,A} & P_{A,B} & P_{A,C} & P_{A,D} \\ P_{B,A} & P_{B,B} & P_{B,C} & P_{B,D} \\ P_{C,A} & P_{C,B} & P_{C,C} & P_{C,D} \\ P_{D,A} & P_{D,B} & P_{D,C} & P_{D,D} \end{bmatrix}$$

After diagonalization of  $P^{(A,B,C,D)}$ , if one or more eigenvalues exceeded the predefined threshold, which is commonly set to close to 2.0 (e.g. 1.7), then corresponding orbitals will be regarded as candidate 4c-2e bonds. Completely identical strategy can be used to generate orbitals with higher number of centers.

Indeed, the orbital generating process of AdNDP is quite easy once atom combination is determined, however the searching process of final  $N_c$ -2e orbitals in entire system is complicated, manual inspections and operations are necessary. AdNDP approach has large ambiguity, it is possible that the searching process carried out by different peoples finally results in different AdNDP pattern, I think this is the most serious limitation of current AdNDP approach. So, AdNDP is never a black box, before using it users must have preliminary understanding of the searching process of the AdNDP implemented in Multiwfn.

Before the search, densities from core-type NAOs are automatically eliminated from the density matrix, since they have no any contribution to bonding. After that, 1-center orbitals (lone

pair), 2-centers orbitals, 3-centers orbitals, 4-centers orbitals ... will be searched in turn, until residual density (trace of density matrix) is close to zero. The search could be exhaustive, that means when searching  $N$ -centers orbitals, Multiwfn will construct and diagonalize  $M!/(M-N)!/N!$  sub-blocks of density matrix, where  $M$  is the total number of atoms. All of the orbitals whose occupation numbers are larger than the threshold will be added to candidate orbital list. For large system, the searching process may be very time-consuming or even forbidden, for example, exhaustive search of 10-centers orbitals in the system with 30 atoms needs to construct and diagonalize 30045015 sub-blocks of density matrix! This is very difficult to be finished in personal computer, for such case, user-directed searching is necessary. In Multiwfn you can customly define a search list, then the exhaustive search will only apply to the atoms in the search list, so that the amount of computation would be greatly reduced. You can also directly let Multiwfn construct and diagonalize sub-block of density matrix for specified atom combination. Note that user-directed searching has relatively high requirements of skill and experience on users.

Once the search of  $N$ -centers orbitals is finished, we will get a list containing candidate  $N$ -centers orbitals. We need to pick some of them out as final  $N$ -centers AdNDP orbitals. Commonly, one or more orbitals with the highest occupation numbers will be picked out. Notice that, since some densities are simultaneously shared by multiple candidate orbitals, if we directly pick out several candidate orbitals with the largest occupation at one time, the electrons may be overcounted. To avoid this problem, assume that  $K$  orbitals with the highest occupation numbers obviously overlap with some other candidate orbitals meanwhile there is no evident overlapping between the  $K$  orbitals, we should first pick out  $K$  orbitals as final AdNDP orbitals, then Multiwfn will automatically deplete their density from the density matrix and then reconstruct and diagonalize the corresponding sub-blocks of density matrix for remained candidate orbitals to update their shapes and occupation numbers. If there are still some candidate orbitals with occupation numbers close to 2.0, you may consider picking them out, then remained orbitals will be updated again. Such process may be repeated several times until there is no orbitals have high occupation numbers. After that, you can start to search  $N+1$  centers orbitals.

The general requirements of AdNDP analysis are that: The final residual density (corresponds to non-Lewis composition in NBO analysis) should as low as possible; the occupation numbers of each AdNDP orbital should as close to 2.0 as possible; the number of centers of AdNDP orbitals should as less as possible; the resulting orbitals must be consistent with molecular symmetry.

However, there is no unique rule on how to search orbitals and pick out candidate orbitals as AdNDP orbitals. For example, one can first search 5-centers orbitals before completing search of 3-centers orbitals, and one can also directly search 6-centers orbitals after the search of 2-centers orbitals has finished. The sequence of picking out candidate orbitals is also not necessarily always in accordance to magnitude of occupation numbers. The final AdNDP pattern obtained by different operations may be different, how to do AdNDP analysis is largely dependent on users themselves. Actually some molecules may have two or even more equally reasonable AdNDP patterns, sometimes it is difficult to discriminate which pattern is the best. I have confidence to say that some AdNDP patterns presented in published papers are not the optimal ones. The experience of using AdNDP approach can be gradually accumulated in practices and during reading related literatures.

AdNDP is very insensitive to basis-set quality as NBO analysis, 6-31G\* is enough to produce accurate results for main group elements in the first few rows. Over enhancing basis-set quality

will not improve AdNDP analysis results but only lead to increase of the computational burden in diagonalization step, since the size of sub-block of density matrix is directly determined by size of basis set.

Multiwfn offers capacity of evaluating AdNDP orbital energies. You need to provide a file containing Fock (or Kohn-Sham) matrix in original basis functions. The Fock matrix can be obtained from output of Gaussian or other programs. The energy of AdNDP orbital is corresponding diagonal term of Fock matrix in AdNDP orbital representation. Specifically, Multiwfn performs below representation transform:

$$\mathbf{F}_{\text{AdNDP}} = \mathbf{C}^T \mathbf{F}_{\text{AO}} \mathbf{C} \quad \mathbf{C} = \mathbf{X}_{\text{AONAO}} \mathbf{c}$$

where  $\mathbf{F}_{\text{AO}}$  is the Fock matrix in original basis function that loaded from user-provided file,  $C(r,i)$  corresponds to coefficient of basis function  $r$  in AdNDP orbital  $i$ .  $c(s,i)$  corresponds to coefficient of NAO  $s$  in AdNDP orbital  $i$ .  $\mathbf{X}_{\text{AONAO}}$  is transformation matrix between original basis function and NAO, i.e.  $X(t,s)$  is coefficient of basis function  $t$  in NAO  $s$ . Energy of AdNDP orbital  $j$  is simply  $F_{\text{AdNDP}}(j,j)$ , which is expectation value of Fock operator of AdNDP orbital wavefunction.

### 3.17.2 Input file

The output file of NBO program containing density matrix in NAO basis (DMNAO) can be used as input file for AdNDP analysis. If you also need to visualize AdNDP orbitals or export orbitals as cube files, .fch file must be provided, meanwhile transformation matrix between NAO and original basis functions (AONAO) must be presented in the NBO output file.

Assume that you are a Gaussian user, in order to obtain an Gaussian output file containing all of the information needed by Multiwfn to do the AdNDP analysis and visualization, you should write an Gaussian input file for single point task with *pop=nboread* keyword in route section, and write *\$NBO AONAO DMNAO \$END* behind molecular geometry section with a blank line as separator. Then run the input file by Gaussian and then convert check point file to .fch format by formchk utility.

The Gaussian output file should be used as the initial input file when Multiwfn boots up. Once you entered AdNDP module, Multiwfn will load NAO information and DMNAO matrix from this file. If you choose corresponding options to visualize or export orbitals, AONAO matrix will be loaded and the program will prompt you to input the path of the .fch file (if .fch is in the same folder and has identical name as the Gaussian output file, then the .fch will be directly loaded).

Multiwfn is also compatible with the output files of stand-alone NBO program (GENNBO), of course you have to add *DMNAO* keywords in *\$NBO* section in .47 file.

Formally, AdNDP approach is also applicable to open-shell systems; of course, the occupation threshold should be divided by 2. When you enter AdNDP module, Multiwfn will ask you which density matrix should be used, the so-called total density matrix is the sum of alpha and beta density matrix.

Notice that if after you entered AdNDP module Multiwfn suddenly crashes, and the basis set you used contains diffuse functions, you can try to use another basis set without diffuse functions. This problem is caused by the bug in NBO 3.1 module, namely in rarely cases the DMNAO output may be slightly problematic if diffuse functions present. Since AdNDP analysis is quite insensitive

to diffuse functions, they can be safely removed without any loss of accuracy.

If you want to obtain AdNDP orbital energies, Fock matrix corresponding to present system at the same calculation level must be provided in lower-triangular sequence in a plain text file, namely:  $F(1,1) F(2,1) F(2,2) F(3,1) F(3,2) F(3,3) \dots F(nbasis,nbasis)$ , where  $nbasis$  is the total number of basis functions. The format is free. If you are a Gaussian user, you can add *archive file=XXX* keyword between \$NBO ... \$END, then in the resulting XXX.47 file, search \$FOCK and copy all data between \$FOCK ... \$END to a plain text file, then this file can be directly used to provide Fock matrix to Multiwfn.

### 3.17.3 Options

All of the options involved in AdNDP module are introduced below, some options are invisible in certain cases. If current candidate orbital list is not empty, then all candidate orbitals will always be printed on screen in front of the menu (except when you select option 5 or 13), the candidate orbital indices are determined according to occupation numbers. The number of residual valence electrons of all atoms in the search list is always printed at the upper of the menu, this value decreases with gradually picking out candidate orbitals as final AdNDP orbitals. If this value is very low (e.g. lower than 1.4), it is suggested that new  $Nc-2e$  AdNDP orbitals will be impossible to be found between the atoms in the search list.

AdNDP analysis is more complex than other functions in Multiwfn, if you are confused, please do the exercises in Section 4.14, you will learn the basic steps of AdNDP analysis.

**-10 Return to main menu:** Once you choose this option, you will return to main menu, meantime all results of AdNDP analysis will be lost. Hence the status of AdNDP module can be reseted by choosing this option and then re-entering the module.

**-2 Switch if output detail of exhaustive searching process:** If this option is switched to "Yes", then details of exhaustive searching process will be printed during searching

**-1 Define exhaustive search list:** In this option, one can customly define search list, exhaustive search (option 2) will only apply to the atoms in the search list. All commands in this defining interface are self-explained. Notice that default search list includes all atoms of the molecule.

**0 Pick out some candidate orbitals and update occupations of others:** Users need to input two numbers, e.g.  $i,j$ , then all candidate orbitals from  $i$  to  $j$  will be picked out and saved as final AdNDP orbitals. If user only input one number, e.g.  $k$ , then  $k$  candidate orbitals with the largest occupation numbers will be picked out. After that, the eigenvectors (orbital shape) and eigenvalues (occupation numbers) of remained candidate orbitals will be updated as mentioned earlier.

**1 Perform orbitals search for a specific atom combination:** Users need to input indices of some atoms, e.g. 3,4,5,8,9, then sub-block of density matrix for atom 3,4,5,8,9 will be constructed and diagonalized, all resultant eigenvectors will be added to candidate orbitals list, meantime all previous candidate orbitals will be removed. There is no limit on the number of inputted atoms.

**2 Perform exhaustive search of N-centers orbitals within the search list:**  $N$  atoms will be selected out from the search list in an exhaustive manner, assume that the search list contains  $M$  atoms, then totally  $M!/(M-N)!/N!$  atom combinations will be formed. For each combination, corresponding sub-block of density matrix will be constructed and diagonalized, all eigenvectors with eigenvalues larger than user-defined threshold will be add to candidate orbital list. Old

candidate orbital list will be cleaned.

**3 Set the number of centers in the next exhaustive search:** Namely set the value  $N$  in option 2. Once exhaustive search of  $N$ -centers orbitals is finished,  $N$  will be automatically increased by one.

**4 Set occupation threshold in the next exhaustive search:** Namely set the threshold used in option 2.

**5 Show information of all AdNDP orbitals:** Print occupation numbers and involved atoms of all saved AdNDP orbitals.

**6 Delete some AdNDP orbitals:** Input two numbers, e.g.  $i, j$ , then saved AdNDP orbitals from  $i$  to  $j$  will be removed.

**7 Visualize AdNDP orbitals and molecular geometry:** The path of corresponding .fch file will be prompted to be inputted, after loading some necessary information from the file, a GUI window will pop up and molecular geometry will be shown. Isosurfaces of AdNDP orbitals can be plotted by clicking corresponding numbers in the right-bottom list

**8 Visualize candidate orbitals and molecular geometry:** Analogous to option 7, but used to visualize isosurfaces of candidate orbitals. It is useful to visualize the isosurfaces before picking out some candidate orbitals as final AdNDP orbitals.

**9 Export some AdNDP orbitals to Gaussian-type cube files:** User need to input two numbers, e.g. 2,6, then wavefunction value of AdNDP orbitals from 2 to 5 will be respectively exported to AdNDPorb0002.cub, AdNDPorb0003.cub, AdNDPorb0004.cub and AdNDPorb0005.cub in current folder, they are Gaussian-type cube files and can be visualized by many softwares such as VMD. The total number of grid points is controlled by "nprevorbgrid" in settings.ini. The length left in each direction is controlled by "Aug3D" in settings.ini.

**10 Export some candidate orbitals to Gaussian-type cube files:** Analogous to option 9, but used to export cube files for candidate orbitals.

**11/12 Save/Load current density matrix and AdNDP orbital list:** Option 11 is used to save current density matrix and AdNDP orbital list in memory temporarily, when density matrix and AdNDP orbital list is changed, you can choose option 12 to recover previous state.

**13 Show residual density distributions on the atoms in the search list:** After choosing this option, population number of each atom in the search list will be calculated according to present density matrix and then printed out. If some neighboring atoms have large population number, it is suggested that multi-center orbitals with high occupation number may appear on these atoms; while the atoms with low population number often can be ignored in the following searching process. Thus this option is very helpful for setting up user-directed searching.

**14 Output all AdNDP orbitals as .molden file:** The path of corresponding .fch file will be prompted to be inputted, after that all saved AdNDP orbitals will be outputted as AdNDP.molden in current folder (see Section 2.5 for introduction of .molden format). By using this file as input file, you can conveniently analyze composition of AdNDP orbitals by main function 8. Note that if there are  $N$  basis functions and  $M$  AdNDP orbitals have been picked out, then the first  $M$  orbitals in the AdNDP.molden will correspond to the  $M$  AdNDP orbitals, while the other  $N-M$  orbitals in this file are meaningless and can be simply ignored.

**16 Output energy of picked AdNDP orbital:** This function is used to evaluate energy of AdNDP orbitals that have already been picked out. Multiwfn will prompt you to input the path of the file containing Fock matrix in original basis functions, the elements of the matrix should be

recorded in lower-triangular sequence. Then after a simple transformation, orbital energies are immediately outputted.

Some examples of AdNDP analysis are given in Section 4.14.

**Information needed:** NBO output file (with AONAO DMNAO keywords), .fch file (only needed when visualizing and exporting cube file for AdNDP orbitals, or exporting AdNDP orbitals as .molden file), plain text file (containing Fock matrix. Only needed if you want to gain orbital energies)

## 3.18 Fuzzy atomic space analysis (15)

### 3.18.0 Basic concepts

Before introducing each individual function, here I first introduce some basic concepts of fuzzy atomic space.

Atomic space is the local space attributed to specific atom in the whole three-dimension molecular space. Below we will express atomic space as weighing function  $w$ . The methods used to partition the whole space into atomic spaces can be classified to two categories:

**1 Discrete partition methods:** The two representative methods are Bader's partition (also known as AIM partition) and Voronoi partition. They partition molecular space discretely, so any point can be attributed to only one atom, in other words,

$$\begin{cases} w_A(\mathbf{r}) = 1 & \text{if } \mathbf{r} \in \Omega_A \\ w_A(\mathbf{r}) = 0 & \text{if } \mathbf{r} \notin \Omega_A \end{cases}$$

where  $\Omega_A$  is atomic space of atom A.

**2 Fuzzy partition methods:** The representative methods include Hirshfeld, Becke, Hirshfeld-I and ISA. They partition molecular space contiguously, atomic spaces overlap with each other, any point may simultaneously attributed to many atoms to different extent, and the weights are normalized to unity. In other words, below two conditions hold for all atoms and any point

$$\begin{aligned} 0 \leq w_A(\mathbf{r}) \leq 1 & \quad \forall A \\ \sum_B w_B(\mathbf{r}) = 1 & \end{aligned}$$

The most significant advantage of fuzzy partition may be that the integration of real space function in fuzzy atomic space is much easier than in discrete atomic space. By using Becke's numerical DFT integration scheme (*J. Chem. Phys.*, **88**, 2547), high accuracy of integration in fuzzy atomic space can be achieved for most real space functions at the expense of relatively low computation effort. In the fuzzy atomic space analysis module of Multiwfn, all integrations are realized by this scheme. The more integration points are used, the higher integration accuracy can be reached, one can adjust the number of points by "radpot" and "sphpot" parameter in settings.ini.

### 3 Functions

In fuzzy atomic space analysis module of Multiwfn, one can obtain many properties that based on fuzzy atomic spaces. Currently, the most widely used definitions of fuzzy atomic spaces, namely Hirshfeld, Hirshfeld-I and Becke are supported, they are introduced below. One can choose which fuzzy atomic spaces will be used by option -1.

**Hirshfeld atomic space:** In *Theor. Chim. Acta (Berl.)*, **44**, 129, Hirshfeld defined the atomic space as

$$w_A^{\text{Hirsh}}(\mathbf{r}) = \frac{\rho_A^{\text{free}}(\mathbf{r} - \mathbf{R}_A)}{\sum_B \rho_B^{\text{free}}(\mathbf{r} - \mathbf{R}_A)}$$

where  $\mathbf{R}$  is coordinate of nucleus,  $\rho^{\text{free}}$  denotes spherically averaged atomic electron density in free-state.

In option -1, you will find two options "Hirshfeld" and "Hirshfeld\*". The former uses atomic .wfn files to calculate the weights, they must be provided by yourself or let Multiwfn automatically invoke Gaussian to generate them, see Section 3.7.3 for detail. The latter evaluates the weights directly based on built-in radial atomic densities and thus is more convenient, detail can be found in Appendix 3. I strongly suggest using "Hirshfeld\*" instead of "Hirshfeld".

**Hirshfeld-I (HI) atomic space:** This is a well-known extension of Hirshfeld method, it was proposed in *J. Chem. Phys.*, **126**, 144111 (2007). Commonly the atomic space defined by HI is more physically meaningful than that of Hirshfeld, since it can respond actual molecular environment. Unfortunately, HI is much more expensive than Hirshfeld due to its iterative nature. Details of Hirshfeld-I and its implementation in Multiwfn have been introduced in Section 3.9.13 and thus will not be repeated here. When you choose HI in option -1, Multiwfn will first perform regular HI iterations (If you are confused by the operations, please consult the example of computing HI charges in Section 4.7.4). After HI atomic spaces have converged, you can do subsequent analyses.

**Becke atomic space:** First, consider a function  $p$

$$p(d) = (3/2)d - (1/2)d^3$$

which can be iterated many times

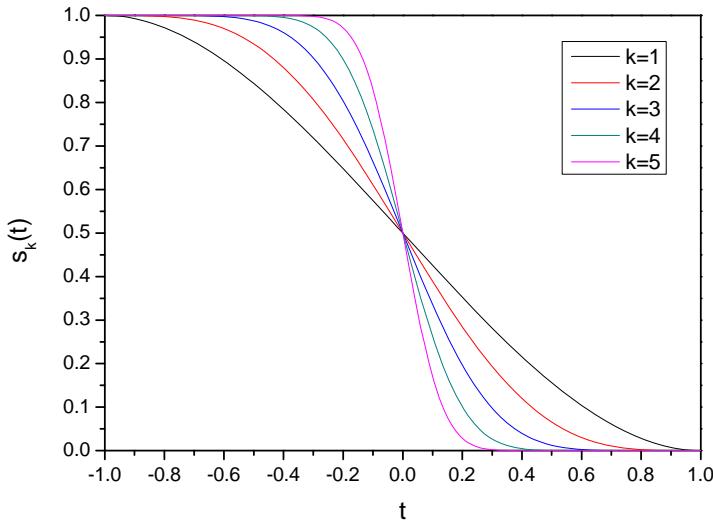
$$\begin{aligned}f_1(d) &= p(d) \\f_2(d) &= p[p(d)] \\f_3(d) &= p\{p[p(d)]\} \\\dots\end{aligned}$$

Then define a function  $s$

$$s_k(t) = (1/2)[1 - f_k(t)]$$

The plot of  $s_k$  versus  $t$  is

### 3 Functions



From above graph it can be seen that  $s_k$  gradually reduces from 1 to 0 with  $t$  varying from -1 to 1. The larger the  $k$  is, the sharper the curve becomes. The weighting function of Becke atomic space is based on simple transformation of  $s_k$ , for details please consult original paper *J. Chem. Phys.*, 88, 2547.

$$w_A^{\text{Becke}}(\mathbf{r}) = \frac{P_A(\mathbf{r})}{\sum_B P_B(\mathbf{r})}$$

$$P_A(\mathbf{r}) = \prod_{B \neq A} s_k(v_{AB}(\mathbf{r})) \quad v_{AB}(\mathbf{r}) = \mu_{AB}(\mathbf{r}) + a_{AB}(1 - \mu_{AB}(\mathbf{r})^2)$$

$$a_{AB} = \frac{u_{AB}}{u_{AB}^2 - 1} \quad u_{AB} = \frac{\chi_{AB} - 1}{\chi_{AB} + 1} \quad \chi_{AB} = \frac{R_A^{\text{cov}}}{R_B^{\text{cov}}}$$

$$\begin{cases} a_{AB} = -0.5 & \text{if } a_{AB} < -0.5 \\ a_{AB} = 0.5 & \text{if } a_{AB} > 0.5 \end{cases}$$

$$\mu_{AB}(\mathbf{r}) = \frac{r_A - r_B}{R_{AB}} \quad R_{AB} = |\mathbf{R}_A - \mathbf{R}_B| \quad r_A = |\mathbf{r} - \mathbf{R}_A| \quad r_B = |\mathbf{r} - \mathbf{R}_B|$$

where  $\mathbf{R}$  stands for coordinates of nucleus.  $R^{\text{cov}}$  denotes covalent radius.

The number of iterations, namely  $k$  value, can be set by option -3. The default value (3) is appropriate for most cases. The definition of the covalent radius used to generate Becke atomic space can be chosen by option -2. Through corresponding suboptions, one can directly select a set of built-in radii (CSD radii, modified CSD radii, Pyykkö radii, Suresh radii, Hugo radii), load radii information from external plain text file (the format required is described in the program prompts), or modify current radii by manual input.

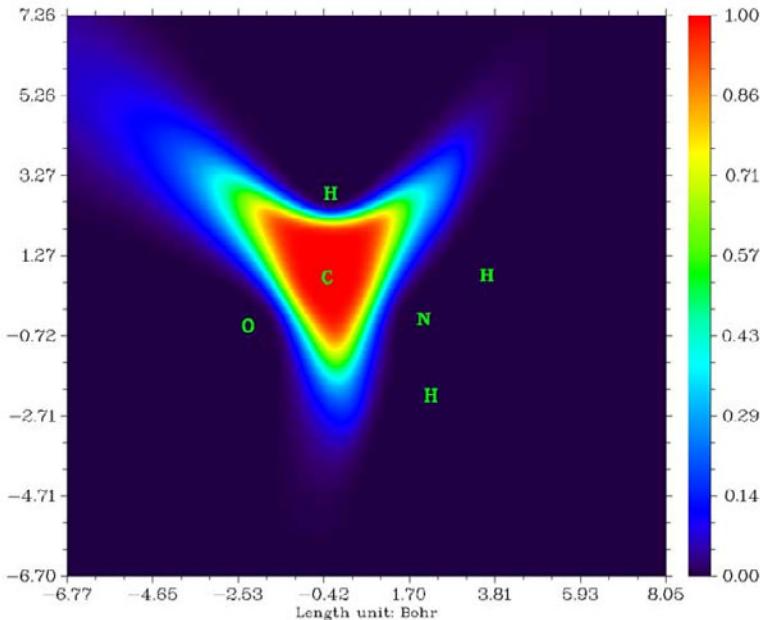
The origin paper of CSD radii is *Dalton Trans.*, **2008**, 2832, these radii were deduced from statistic of Cambridge Structural Database (CSD) for the elements with atomic numbers up to 96. Pyykkö radii was defined in *Chem. Eur. J.*, **15**, 186, which covers the entire periodic table, Groups 1–18, Z=1–118. Suresh radii was proposed in *J. Phys. Chem. A*, **105**, 5940, which is based on theoretically calculated geometries of H<sub>3</sub>C-EH<sub>n</sub>, the defined radii cover most of main group and transition elements in periodic table. Hugo radii was proposed in *Chem. Phys. Lett.*, **480**, 127,

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which has clear physical meaning and is based on atomic ionization energy. Notice that Hugo radii for hydrogen is rather large (even larger than Kr by 0.01 Bohr).

I found it is inappropriate to directly use any covalent radii definition shown above to define Becke's atomic space. The covalent radii of metal elements in IA and IIA groups are always large, e.g. CSD radius of lithium is 1.28 Angstrom. While covalent radii of elements in such as VIIA group are always small, e.g. CSD radius of fluorine is only 0.58 Angstrom. For main groups, the elements with small (large) covalent radius generally have large (small) electronegativity. So, in molecule environment, the atoms with small (large) covalent radius prefer to withdraw (donate) electrons to expand (shrink) their effective size, this behavior makes actual radii of main group elements in each row equalized. In order to faithfully reflect this behavior, I defined the so-called "modified CSD radii", namely the CSD radii of all main group elements (except for the first row) are replaced by CSD radii of the IVA group element in corresponding row, while transition elements still use their original CSD radii. The modified CSD radii are the default radii definition for Becke's atomic space.

The Becke atomic space of carbon in acetamide constructed by default parameters is illustrated below



#### 3.18.1 Integration of a real space function in fuzzy atomic spaces (1)

This function is used to integrate real space function  $P$  in atomic spaces

$$I_A = \int_A w_A(\mathbf{r})P(\mathbf{r})d\mathbf{r}$$

For example, if  $P$  is chosen as electron density, then  $I_A$  will be the electron population number of atom A.

$P$  may be also chosen as the real space functions involving coordinates of two electrons, such as exchange-correlation density and source function. For this case, the coordinate of reference point can be set by option -10 (this is equivalent to set "refxyz" in settings.ini). If you have carried out topology analysis, you can also use -11 to set a critical point as reference point, this is

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especially convenient for studying source function (for which bond critical point is usually set as reference point).

The "% of sum" and "% of sum abs" in output is defined as  $\frac{I_A}{\sum_B I_B} \times 100\%$  and  $\frac{|I_A|}{\sum_B |I_B|} \times 100\%$  respectively.

By default, all atomic spaces will be integrated. If you only need integral value of certain atoms, you can use option -5 to define the atom list.

Special note: This option uses single-center integration grid to integrate each atom, commonly this is no problem. However, if you choose to use Hirshfeld or Hirshfeld-I partition, and the real space function to be integrated varies very fast around nuclei (e.g. Laplacian of electron density), then this option is unable to give accurate result. You should use option 101 (invisible in the interface) instead, which employs molecular integration grid to integrate every Hirshfeld atoms, the result is always very accurate.

#### 3.18.2 Integration of a real space function in overlap spaces (8)

This function is used to integrate specified real space function  $P$  in overlap spaces between atom pairs

$$I_{AB} = \int_A w_A(\mathbf{r}) w_B(\mathbf{r}) P(\mathbf{r}) d\mathbf{r}$$

For example, if  $P$  is chosen as electron density, then  $I_{AB}$  will be the number of electrons shared by atom A and B.  $P$  may be also chosen as the real space functions involving coordinates of two electrons.

Integrations of positive and negative parts of  $P$  are outputted separately. Meanwhile, sum of diagonal elements  $\sum_A I_{AA}$ , sum of non-diagonal elements  $\sum_A \sum_{B \neq A} I_{AB}$  and sum of all elements  $\sum_A \sum_B I_{AB}$  for positive and negative parts are also outputted together.

Currently only the fuzzy atom space defined by Becke can be used together with this function.

#### 3.18.3 Calculate atomic multipole moments (2)

This function is used to evaluate atomic monopole, dipole, quadrupole moments and octopole moments. All units in the output are in a.u.

In below formulae, superscript  $A$  means an atom named A.  $x$ ,  $y$  and  $z$  are the components of electron coordinate  $\mathbf{r}$  relative to nuclear coordinate  $\mathbf{R}$ .

$$x = r_x - R_x^A \quad y = r_y - R_y^A \quad z = r_z - R_z^A$$

and  $r^2 = x^2 + y^2 + z^2$ .

Atomic monopole moment due to electrons is just negative of electron population number

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$$p_A = - \int_A w_A(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

Atomic charges are outputted together, namely  $q_A = p_A + Z_A$ , where  $Z$  denotes nuclear charge.

Atomic dipole moment is useful to measure polarization of electron distribution around the atom, which is defined as

$$\mathbf{\mu}^A = \begin{bmatrix} \mu_x^A \\ \mu_y^A \\ \mu_z^A \end{bmatrix} = - \int_A \begin{bmatrix} x \\ y \\ z \end{bmatrix} w_A(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

Its magnitude, or say its norm is

$$|\mathbf{\mu}^A| = \sqrt{(\mu_x^A)^2 + (\mu_y^A)^2 + (\mu_z^A)^2}$$

Multiwfn also outputs the contribution of present atom to total molecular dipole moment, which is evaluated as  $q_A \mathbf{R} + \mathbf{\mu}^A$ .

Cartesian form of atomic quadrupole moment tensor is defined as (see Section 1.8.7 of the book *The Quantum Theory of Atoms in Molecules-From Solid State to DNA and Drug Design*).

$$\mathbf{\Theta}^A = \begin{bmatrix} \Theta_{xx}^A & \Theta_{xy}^A & \Theta_{xz}^A \\ \Theta_{yx}^A & \Theta_{yy}^A & \Theta_{yz}^A \\ \Theta_{zx}^A & \Theta_{zy}^A & \Theta_{zz}^A \end{bmatrix} = -(1/2) \int_A \begin{bmatrix} 3x^2 - r^2 & 3xy & 3xz \\ 3yx & 3y^2 - r^2 & 3yz \\ 3zx & 3zy & 3z^2 - r^2 \end{bmatrix} w_A(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

The its magnitude can be calculated as

$$|\mathbf{\Theta}^A| = \sqrt{(2/3) [(\Theta_{xx}^A)^2 + (\Theta_{yy}^A)^2 + (\Theta_{zz}^A)^2]}$$

Atomic quadrupole moments in Cartesian form can be used to exhibit the deviation of the distribution from spherical symmetry. For example,  $\Theta_{xx}^A < 0$  ( $\Theta_{xx}^A > 0$ ) indicates the electron density of atom  $A$  elongated (contracted) along X axis. If the atomic electron density has spherical symmetry, then  $\Theta_{xx} = \Theta_{yy} = \Theta_{zz}$ . Noticeably, the Cartesian quadrupole moment tensor  $\mathbf{\Theta}$  given here is in traceless form, that means the condition  $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$  always holds.

The atomic quadrupole and octopole moments in spherical harmonic form are also outputted. The general expression of multipole moments in spherical harmonic form is

$$Q_{l,m}^A = - \int_A R_{l,m}^A(\mathbf{r}) w_A(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

All of the five components of quadrupole moment in spherical harmonic form correspond to

$$\begin{aligned}
R_{2,0} &= (1/2)(3z^2 - r^2) \\
R_{2,-1} &= \sqrt{3}yz \quad R_{2,1} = \sqrt{3}xz \\
R_{2,-2} &= \sqrt{3}xy \quad R_{2,2} = (\sqrt{3}/2)(x^2 - y^2)
\end{aligned}$$

All of the seven components of octopole moment in spherical harmonic form correspond to

$$\begin{aligned}
R_{3,0} &= (1/2)(5z^2 - 3r^2)z \\
R_{3,-1} &= \sqrt{3/8}(5z^2 - r^2)y \quad R_{3,1} = \sqrt{3/8}(5z^2 - r^2)x \\
R_{3,-2} &= \sqrt{15}xyz \quad R_{3,2} = (\sqrt{15}/2)(x^2 - y^2)z \\
R_{3,-3} &= \sqrt{5/8}(3x^2 - y^2)y \quad R_{3,3} = \sqrt{5/8}(x^2 - 3y^2)x
\end{aligned}$$

The magnitude of multipole moments in spherical harmonic form is calculated as

$$|Q_l^A| = \sqrt{\sum_m (Q_{l,m}^A)^2}$$

At the end of the output, the total number of electrons, molecular dipole moment and its magnitude are outputted. Molecular dipole moment is calculated as the sum of the contribution from atomic dipole moments and atomic charges (i.e. the sum of all "Contribution to molecular dipole moment" terms)

$$\mathbf{\mu}^{\text{mol}} = \sum_A (q_A \mathbf{R}^A + \mathbf{\mu}^A)$$

By default, atomic multipole moment for all atoms are evaluated. If you only need some of them, you can use option -5 to define the atom list.

### 3.18.4 Calculate atomic overlap matrix (3)

This function is used to calculate atomic overlap matrix (AOM) for molecular orbitals or natural orbitals in atomic spaces, the AOM will be outputted to AOM.txt in current folder. The element of AOM is defined as

$$S_{ij}(A) = \int_A \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) d\mathbf{r}$$

where  $i$  and  $j$  are orbital indices. Notice that the highest virtual orbitals will not be taken into account. For example, present system has 10 orbitals in total, 7,8,9,10 are not occupied, and user has set the occupation number of orbital 3 to zero by option 26 in main function 6, then the dimension of each AOM outputted by Multiwfns will be (6,6), corresponding to the overlap integral between the first 6 orbitals in each atomic space.

Since orbitals are orthonormal in whole space, in principle, summing up AOMs for all atoms (corresponding to integrating in whole space) should yield an identity matrix

$$\mathbf{SUM} = \sum_A \mathbf{S}(A) = \mathbf{I}$$

Of course, this condition does not strictly hold, because the integration is performed numerically as mentioned earlier. The deviation of **SUM** to identity matrix is a good measure of numerical integration accuracy

### 3 Functions

$$\text{ERROR} = \frac{\sum_i \sum_j |\text{SUM}_{i,j} - \mathbf{I}_{i,j}|}{N_{Atom}}$$

Multiwfn automatically calculates and outputs the ERROR value. If ERROR is not small enough, e.g. >0.001, you may want to improve the integration accuracy by increasing "radpot" and "sphpot" in settings.ini.

For unrestricted HF/DFT or unrestricted post-HF wavefunction, AOM for  $\alpha$  and  $\beta$  orbitals will be outputted respectively.

#### 3.18.5 Calculate localization and delocalization index (4)

Delocalization index  $\delta$  (DI) is a quantitative measure of the number of electron pairs delocalized (or say shared) between two atomic spaces, while localization index  $\lambda$  (LI) quantitatively measures how many electron are localized in an atomic space. (Only the expression for  $\alpha$  electrons is given below. For  $\beta$  electrons, just replace  $\alpha$  by  $\beta$ , similarly hereinafter)

$$\begin{aligned}\delta^\alpha(A, B) &= -2 \int_A \int_B \Gamma_{XC}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ \lambda^\alpha(A) &= - \int_A \int_A \Gamma_{XC}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \delta^\alpha(A, A) / 2\end{aligned}$$

where  $\Gamma_{XC}$  is exchange-correlation density, if you are not familiar with it, please consult the discussion in part 17 of Section 2.6. Using the approximate expression of  $\Gamma_{XC}$ , DI and LI can be explicitly written as

$$\begin{aligned}\delta^\alpha(A, B) &= 2 \sum_{i \in \alpha} \sum_{j \in \alpha} \sqrt{\eta_i \eta_j} S_{ij}(A) S_{ij}(B) \\ \lambda^\alpha(A) &= \sum_{i \in \alpha} \sum_{j \in \alpha} \sqrt{\eta_i \eta_j} S_{ij}(A) S_{ij}(A)\end{aligned}$$

The relationship between LI, DI and the population number of electrons in atomic space is

$$\lambda^\alpha(A) + \sum_{B \neq A} \delta^\alpha(A, B) / 2 = - \int_A \int_B \Gamma_{XC}^{\alpha,tot}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \int_A \rho^\alpha(\mathbf{r}) d\mathbf{r} = N_A^\alpha$$

Total DI and LI are the summation of  $\alpha$  part and  $\beta$  part

$$\begin{aligned}\delta(A, B) &= \delta^\alpha(A, B) + \delta^\beta(A, B) \\ \lambda(A) &= \lambda^\alpha(A) + \lambda^\beta(A)\end{aligned}$$

For close-shell cases, since  $\delta^\alpha(A, B) = \delta^\beta(A, B)$ , one can evaluate total DI as

$$\delta(A, B) = 2\delta^\alpha(A, B) = 2 * 2 \sum_m \sum_n \sqrt{\frac{\eta_m}{2} \frac{\eta_n}{2}} S_{mn}(A) S_{mn}(B) = 2 \sum_m \sum_n \sqrt{\eta_m \eta_n} S_{mn}(A) S_{mn}(B)$$

where  $m$  and  $n$  denote close-shell natural orbitals. Similarly, the total LI for close-shell cases is

$$\lambda(A) = \sum_m \sum_n \sqrt{\eta_m \eta_n} S_{mn}(A) S_{mn}(A)$$

If single-determinant wavefunction, because of integer occupation number of orbitals, LI and DI can be simplified as

### 3 Functions

$$\delta^\alpha(A, B) = 2 \sum_{i \in \alpha}^{\text{occ}} \sum_{j \in \alpha}^{\text{occ}} S_{ij}(A) S_{ij}(B)$$

$$\delta(A, B) = 4 \sum_m^{\text{occ}} \sum_n^{\text{occ}} S_{mn}(A) S_{mn}(B)$$

$$\lambda^\alpha(A) = \sum_{i \in \alpha}^{\text{occ}} \sum_{j \in \alpha}^{\text{occ}} S_{ij}(A) S_{ij}(A)$$

$$\lambda(A) = 2 \sum_m^{\text{occ}} \sum_n^{\text{occ}} S_{mn}(A) S_{mn}(A)$$

Conventionally, LI and DI are calculated in AIM atomic space (also called as AIM basin), while in fuzzy atomic space analysis module of Multiwfn, they are calculated in fuzzy atomic space, the physical nature is the same.

According to the discussion presented in *J. Phys. Chem. A*, **109**, 9904 (compare Eq.13 and Eq. 18), the DI calculated in fuzzy atomic space is just the so-called fuzzy bond order, which was defined by Mayer in *Chem. Phys. Lett.*, **383**, 368.

For close-shell system, atomic valence can be calculated as the sum of its fuzzy bond orders

$$V(A) = \sum_{B \neq A} \delta(A, B)$$

In Multiwfn, before calculating LI and DI, AOM is calculated first automatically, this is the most time-consuming step. For open-shell systems, the LI and DI for  $\alpha$  and  $\beta$  electrons, as well as for all electrons are outputted respectively. Notice that the diagonal terms of DI matrix are calculated as the sum of corresponding off-diagonal row (or column) elements. For close-shell system, as stated above, they correspond to atomic valence.

For strictly planar molecules, because overlap integral of  $\sigma$  orbital and  $\pi$  orbital is exactly zero in atomic space, the contributions from  $\sigma$  and  $\pi$  electrons to DI can be exactly decomposed as DI- $\sigma$  and DI- $\pi$

$$\delta^\alpha(A, B) = \delta_\sigma^\alpha(A, B) + \delta_\pi^\alpha(A, B)$$

$$\delta_\sigma^\alpha(A, B) = 2 \sum_{i \in \alpha}^{\sigma} \sum_{j \in \alpha}^{\sigma} \sqrt{\eta_i \eta_j} S_{ij}(A) S_{ij}(B)$$

$$\delta_\pi^\alpha(A, B) = 2 \sum_{i \in \alpha}^{\pi} \sum_{j \in \alpha}^{\pi} \sqrt{\eta_i \eta_j} S_{ij}(A) S_{ij}(B)$$

Similarly, LI can be decomposed as LI- $\sigma$  and LI- $\pi$ . Summing up corresponding off-diagonal elements in DI- $\sigma$  and DI- $\pi$  matrix gives  $\sigma$ -atomic valence and  $\pi$ -atomic valence, respectively. If you want to compute DI/LI- $\sigma$  (DI/LI- $\pi$ ), before the DI/LI calculation, you should set the occupation numbers of all  $\pi$  orbitals ( $\sigma$  orbitals) to zero by subfunction 26 of main function 6.

By the way, in some literatures, especially the ones written by Bernard Silvi, the variance of electronic fluctuation in atomic space  $\sigma^2(A)$  and the covariance of fluctuation of electron pair between two atomic spaces  $\text{cov}(A, B)$  are discussed. They are not directly outputted by Multiwfn,

because there is a very simple relationship correlates  $\sigma^2(A)$ ,  $\text{cov}(A,B)$  and  $\text{DI}(A,B)$ , thus you can calculate them quite easily, see *Chem. Rev.*, **105**, 3911 for derivation

$$\text{cov}(A,B) = -\delta(A,B)/2$$

$$\sigma^2(A) = N_A - \lambda(A) = -\sum_{B \neq A} \text{cov}(A,B) = \sum_{B \neq A} \delta(A,B)/2$$

where  $N_A$  is the electron population number in A. As mentioned above, the diagonal terms of the DI matrix outputted by Multiwfn are calculated as the sum of off-diagonal elements in the corresponding row (or column), hence you can simply obtain  $\sigma^2$  by dividing corresponding diagonal term of DI matrix by two.

A quantity closely related to  $\sigma^2$  is the relative fluctuation parameter introduced by Bader, which indicates the electronic fluctuations for a given atomic space relative to its electron population, you can calculate it manually if you want

$$\lambda_F(A) = \sigma^2(A) / N_A$$

Alternatively, you can calculate below value to measure the proportion of the electrons localized in the atomic space

$$l(A) = \lambda(A) / N_A$$

### 3.18.6 Calculate PDI (5)

Para-delocalization index (PDI) is a quantity used to measure aromaticity of six-membered rings. PDI was first proposed in *Chem. Eur. J.*, **9**, 400, also see *Chem. Rev.*, **105**, 3911 for more discussion. PDI is essentially the averaged para-delocalization index (para-DI) in six-membered rings.

$$PDI = \frac{\delta(1,4) + \delta(2,5) + \delta(3,6)}{3}$$

The basic idea behind PDI is that Bader and coworkers reported that DI in benzene is greater for para-related than for meta-related carbon atoms. Obviously, the larger the PDI, the larger the delocalization, and the stronger the aromaticity. The main limitation of the definition of PDI is that it can only be used to study aromaticity of six-membered rings, and it was shown that PDI is inappropriate for the cases when the ring plane has an out-plane distortion.

In Multiwfn, before calculating PDI, AOM and DI are first calculated automatically. Then you will be prompted to input the indices of the atoms in the ring that you are interested in, the input order must be consistent with atom connectivity.

PDI currently is only available for close-shell systems, although theoretically it may be possible to be extended to open-shell cases.

Note that for completely planar systems, since DI can be decomposed to  $\alpha$  and  $\pi$  parts, PDI can also be separated as PDI- $\alpha$  and PDI- $\pi$  to individually study  $\alpha$  aromaticity and  $\pi$  aromaticity. In order to calculate PDI- $\alpha$  (PDI- $\pi$ ), before enter present module, you should first manually set occupation number of all MOs except for  $\pi$  ( $\alpha$ ) MOs to zero (or you can utilize option 22 in main function 100 to do this step, which will be much more convenient).

### 3.18.7 Calculate FLU and FLU- $\pi$ (6,7)

Aromatic fluctuation index (FLU) was proposed in *J. Chem. Phys.*, **122**, 014109, also see *Chem. Rev.*, **105**, 3911 for more discussion. Like PDI, FLU is an aromaticity index based on DI, but can be used to study rings with any number of atoms. The FLU index was constructed by following the HOMA philosophy (see Section 3.100.13), i.e. measuring divergences (DI differences for each single pair bonded) from aromatic molecules chosen as a reference. FLU is defined as below

$$\text{FLU} = \frac{1}{n} \sum_{A-B}^{\text{RING}} \left[ \left( \frac{V(B)}{V(A)} \right)^\alpha \left( \frac{\delta(A, B) - \delta_{\text{ref}}(A, B)}{\delta_{\text{ref}}(A, B)} \right) \right]^2$$

where the summation runs over all adjacent pairs of atoms around the ring,  $n$  is equal to the number of atoms in the ring,  $\delta_{\text{ref}}$  is the reference DI value, which is precalculated parameter.  $\alpha$  is used to ensure the ratio of atomic valences is greater than one

$$\alpha = \begin{cases} 1 & V(B) > V(A) \\ -1 & V(B) \leq V(A) \end{cases}$$

The first factor in the formula of FLU penalizes those with highly localized electrons, while the second factor measures the relative divergence with respect to a typical aromatic system. Obviously, lower FLU corresponds to stronger aromaticity.

The dependence on reference value is one of main weakness of FLU. The default  $\delta_{\text{ref}}$  in Multiwfn for C-C, C-N, B-N are 1.468, 1.566 and 1.260 respectively, they are obtained from calculation of benzene, pyridine and borazine respectively under HF/6-31G\* (geometry is optimized at the same level. Becke's atomic space with modified CSD radii and with sharpness parameter  $k=3$  is used to derive  $\delta_{\text{ref}}$ ). Users can modify or add  $\delta_{\text{ref}}$  through option -4.

The original paper of FLU also defined FLU- $\pi$ , which is based on DI- $\pi$  and  $\pi$ -atomic valence

$$\text{FLU}_\pi = \frac{1}{n} \sum_{A-B}^{\text{RING}} \left[ \left( \frac{V_\pi(B)}{V_\pi(A)} \right)^\alpha \left( \frac{\delta_\pi(A, B) - \delta_{\text{Avg}}}{\delta_{\text{Avg}}} \right) \right]^2$$

where  $\delta_\pi$  is the average value of the DI- $\pi$  for the bonded atom pairs in the ring, and the other symbols denote the aforementioned quantities calculated using  $\pi$ -orbitals only. The advantage of FLU- $\pi$  over FLU is that FLU- $\pi$  does not rely on predefined reference DI value, while the disadvantage is that FLU- $\pi$  can only be exactly calculated for planar molecules.

Akin to FLU, the lower the FLU- $\pi$ , the stronger aromatic the ring. If FLU- $\pi$  is equal to zero, that means DI- $\pi$  is completely equalized in the ring. The reasonableness to measure aromaticity by FLU- $\pi$  is that aromaticity for most aromatic molecules are almost purely contributed by  $\pi$  electrons, rather than  $\sigma$  electrons.

In fuzzy atomic space analysis module of Multiwfn, PDI, FLU and FLU- $\pi$  are calculated in fuzzy atomic spaces. In *J. Phys. Chem. A*, **110**, 5108, the authors showed that the correlation between the PDI, FLU and FLU- $\pi$  calculated in fuzzy atomic space and the ones calculated in AIM atomic space is excellent.

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In Multiwfn, before calculating FLU and FLU- $\pi$ , AOM will be calculated automatically. If you are calculating FLU- $\pi$ , you will be prompted to input the indices of  $\pi$  orbitals, you can find out their indices by checking isosurface of all orbitals by main function 0. Then DI or DI- $\pi$  matrix will be generated. Next, you should input the indices of the atoms in the ring, the input order must be consistent with atom connectivity. Besides FLU or FLU- $\pi$  value, the contributions from each bonded atom pair are outputted too.

FLU and FLU- $\pi$  are only available for close-shell system in Multiwfn. It is not well known whether FLU and FLU- $\pi$  are also applicable for open-shell systems.

#### 3.18.8 Calculate condensed linear response kernel (9)

Linear response kernel (LRK) is an important concept defined in DFT framework, which can be written as

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \left( \frac{\delta^2 E}{\delta v(\mathbf{r}_1) \delta v(\mathbf{r}_2)} \right)_N = \left( \frac{\delta \rho(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)} \right)_N$$

This quantity reflects the impact of the perturbation of external potential at  $\mathbf{r}_2$  on the electron density at  $\mathbf{r}_1$ , which may also be regarded as the magnitude coupling between electron at  $\mathbf{r}_1$  and  $\mathbf{r}_2$ .

In Multiwfn, LRK is evaluated by an approximation form based on second-order perturbation theory (see Eq.3 of *Phys. Chem. Chem. Phys.*, **14**, 3960)

$$\chi(\mathbf{r}_1, \mathbf{r}_2) \approx 4 \sum_{i \in \text{occ}} \sum_{j \in \text{vir}} \frac{\varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_2)}{\varepsilon_i - \varepsilon_j}$$

where  $\varphi$  is molecular orbital,  $\varepsilon$  stands for MO energy. Note that this approximation form is only applicable to HF/DFT close-shell systems, therefore present function only works for HF/DFT close-shell systems.

Condensed linear response kernel (CLRK) is calculated as

$$\chi_{A,B} = \int_A \int_B \chi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = 4 \sum_{i \in \text{occ}} \sum_{j \in \text{vir}} \frac{S_{ij}(A) S_{ji}(B)}{\varepsilon_i - \varepsilon_j}$$

where  $A$  and  $S(A)$  denote fuzzy atomic space and atomic overlap matrix for atom A, similar for atom B. In *Phys. Chem. Chem. Phys.*, **15**, 2882 (2013), it was shown that CLRK is useful for investigation of aromaticity and anti-aromaticity.

Present function is used to calculate CLRK between all atom pairs in current system, and the result will be outputted as a matrix. Due to evaluation of LRK requires virtual MO information, in current version .fch/.molden/.gms file must be used as input file.

Note that CLRK can be decomposed to orbital contribution, e.g. for MO  $i$

$$\chi_{A,B}^{(i)} = 4 \sum_{j \in \text{vir}} \frac{S_{ij}(A) S_{ji}(B)}{\varepsilon_i - \varepsilon_j}$$

For instances, assume that you want to evaluate the contribution from MO 3,4,7, then before calculating CLRK, you should enter main function 6 and use option 26 to set occupation number of all MOs except for 3,4,7 to zero. (Note that the virtual MOs used to calculate LRK will automatically still be the original virtual MOs, rather than the ones after modification of MO occupation numbers.)

### 3.18.9 Calculate para linear response index (10)

The definition of para linear response index (PLR) has an analogy to PDI, the only difference is that DI is replaced by CLRK

$$PLR(A, B) = \frac{\chi_{1,4} + \chi_{2,5} + \chi_{3,6}}{3}$$

In *Phys. Chem. Chem. Phys.*, **14**, 3960 (2012), the authors argued that PLR is as useful as PDI in quantitatively measuring aromaticity, and it is found that the linear relationship between PLR and PDI is as high as  $R^2=0.96$ .

Present function is used to calculate PLR. Multiwfn will first calculate CLRK, and then you should input the indices of the atoms constituting the ring in quesiton, e.g. 3,5,6,7,9,2. The input order must be consistent with atom connectivity. Then PLR will be immediately outputted on screen. PLR is only applicable to HF/DFT close-shell systems, and currently .fch/.molden/.gms must be used as input file.

Note that for completely planar systems, PLR can be exactly separated as PLR- $\alpha$  and PLR- $\pi$  to individually study  $\alpha$  aromaticity and  $\pi$  aromaticity. In order to calculate PLR- $\alpha$  (PLR- $\pi$ ), before enter present module, you should first manually set occupation number of all MOs except for  $\pi$  ( $\alpha$ ) MOs to zero (or you can utilize option 22 in main function 100 to do this step, which will be much more convenient).

### 3.18.10 Calculate multi-center delocalization index (11)

$n$ -center multi-center DI is calculated as

$$\delta(A, B, C \dots H) = 2^{n-1} \sum_i \sum_j \sum_k \dots \sum_q S_{ij}(A) S_{jk}(B) S_{kl}(C) \dots S_{qi}(H)$$

where  $i, j, k \dots$  only cycle occupied orbitals. The normalized form of multi-center DI is defined as  $\delta^{1/n}$ , and may be compared between rings with different number of members.

Currently this function is only available for single-determinant close-shell wavefunctions, and supports up to 10 centers. Note that for relatively large size of systems, calculating multi-center DI for more than 6 centers may be quite time-consuming.

**Information needed:** GTFs, atom coordinates, basis functions (only for calculating condensed linear response kernel and PLR)

## 3.19 Charge decomposition analysis and plotting orbital interaction diagram (16)

### 3.19.1 Theory

The charge decomposition analysis (CDA) proposed by Dapprich and Frenking (*J. Phys. Chem.*, **99**, 9352) is used to provide deep insight on how charges are transferred between fragments in a complex to achieve charge equilibrium. The idea of CDA is based on fragment

orbital (FO), which denotes the molecular orbital (MO) of fragment in its isolated state. Besides, once the compositions of FOs in MOs of complex are obtained, the orbital interaction diagram can be directly plotted, which allows one visually and directly understand how orbitals of fragments are mixed to form orbitals of complex.

For simplicity, in this section we assume that the complex consists of only two fragments. However, the CDA can be straightforwardly used for more than two fragments cases.

### Fragment orbital

Consider we are studying a complex AB,  $NA$  basis functions are located in the atoms of fragment A,  $NB$  basis functions in fragment B, then each MO of complex will be linearly expanded by  $NA+NB$  basis functions, and meanwhile, the complex has  $NA+NB$  MOs. By using the same basis-set, and maintaining the same geometry as in complex, if we calculate the two fragments respectively, we can obtain  $NA$  MOs of fragment A, and  $NB$  MOs of fragment B, they are collectively called as fragment orbital (FO). We can take these FOs as basis functions to linearly expand the MOs of complex. Since the dimension (the number of basis functions) is still  $NA+NB$ , the expansion is exact. In other words, we equivalently transformed the basis.

### Charge decomposition analysis

In the original paper of CDA, the authors defined three terms:

$$\begin{aligned} d_i &= \sum_{m \in A}^{\text{occ}} \sum_{n \in B}^{\text{vir}} \eta_i C_{m,i} C_{n,i} S_{m,n} \\ b_i &= \sum_{m \in A}^{\text{vir}} \sum_{n \in B}^{\text{occ}} \eta_i C_{m,i} C_{n,i} S_{m,n} \\ r_i &= \sum_{m \in A}^{\text{occ}} \sum_{n \in B}^{\text{occ}} \eta_i C_{m,i} C_{n,i} S_{m,n} \end{aligned}$$

where  $i$  and  $\eta$  are index and occupation number of MO of complex, respectively.

$S_{m,n} = \int \varphi_m(\mathbf{r}) \varphi_n(\mathbf{r}) d\mathbf{r}$  is overlap integral between FO  $m$  and FO  $n$ . Note that though the  $NA$  and  $NB$  FOs are respectively orthonormalization sets, the  $NA$  set are in common not normal to the  $NB$  set, so  $S$  is not an identity matrix.  $C_{m,i}$  denotes the coefficient of FO  $m$  in MO  $i$  of complex. The superscript "vir" and "occ" mean virtual (viz. unoccupied) and occupied, respectively.

The term  $d_i$  denotes the amount of electron donated from fragment A to B via MO  $i$  of complex; similarly, the term  $b_i$  denotes the electron back donated from B to A. In fact,  $\eta_i C_{m,i} C_{n,i} S_{m,n}$  can be regarded as the half of overlap population between FO  $m$  and  $n$  in MO  $i$ .

Hence, the difference between term  $d$  and  $b$  is that which fragment provides its electrons from its occupied FOs to virtual FOs of another fragment. The term  $r$  reveals close-shell interaction between two occupied FOs in different fragments; positive value of  $r_i$  means that owing to MO  $i$ , the electrons of the two fragments are accumulated in their overlap region and shows bonding character, while negative value indicates that the electrons are depleted from the overlap region and thus reflecting electron repulsive effect. The sum of all  $r_i$  terms is in general negative, because overall interaction between filled orbitals are generally repulsive.  $r$  is also known as "repulsive polarization" term

Beware that although the CDA formulae given in original paper are correct, by carefully inspecting the data, I found the  $d$ ,  $b$  and  $r$  terms in the examples presented in the original paper are erroneous (the data should be divided by two).

### Generalizing CDA

The original definition of CDA has two drawbacks. First, it is only applicable to close-shell cases (namely, complex and each fragment must be close-shell) and hence unable to be used when the two fragments are bound by covalent bonding. Second, in post-HF calculations, though the MOs of complex can be replaced by natural orbitals (NOs), the FOs can only be produced by HF or DFT calculation, because occupation numbers of FOs are not explicitly considered in the original CDA formulae.

To address the limitations of the original definition, in *J. Adv. Phys. Chem.*, **4**, 111-124 (2015) (<http://dx.doi.org/10.12677/JAPC.2015.44013>) I proposed a generalized form of CDA, which is the form used in CDA module of Multiwfn:

$$t_i = \sum_{m \in A} \sum_{n \in B} \eta_i \frac{|\eta_m^{\text{FO}} - \eta_n^{\text{FO}}|}{\eta_{\text{ref}}} C_{m,i} C_{n,i} S_{m,n}$$

$$r_i = \sum_{m \in A} \sum_{n \in B} 2 \frac{\min(\eta_m^{\text{FO}}, \eta_n^{\text{FO}})}{\eta_{\text{ref}}} \eta_i C_{m,i} C_{n,i} S_{m,n}$$

In the generalized CDA, orbitals of complex and fragments can be produced either by HF/DFT or by post-HF method, corresponding to MOs and NOs, respectively.  $\eta_m^{\text{FO}}$  stands for occupation number of FO  $m$ . For open-shell cases,  $\eta_{\text{ref}}$  is 1.0, CDA will be performed for alpha spin and beta spin separately; for the former,  $i$  denotes alpha orbital of complex,  $m$  and  $n$  run over all alpha FOs; for the latter,  $i$  denotes beta orbital of complex,  $m$  and  $n$  run over all beta FOs. For close-shell cases,  $\eta_{\text{ref}}$  is 2.0,  $m$  and  $n$  run over space orbitals.  $\min()$  is the function used to extract minimum from two values. During calculation of  $t$ , if the values are only accumulated for the cases  $\eta_m^{\text{FO}} > \eta_n^{\text{FO}}$ , then the resulting  $t$  is  $d$ ; if only for the cases  $\eta_m^{\text{FO}} < \eta_n^{\text{FO}}$ , then  $t$  will be  $b$ .

For the situations when the original CDA is applicable, the  $b$  and  $d$  calculated by the generalized form are exactly identical to the ones obtained via original definition; while  $r$  will be exactly twice of the one produced via original definition. The reason why the factor 2 is introduced into the generalized form of  $r$  is because after doing so,  $r$  has more clear physical meaning, namely it equals to overlap population (also known as Mulliken bond order) between the occupied FOs in the two fragments.

Because the CDA has been generalized, below, FO will stand for MO or NO of fragment, "complex orbital" will denote MO or NO of complex. The orbitals can either be spin-space orbital (for open-shell) or space orbital (for close-shell).

It is clear that the  $d$ ,  $b$  and  $r$  terms can be decomposed into FO pair contributions, this kind of decomposition is supported by Multiwfn and greatly facilitates analysis of the nature of FO interaction.

### Composition of FO in complex orbital and orbital interaction diagram

By using the methods discussed in Section 3.10, the composition of FO in complex orbital

### 3 Functions

can be calculated. In common, Mulliken method is the best choice for this purpose, the composition of FO  $m$  in complex orbital  $i$  is calculated as

$$\Theta_{m,i} = \left( C_{m,i}^2 + \sum_{n \neq m} C_{m,i} C_{n,i} S_{m,n} \right) \times 100\%$$

Although using SCPA method to calculate composition is more convenient (since overlap matrix is not involved), if  $i$  is a high-lying virtual orbital, the calculated composition is not very reasonable. Note that due to a well-known drawback of Mulliken method, sometimes negative contributions occur, since the values are often not large, you can simply ignore them.

From  $\Theta$ , we can clearly understand how each complex orbital is formed by mixing FOs of the two fragments. Furthermore, one can plot orbital interaction diagram to visually and intuitively study the relationship between complex orbitals and FOs, namely plot a bar for each complex orbital and FO according to its energy, and then check each  $\Theta$  to determine how to link the bars, e.g. if the value of  $\Theta_{m,i}$  is larger than 5%, then the two bars corresponding to FO  $m$  and complex orbital  $i$  will be linked. Consequently, from the graph we will directly know that FO  $m$  has important contribution to complex orbital  $i$ .

#### Extended charge decomposition analysis

The difference between the total number of donation and back donation electrons, that is  $d - b$ , may be regarded as the net transferred electrons. However, in *J. Am. Chem. Soc.*, **128**, 278, the authors argued that this viewpoint is not correct, because  $b$  and  $d$  terms not only represent charge transfer effect (CT), but also electron polarization effect (PL); the latter describes the adjustment of electron distribution within the fragment, which is caused by mixing virtual and occupied FOs of the same fragment during formation of the complex, and should be excluded in the calculation of the amount of net transferred electrons. In this paper they proposed extended charge decomposition analysis (ECDA) method, by which they argued that the number of net transferred electrons can be calculated more reasonably.

In ECDA viewpoint, four terms can be defined as follows

1.  $PL(A) + CT(A \rightarrow B)$  = The sum of compositions of occupied FOs of fragment A in all virtual orbitals of complex, multiplied by Occ
2.  $PL(A) + CT(B \rightarrow A)$  = The sum of compositions of virtual FOs of fragment A in all occupied orbitals of complex, multiplied by Occ
3.  $PL(B) + CT(B \rightarrow A)$  = The sum of compositions of occupied FOs of fragment B in all virtual orbitals of complex, multiplied by Occ
4.  $PL(B) + CT(A \rightarrow B)$  = The sum of compositions of virtual FOs of fragment B in all occupied orbitals of complex, multiplied by Occ

where Occ is 1.0 and 2.0 for open-shell and close-shell cases, respectively.

After the four terms are calculated, the number of net transferred electrons from A to B can be directly obtained as

$$CT(A \rightarrow B) - CT(B \rightarrow A) = [ PL(A) + CT(A \rightarrow B) ] - [ PL(B) + CT(A \rightarrow B) ]$$

The composition of complex orbitals can be calculated by various methods, leading to different ECDA result. The method used in Multiwfn is identical to the one in ECDA original paper, namely Mulliken method.

Note that ECDA can neither be applied to post-HF calculation nor the system consisting more

than two fragments.

According to the name, ECDA is as if an extension of CDA, however in my personal opinion, ECDA is irrelevant to CDA, their basic ideas are quite different, and thus the amount of net transferred electron calculated by ECDA is not comparable with the  $d - b$  produced by CDA at all. In addition, though ECDA is realized in Multiwfn, I do not think this is a useful method. The most remarkable feature of CDA is that the electron transfer can be decomposed to contribution of complex orbitals, however ECDA is incapable to do this; ECDA can only reveal how many electrons is transferred between two fragments, but this quantity actually can be obtained by a more straightforward approach, namely calculating the fragment charge by summing up all atomic charges in the fragment, and then subtracting it by the net charge of the fragment in its isolated state.

### 3.19.2 Input file

There are several points you should note:

In Multiwfn, infinite number of fragments can defined; however, if more than two fragments are defined, ECDA analysis will be unavailable.

If the complex or any one fragment is an open-shell system, then CDA will be performed separately for alpha and beta electrons.

If in the calculation of the complex or any one fragment post-HF method is employed to produce natural orbitals, then ECDA analysis cannot be performed, and orbital interaction diagram cannot be drawn (since orbital energy of natural orbitals is not well-defined).

#### For Gaussian users

Below files are required as input files of CDA module:

(1) Gaussian output file of single point task of complex. The keywords *nosymm pop=full IOp(3/33=1)* must be specified in route section; in which  $3/33=1$  makes Gaussian output overlap matrix between basis functions.

(2) Gaussian output file of single point task of each fragment. The keywords *nosymm pop=full* must be specified in route section.

Notice that the atomic coordinates in fragment calculations must be exactly in accordance with that in complex calculation, therefore do not optimize geometry for each fragment, you only need to directly extract fragment coordinates from the optimized complex coordinate. The atomic sequence in fragments and complex must be identical, that means the atomic sequence in the complex can be retrieved by successively combining the atoms in fragment 1, 2, 3 ...  $n$ . Molecular geometry must be given in Cartesian coordinate. The basis-set used in the complex and fragment calculations must be completely the same. Notice that if you intent to use mixed basis-set, and in particular when Pople type basis-set is involved (such as 6-31G\*), you'd better specify "**5d 7f**" keywords in the fragment calculations to force Gaussian to use spherical-harmonic type basis functions.

By default Gaussian automatically eliminates linearly dependant basis functions, hence in some cases the number of basis functions will not be equal to the number of orbitals and thus CDA cannot be performed, in this case *IOp(3/32=2)* should be specified, which avoids Gaussian eliminating linearly dependant basis functions. The common reason of this problem comes from the use of diffuse basis functions. According to my experiences, when diffusion basis functions are presented, the CDA results are often unreasonable or even completely meaningless. So, **DO NOT**

### use diffuse functions in CDA analysis!

The theoretical method used in the calculations can be HF/DFT or post-HF. Closed-shell and unrestricted open-shell wavefunctions are supported (In fact ROHF/ROKS is also supported and closed-shell form of CDA will be employed, however the result is often not very useful). For post-HF calculation, in order to output coefficient and occupation number for natural orbitals, do not use "pop=full" but use "density pop=NO" and "density pop=NOAB" for close-shell and open-shell cases, respectively.

**It is also completely OK to use the corresponding .fch as input file of CDA module instead of Gaussian output file for HF/DFT,** and in this case *IOP(3/33=1)* and *pop=full* are not needed. However for post-HF case, you need to follow the steps given in the beginning of Chapter 4 to save natural orbitals into .fch file, this is somewhat cumbersome and not as straightforward as using Gaussian output file.

### For other ab-initio program users

You can also use CDA module as long as your favourite *ab-initio* program is able to produce Molden input file (.molden), such as ORCA and Molpro. Note that not the .molden outputted by all of quantum chemistry codes can be properly recognized by Multiwfn, see part 4 of Section 2.3 for explanation. In addition, .gms file (GAMESS-US output file) may also be used as input file.

Similar to the case of Gaussian, you need to use your *ab-initio* program generate .molden or .gms file for complex and all fragments. All of the points mentioned above must be fulfilled, namely the avoidance of elimination of linearly dependant basis functions, the consistency of the atomic coordinates and the correspondence of atomic sequence in complex and fragments .molden files. An example is given in "examples\CDA\COBH3\_ORCA" folder, the .molden files were generated by ORCA 3.0.1.

## 3.19.3 Usage

After booting up Multiwfn, first you should input the path of the file (i.e. Gaussian output file or .fch or .molden or .gms) for complex, and then enter the CDA module. Next, you should set the number of fragments, and then input the path of the file for each fragment in turn, the orbital information recorded in which will be loaded into memory.

For the open-shell fragments, you will be prompted to select if flip its spin. If select "y", then orbital information of its alpha and beta orbitals will be exchanged. The reason for introduction of this step is obvious, for example, we want to use CDA to decompose electron transfer between fragment CH<sub>3</sub> and NH<sub>2</sub> in CH<sub>3</sub>NH<sub>2</sub>; CH<sub>3</sub>NH<sub>2</sub> has 9 alpha and 9 beta electrons, while in the calculations of quantum chemistry codes, both CH<sub>3</sub> and NH<sub>2</sub> will be regarded as having 5 alpha and 4 beta electrons. In order to carry out CDA, we have to flip electron spin of either CH<sub>3</sub> or NH<sub>2</sub>, otherwise the total numbers of alpha and beta electrons in the two fragments, namely 5+5 and 4+4 respectively, will be unequal to the ones of complex, namely 9 and 9, respectively.

After the loading is finished, Multiwfn will calculate some data. If only two fragments are defined, CDA and ECDA result will be directly shown. Then you will see a menu:

**-2 Switch output destination (for options 0 and 1):** By default the options 0 and 1 output results on screen; if you select this option once, then their results will be outputted to CDA.txt in current folder.

**0 Print CDA result and ECDA result:** Input the index of two fragments, then the CDA and ECDA analysis result between them will be outputted.

**1 Print full CDA result:** If you select this option, the CDA result for all complex orbitals will be outputted. By default, Multiwfn does not output CDA result for the complex orbitals lying higher than LUMO+5, because the number of such orbitals is too large, whereas their contributions to *d*, *b* and *r* terms are often completely negligible due to their occupation numbers are often quite small. (For HF/DFT wavefunctions, the occupation numbers of the orbitals lying higher than HOMO are exactly zero, and thus have no contribution to *d*, *b* and *r* terms at all. So for this case this option is meaningless)

**2 Show fragment orbital contributions to specific complex orbital:** If you input *x*, then the composition of complex orbital *x* will be outputted (for open-shell cases, the *x*th alpha and the *x*th beta complex orbital will be outputted respectively). By default only the FOs having contribution  $\geq 1\%$  will be shown, but this threshold can be altered by "comphresCDA" parameter in settings.ini.

If you want to obtain composition of a fragment orbital in all complex orbitals, you can input for example *1,6*, which means orbital 6 of fragment 1 is selected.

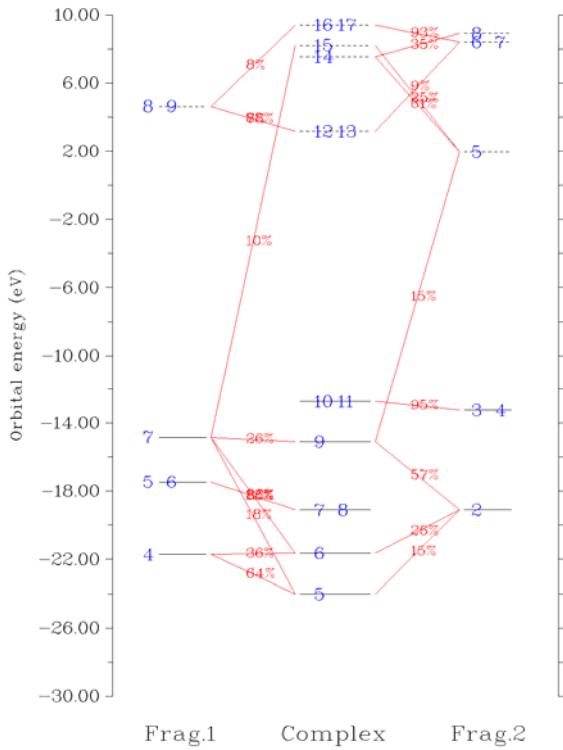
**3 Export coefficient matrix of complex orbitals in fragment orbital basis:** The coefficient matrix corresponding to all FOs in all complex orbitals will be outputted to "coFO.txt" in current folder.

**4 Export overlap matrix between fragment orbitals:** The overlap matrix between all FOs will be outputted to "ovlpint.txt" in current folder.

**6 Decompose complex orbital contribution to CDA:** You need to input index of a complex orbital and set threshold for printing, if contribution of a pair of fragmental orbitals to any of *d*, *b* and *r* term of this complex orbital is larger than the threshold then the contribution value will be shown. This greatly facilitates analysis of interaction between fragment orbitals.

**5 Plot orbital interaction diagram:** This option is only available for HF/DFT wavefunctions. If you select this option, you will enter a new menu, in which by corresponding options you can plot and save orbital interaction diagram and adjust plotting parameters, such as size of labels, energy range (namely Y-axis range) and the criterion for linking bars. The orbital interaction diagram plotted under default settings looks like this:

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In above graph, occupied and virtual orbitals are represented as solid and dashed bars, respectively, the vertical positions are determined by their energies. The bars at left and right sides correspond to the FOs of the two fragments you selected; the bars in the middle correspond to complex orbitals. Orbital indices are labelled by blue texts. If two or more labels occur in the same bar, that means these orbitals are degenerate in energy. If composition of a FO in a complex orbital is larger than specific criterion, then the corresponding two bars will be connected by red line, so that simply by viewing the diagram one can directly understand the complex orbitals are constructed by mainly mixing which FOs. The compositions are labelled in the center of the lines.

By default, all FOs and complex MOs are plotted, and if the contribution of a FO of fragment A or B to a complex MO is larger than 10% then they will be connected. For large systems, usually there are too many bars and linking lines in the diagram, and it is hence difficult to identify the orbital interaction mode based on the diagram. In these cases, you should properly use the option "4 Set the rule for connecting and drawing orbital bars" to manually set up the rule for connecting and plotting the orbital bars. See the prompt shown on the screen on how to use this option.

Sometimes the difference between orbital energies of the two fragments in the orbital interaction diagram is too large and thus hinders one to analyze the diagram, so you may want to equalize their energies. In this case, you can use the option "12 Set orbital energy shifting value" to set the value used to shifting orbital energies of the complex or the two fragments presented at the left and right side of the diagram; their orbital energies will be augmented by the given value.

Some examples of CDA are given in Section 4.16.

**Information needed:** Gaussian output files of complex and fragments

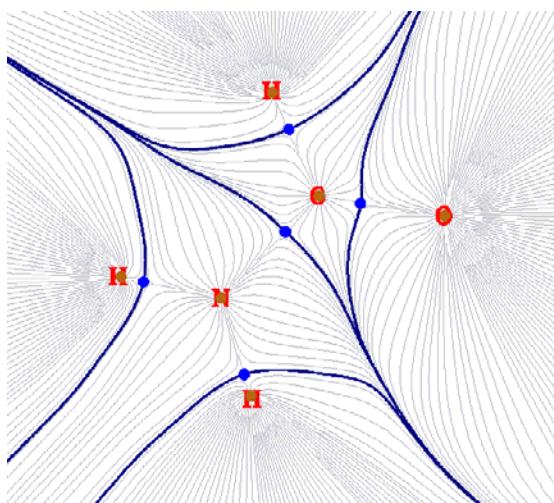
## 3.20 Basin analysis (17)

### 3.20.1 Theory

The concept of basin was first introduced by Bader in his atom in molecular (AIM) theory, after that, this concept was transplant to the analysis of ELF by Savin and Silvi. In fact, basin can be defined for any real space function, such as molecular orbital, electron density difference, electrostatic potential and even Fukui function.

A real space function in general has one or more maxima, which are referred to as attractors or (3,-3) critical points. Each basin is a subspace of the whole space, and uniquely contains an attractor. The basins are separated with each other by interbasin surfaces, which are essentially the zero-flux surface of the real space functions; mathmatically, such surfaces consist of all of the points  $\mathbf{r}$  satisfying  $\nabla f(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$ , where  $\mathbf{n}(\mathbf{r})$  stands for the unit normal vector of the surface at position  $\mathbf{r}$ .

Below figure illustrates the basins of total electron density of  $\text{NH}_2\text{COH}$ , such figure is often involved in AIM analysis. Brown points are attractors; in this case they correspond to maxima of total electron density and thus are very close to nuclei. Blue bolded lines correspond to interbasin surfaces, they dissect the whole molecular space into basins, which in present case are also known as AIM atomic space or AIM basin. Grey lines are gradient paths of total electron density, they are emanated from attractors.



Multiwfn is able to generate basins for any supported real space functions, such as electron density, ELF, LOL, electrostatic potential. Alternatively, one can let Multiwfn load the grid file generated by third-part programs (e.g. cube file or .grd file) and then generate basins for the real space function recorded in the grid data.

After the basins were generated, some analyses based on the basins can be conducted to extract information of chemical interest. The three most useful types of basin analyses are supported by Multiwfn and are briefed below. All of them require performing integration in the basin.

(1) Study integral of a real space function in the basins. For example, one can first use electron density to define the basins, and then integrate electron density in the basins to acquire

electron population numbers in the basins; this quantity is known as AIM atomic population number. Another example, one can first partition the space into basins according to ELF function, and then calculate integral of spin density in the basins.

(2) Study electric multipole moments in the basins. In Multiwfn electric monopole, dipole and quadrupole moments can be calculated in the basins. This is very useful to gain a deep and quantitative insight on how the electrons are distributed in different regions of a system. Based on these data, one can clearly understand such as how lone pair electrons contribute to molecular dipole moment (see *J. Comput. Chem.*, **29**, 1440 for example, in which ELF basins are used), how the electron density around an atom is polarized as another molecule approaching.

(3) Study localization index and delocalization index in the basins. The former one measures how many electrons are localized in a basin in average, while the latter one is a quantitative measure of the number of electrons delocalized (or say shared) between two basins. They have been very detailedly introduced in Section 3.18.5 and hence will not be reintroduced here. The only difference relative to Section 3.18.5 is that the range of integration in our current consideration is basins rather than fuzzy atom spaces.

### 3.20.2 Numerical aspects

This section I will talk about many numerical aspects involved in basin analysis, so that you can understand how the basin analysis module of Multiwfn works.

#### Algorithms for generating basins

The algorithms used to generate/integrate basins can be classified into three categories:

(1) Analytical methods. Due to the popularity and importance of AIM theory, and the complex shape of AIM basins, since long time ago numerous methods have been proposed to attempt to speed up integration efficiency and increase integration accuracy for AIM basins, e.g. *J. Comput. Chem.*, **21**, 1040 and *J. Phys. Chem. A*, **115**, 13169. All of these methods are analytical, and they are employed by almost all old or classical AIM programs, such as AIMPAC, AIM2000, Morphy and AIMAll. This class of methods suffers many serious disadvantages: 1. The algorithm is very complicated 2. High computational cost 3. Only applicable to the analysis of total electron density 4. Before generating basins, (3,-3) and (3,-1) critical points must be first located in some ways. The only advantage of these methods is that the integration accuracy is very satisfactory.

(2) Grid-based methods. This class of methods relies on cubic (or rectangle) grid data. Since the publication of TopMoD program, which aims to analyze ELF basin and for the first time uses a grid-based methods, grid-based methods continue to be proposed and incurred more and more attention. Grid-based methods solved all of the drawbacks in analytical methods; they are easy to be coded, the computational cost is relative low, and more important, they are suitable for any type of real space function. Unfortunately these methods are not free of shortcomings, the central one is that the integration accuracy is highly dependent on the quality of grid data; to obtain a high accuracy of integral value the grid spacing must be small enough.

(3) Mixed analytical and grid-based method. The only instance in this class of method is described in *J. Comp. Chem.*, **30**, 1082, in which Becke's multicenter integration scheme is used to integrate basins. This method is faster than analytical method, and more accurate than grid-based method, but it is only suitable to analyze total electron density, thus the application range is seriously limited. Since the basin analysis module of Multiwfn focuses on universality, this

method is not currently implemented.

Currently the best grid-based method is near-grid method (*J. Phys.: Condens. Matter*, **21**, 084204), which is employed in Multiwfn as default method to generate basins. Multiwfn also supports on-grid method (*Comput. Mat. Sci.*, **36**, 354), which is the predecessor of near-grid method.

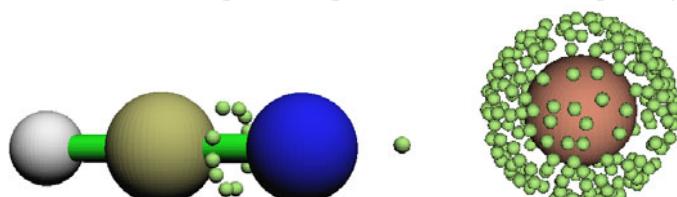
### Basic steps of generating basins and locating attractors in Multiwfn

In Multiwfn, generating basin and locating attractor are carried out simultaneously; the basic process can be summarized as follows: Given a grid data, all grids (except for the grids at box boundary) are cycled in turn. From each grid, a trajectory is evolved continuously in the direction of maximal gradient. Each step of movement is restricted to its neighbour grid, and the gradient in each grid is evaluated via one direction finite difference by using the function values of it and its neighbour grids. There are four circumstances to terminate the evolvement of present trajectory and then cycle the next grid (a) The trajectory reached a grid, in which the gradients in all directions is equal or less than zero; such a grid will be regarded as an attractor, meanwhile all grids contained in the trajectory will be assigned to this attractor. (b) The trajectory reached a grid that has already been assigned; all of the grids contained in the trajectory will be assigned to the same attractor. This treatment greatly reduced computational expense. (c) The upper limit of step number is reached (d) The trajectory reached the grids at box boundary; all of the grids in the trajectory will be marked as "travelled to boundary" status.

After all grids have been cycled, we obtained position of all attractors covered by the spatial scope of the grid data. Each set of grids that assigned to a same attractor collectively constitutes the basin corresponding to the attractor. Interbasin grids will then be detected, according to the criterion that if any neighbour grid belongs to different attractor. Note that sometimes after finished above processes, some grids may remain unassigned, and some grids may have the status "travelled to boundary". Such grids are often far away from atoms and thus unimportant, in general you can safely ignore them.

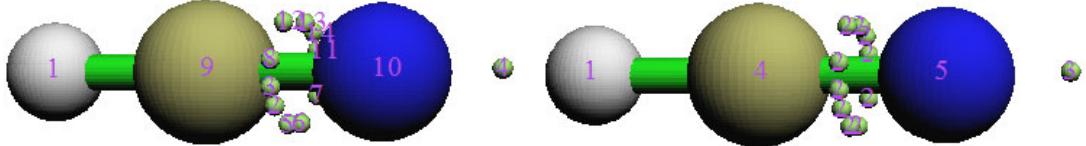
The only difference between on-grid method and near-grid method is that in the latter one, the so-called "correction step" is introduced to continuously calibrate the evolvement direction of the trajectory, which greatly eliminates the artificiality problem of interbasin surfaces due to on-grid method, and in turn makes the basin integration more close to actual values. Near-grid method can be supplemented by a refinement step for interbasin surfaces at the final stage, so that the partition of basin can be even more accurate, this additional step is not very time-consuming.

For ELF (and may be other real space functions), if sphere- or ring-shape attractors exist in the system, in corresponding regions a large number of attractors having basically the same value will be found. Below two examples illustrated the existence of the ring-shape ELF attractor encircling N-C bond of HCN and the sphere-shape ELF attractor encompassing the Ar atom.



Based on nearest neighbour algorithm, Multiwfn automatically checks the distances and the relative value differences between all pairs of located attractors, and then clusters some attractors

together. The resulting attractors thus have multiple member attractors, and will be referred to as "degenerate attractors" later. For example, the left graph and right graph given below displayed the attractor indices before and after clustering, respectively. As you can see, after clustering, all of the attractors constituting the ring-shape ELF attractor now have the same index, suggesting that the corresponding basins have been merged together as basin #2.



For certain cases, in the regions far beyond the systems, some artificial or physically meaningless attractors are located. These attractors have very low function value and thus are called as "insignificant" attractors; in contrast, other attractors can be called as "significant" attractors. The presence of insignificant attractors is because in corresponding regions the function values are rather small, hence the function behavior is not very definitive, even a very slight fluctuation of function value or trivial numerical perturbation is enough to result in new attractors. When insignificant attractors are detected, Multiwfn will prompt you to select how to deal with them, there are three options: (1) Do nothing, namely do not remove these attractors (2) Remove these attractors meanwhile set corresponding grids as unassigned grids (3) Remove these attractors meanwhile assign corresponding grids to the nearest significant attractors. The third option is generally recommended.

If the real space function simultaneously possesses positive and negative parts, e.g. electrostatic potential, Multiwfn will automatically invert the sign of negative part of the grid data and then locate attractors and generate basins as usual, after that the sign will be retrieved. Therefore, for negative parts, the "attractors" located by Multiwfn actually are "repulsors".

### Integration of basins

Once the basins have been generated by grid-based method, the integral of a real space function  $f$  in a basin  $P$  can be readily evaluated as  $F = \sum_{i \in P} f(\mathbf{r}_i) \times dV$ , where  $i$  is grid index,  $dV$

is volume differential element. Evidently, the finer the grid data (smaller grid spacing) is used, the more accurate the integral values will be, and correspondingly, the more computational effort must be paid.

Since the arrangement of grids in general is not in coincident with system symmetry, one should not expect that the integral values always satisfy system symmetry well, unless very fine grid is used.

Note that different functions have different requirement on the quality of grid data. For the same grid spacing, the faster the function varies, the lower the integration accuracy will be. Due to Laplacian of electron density, source function and kinetic density function etc. fluctuate violently near nuclei, it is impossible to directly integrate these functions in AIM basins solely by grid-based method at satisfactory accuracy (since only uniform grids are used, which is incapable to represent nuclear region well enough). In order to tackle this difficulty, an integration method based on mixed atomic-center and uniform grids is supported by Multiwfn, in which the regions

close to nuclei are integrated by atomic-center grids, while the other regions are integrated by uniform grids. This method is able to integrate AIM basin for any real space function, including the ones having complicated behavior at generally acceptable accuracy without evident additional computational cost with respect to grid-based method. In order to further improve the integration accuracy for AIM basins, Multiwfn also enables one to exactly refine the assignment of the grids at basin boundary. An exact steepest ascent trajectory is emitted from each boundary grid, and terminates when reaches an attractor. Since there are often very large number of boundary grids and each steepest ascent step requires evaluating gradient of electron density once, this process is time-consuming. In Multiwfn these gradients can also be approximately evaluated by trilinear interpolation based on pre-calculated grid data of gradient, 1/3~1/2 of overall time cost of the AIM basin integration can be saved. Note that if the mixed type of atomic-center and uniform grids is employed, and especially when the exact refinement process of boundary basin is enabled at the same time, then the requirement on quality grid will be markedly lowered, usually accurate result can be obtained at "Medium-quality grid" level (grid spacing=0.1 Bohr).

It is worth noting that even though basin analysis module of Multiwfn can be used to acquire position of attractors, the accuracy is directly limited by the quality of grid data, since the attractors will be located on a grid point. Moreover, this module is unable to be used to search other types of critical points (attractor corresponds to (3,-3) type critical point); So if you want to obtain accurate coordinate and value for all types of critical points, you should make use of main function 2, namely topology analysis function.

### 3.20.3 Usage

The basin analysis module in Multiwfn is very powerful, fast and flexible. Basins can be generated and visualized for any real space function, meanwhile any real space function can be integrated in the generated basins. Electric multipole moments and localization index in the basins and delocalization index between basins can be calculated.

#### Basic steps

To perform basins analysis in Multiwfn, there are five basic steps you need to do

(1) Load input file into Multiwfn and then enter main function 17.

(2) Select option 1 to generate basins and locate attractors. Before doing this, you can change the method used to generate basins via option -1, or adjust the parameters for clustering attractors via option -6.

(3) Visualize attractors and basins by option 0. This step is optional.

(4) Perform the analyses you want. Integral of a real space function in generated basins, electric multipole moments in the basins and localization/delocalization index of the basins can be calculated by option 2 (or 7), 3 (or 8) and 4, respectively.

You can export the generated basins as cube files by option -5, export attractors as .pdb file by option -4, check the coordinate of the located attractors by option -3, measure the distances, angles and dihedrals angles between attractors or atoms by option -2. Also you can use suboption 3 in option -6 to manually merge specified basins as a single one. If you want to regenerate basins and locate attractors for other real space functions or under new settings, you can select option 1 again.

### About input file and grid data

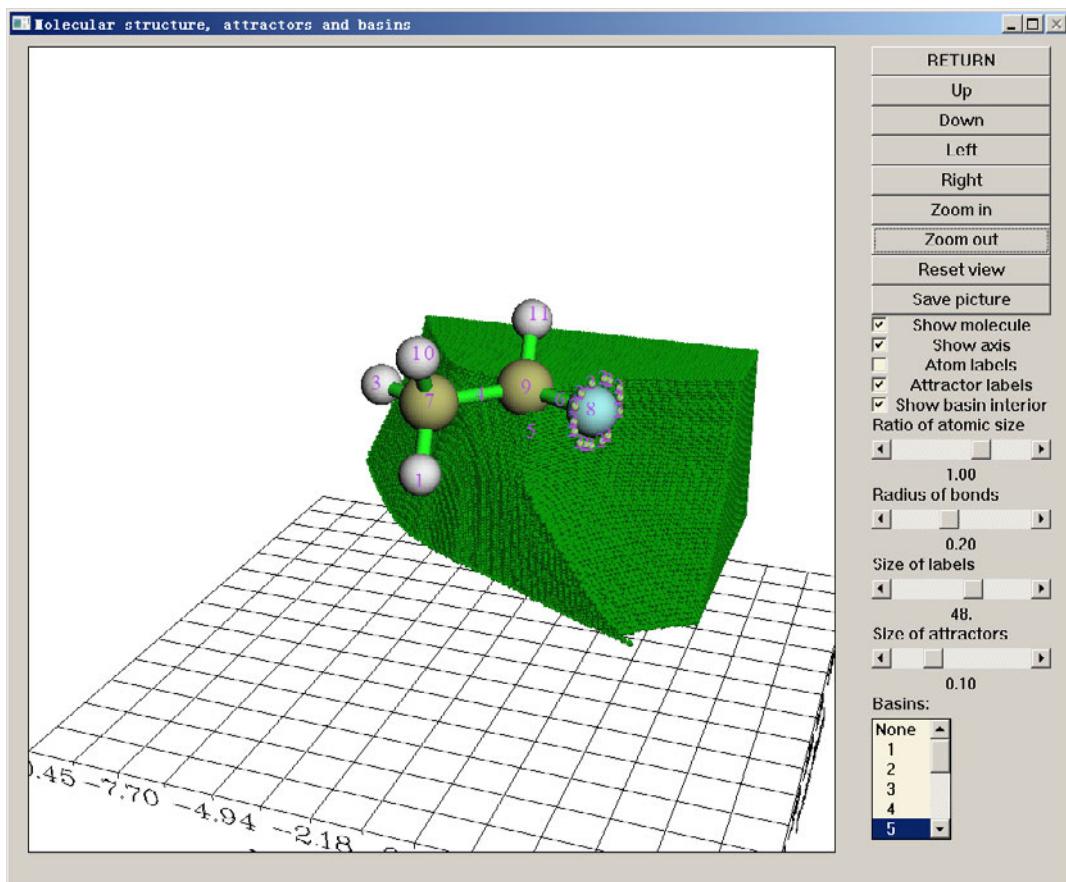
Grid data must be obtained first before generating basins. In option 1 of basin analysis module, you can let Multiwfn calculate the grid data. However, if a grid data has already been stored in memory, you can directly choose to use it. There are two circumstances in which grid data will be stored in memory: (1) The input file contains grid data, e.g. .cub and .grd file (2) You have used main function 5 or 13 to calculate grid data before entering main function 17. This design makes Multiwfn rather flexible: you can use Multiwfn to generate basins for a real space function recorded in a .cub or .grd file, which may be outputted by a third-part program; and you can also first use main function 5 or 17 to generate grid data for electron density difference, Fukui function, dual descriptor and so on, and then generate basins for them.

In the function of basin integration, namely option 2, the value of integrand at each grid must be available so that the integral can be evaluated. These values can come from three ways, you can choose any one: (1) Let Multiwfn directly calculate them (2) Load and use the grid data in a .cub/.grd file, note that this operation will not overwrite the grid data already stored in memory (3) Use the grid data already stored in memory. Beware that the grid setting of the grid data stored in memory or the grid data recorded in a .cub/.grd must be exactly in coincidence with that of the grid data used to generate basin, otherwise the integral is meaningless.

Note that if you have made Multiwfn calculate grid data for a real space function, then this grid data will be stored in memory and hence you can directly use it in the basin integration step.

### Visualization

In option 0, you can visualize attractors and basins, for example



Most of buttons are self-explained, please feel free to play with them. You can plot basin by choosing corresponding term in the basin list at right-bottom corner. By default, only the grids at basin boundary are shown. If you want the entire basin to be portrayed, "Show basin interior" check box should be selected. At the end of the list, the "Unas" term means unassigned grid during basin generation, while "Boun" term means the grid travelled to box boundary, you can select them to plot the corresponding grids. Some basins are very small and very close to nucleus, such as core-type basin of ELF, they are often screened by molecular structure; if you want to inspect these basins you should deselect "Show molecule" check box.

Light green spheres denote attractors, and corresponding basins are colored as green. If the real space function simultaneously has positive and negative parts, the "attractors" in negative regions (in fact they are repulsors) will be shown as light blue spheres, and corresponding basin will be portrayed as blue color.

If a set of attractors have been clustered as a single one, although all of them will be displayed in the GUI, the index labels shown above them will be the same, which is the index of corresponding degenerate attractor.

After using option 1 to locate the attractors, if you visualize isosurface by the GUI of main function 5 or 13, you can also see the attractors and their labels. This design facilitates comparative study of attractors and isosurfaces.

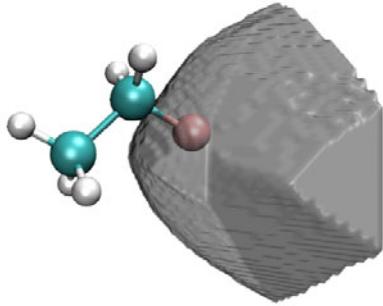
### **Detail of all options**

All of the options involved in basin analysis module are described below; some options have been partially discussed above.

**-6** This option controls the parameter used in attractor clustering. If the parameters in suboption 1 and 2 are set as A and B, respectively, that means for any two attractors, if between them the relative value difference is smaller than A, meanwhile their interval is less than  $B * \sqrt{dx^2 + dy^2 + dz^2}$ , where dx,dy,dz are grid spacings in X,Y,Z, then they will be clustered together. If you want to nullify the automatic clustering step after generating basins, simply set the parameter in suboption 2 to 0.

After basins have been generated, you can also use suboption 3 to manually cluster specified attractors.

**-5** Export basins as cube file. The basins in the specified index range will be successively outputted to basinXXXX.cub in current folder, where XXXX is the index of the basin. In the cube file, the value 1 and 0 denote the corresponding grid belongs and not belongs to the basin, respectively. Therefore you can plot isosurface with isovalue=0.5 to visualize the basins in your favourite visualization software. For example, below graph is plotted by VMD, the grey isosurface corresponds to AIM basin of fluorine atom



Note that when Multiwfn asking you "If output internal region of the basin?", if you input "n" rather than "y", then in the exported cube file, only boundary grids of the basin will have value of 1, and the other grids will have value 0. Therefore only interbasin surface will be shown when you visualizing isosurface.

You can also choose 0,0, then basin.cub will be outputted, in which grid value corresponds to basin index. This is important if you would like to

**-10** Return to main menu.

**-4** Export attractors as pdb file. The coordinate of all attractors will be outputted to attractors.pdb in current folder. In this file, the atom indices correspond to the attractor indices before clustering, while the residue indices indicate the attractor indices after clustering.

**-3** Show information of attractors. The coordinate and value of all attractors will be outputted on screen. For degenerate attractors, the shown coordinates and values are the average ones of their member attractors, the coordinate and the value of all of the member attractors will also be individually shown on screen.

**-2** Measure distances, angles and dihedral angles between attractors or atoms. As the title says. Please follow the prompts shown on the screen.

**-1** Select the method for generating basins. Three methods are available now: (1) On-grid method (2) near-grid method (3) near-grid method with boundary refinement step. Note that the near-grid method used in Multiwfn has been adapted by me, and thus became more robust. In general I recommend method 3, and this is also the default method.

**0** Visualize attractors and basins. This option has already been introduced above.

**1** Generate basins and locate attractors. Choose a real space function, and select a grid setting, then Multiwfn will calculate grid data, and then generate basins meanwhile locate attractors. After that, as mentioned earlier, if there are some attractors having similar value and closely placed then they will be automatically clustered. If a grid data has been stored in memory, you can directly choose to use this grid data to avoid calculating new grid data. You can use this option to regenerate basins again and again.

Multiwfn provided a lot of ways to define the grid setting. If you want to study the basins in the whole system, in commonly "medium quality grid" is recommended for qualitative analysis purposes; while if you want to obtain higher integration accuracy, "high quality grid" is in general recommended. If you only need to study the basins in a local region of the whole system, you can make the spatial scope of the grid data only cover this region; for this purpose, I suggest you to use the option "Input center coordinate, grid spacing and box length", by which you can easily define the spatial scope of the grid data.

**2** Integrate real space functions in the basins. Select a real space function, or select the grid data stored in memory, or choose to use external .cub/.grd file, then the real space function you

selected or the real space function recorded in the grid data will be integrated in the basins that have been generated by option 1, the integral in each basin and basin volumes will be outputted. If there are some unassigned grids or the grids travelled to box boundary, their integrals will also be shown.

If the basins you analyzed are AIM basins, it is highly recommended to use option 7 instead to gain much better integration accuracy.

**3** Calculate electric multipole moments in the basins. Please consult Section 3.18.3. The differences relative to Section 3.18.3 are that the ranges of integration in our current consideration are basins rather than fuzzy atom spaces, and nuclear positions should be replaced by attractor positions. The multipole moments are outputted up to quadrupole, while octopole and higher orders are not supported, because based on grid integration they are difficult be evaluated accurately.

If the basins you analyzed are AIM basins, it is highly recommended to use option 8 instead to gain much better integration accuracy.

**4** Calculate localization index and delocalization index for the basins. Please consult Section 3.18.5. The only difference relative to Section 3.18.5 is that the range of integration in our current consideration is basins rather than fuzzy atom spaces.

**5** Calculate and output orbital overlap matrix in all basins to BOM.txt in current folder. All virtual orbitals are ignored.

*Below options are available only when the real space function used to define the basins is chosen as electron density*

**7** Integrate real space functions in AIM basins with mixed type of grids. This option is specific for integrating AIM basins; there are three different ways to realize it:

Hint: Accuracy:  $(2) \geq (3) >> (1)$ . Time spent:  $(2) > (3) >> (1)$ . Memory requirement:  $(3) > (2) = (1)$

**(1)** Integrate a specific function with atomic-center + uniform grids: Atomic-center grids are mainly used to integrate the real space function near nuclei, while uniform grids are mainly used for other regions. The accuracy is much better than solely using uniform grids (namely option 2 in basin analysis module).

**(2)** The same as (1), but with exact refinement of basin boundary: Compared to option (2), when integrating the grids at basin boundary, the assignment of these grids will be exactly refined by steepest ascent scheme, hence the result will be more accurate than using option (1), unfortunately the refinement step is time consuming.

**(3)** The same as (2), but with approximate refinement of basin boundary: This is an approximate version of option (2). The gradient of electron density used in refinement step will not be evaluated exactly, but obtained by trilinear interpolation of pre-calculated grid data of gradient. Although evaluating the grid data of gradient is also time consuming, the overall time cost is lower than option (2), and the loss of accuracy is trivial.

After you used option (2) or (3) once, the assignment of the boundary grids will be updated permanently, that means then if you use option (1), the result will be identical to (2) or (3).

Not only the basin volumes are outputted along with the integrals, the basin volumes with electron density  $> 0.001$  are also outputted, which can be regarded as atomic sizes.

**8** Calculate electric multipole moments in AIM basins with mixed type of grids. Similar to option 3, but use mixed atomic-center and uniform grids to calculate electric multipole moments to gain better accuracy without bringing evident additional computational cost. This option is only applicable to AIM basins.

**9** Obtain atomic contribution to population of external basins. The external basins means the basin defined by a cube file named basin.cub in current folder, in which the grid value corresponds to basin index. This option aims to obtain atomic contribution to population of ELF bond basins (or other type of basins) based on AIM partition. Please check Section 4.17.7 for example.

Notice that if you use option 7 and 8, when you generating AIM basin, the spatial range of the grid data must cover the whole system. If effective core potential (ECP) is used for an atom, then many attractors will occur at valence region of the atom; before entering option 7 and 8, you have to manually cluster these attractors as single one by suboption 3 in option -6, otherwise the program does not know which attractors correspond to this atom.

For option 3, 4, 5, 7 and 8, if the input file you used does not contain GTF information (e.g. .cub file), then Multiwfn will prompt you to input a new file, which should contain GTF information of present system, you can use for example .wfn/.wfx/.fch/.molden/.gms file as input.

**Information needed:** GTFs or grid data, atom coordinates

## 3.21 Electron excitation analysis (18)

### 3.21.1 Analyze and visualize hole-electron distribution, transition dipole moment and transition density (1)

This very powerful module is used to analyze and visualize hole-electron distribution, transition density, transition dipole moment density and charge difference density. Moreover, transition density matrix can be generated, and transition dipole moment can be decomposed to MO pair contributions, hole and electron can be decomposed to MO contributions.

#### 3.21.1.1 Theory

This module involves many theories, which will be described below in turn.

##### Theory 1: Hole and electron

In single-electron excitation process, an electron leaves A and goes to B; where A and B are real space functions, and they will be respectively named as "hole" and "electron" in the following texts. If the excitation can be perfectly described as HOMO→LUMO transition, then A and B are just HOMO and LUMO, respectively. However, in most practical cases, this single-orbital pair model is not suitable, and the excitations have to be represented as the transition of multiple MO pairs with proper weighting coefficients. The most straightforward way to deal with electron excitation problem is CIS, the CIS excited state wavefunction is written as

$$\Psi^{\text{exc}} = \sum_{i \rightarrow l} w_i^l \Phi_i^l$$

where  $i$  and  $l$  respectively run over all occupied and all virtual MOs, similarly hereafterin.  $\Phi_i^l$  is the configuration state wavefunction corresponding to moving the electron from originally occupied MO  $i$  to virtual MO  $l$ .  $w$  is configuration coefficient.

### 3 Functions

I and my collaborator Cheng Zhong have shown (to be published) that the density distribution of hole and electron can be gracefully defined as

$$\begin{aligned}\rho^{\text{hole}}(\mathbf{r}) &= \rho_{\text{(loc)}}^{\text{hole}}(\mathbf{r}) + \rho_{\text{(cross)}}^{\text{hole}}(\mathbf{r}) = \sum_{i \rightarrow l} (w_i^l)^2 \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}) + \sum_{i \rightarrow l} \sum_{j \neq i \rightarrow l} w_i^l w_j^l \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \\ \rho^{\text{ele}}(\mathbf{r}) &= \rho_{\text{(loc)}}^{\text{ele}}(\mathbf{r}) + \rho_{\text{(cross)}}^{\text{ele}}(\mathbf{r}) = \sum_{i \rightarrow l} (w_i^l)^2 \varphi_l(\mathbf{r}) \varphi_l(\mathbf{r}) + \sum_{i \rightarrow l} \sum_{i \rightarrow m \neq l} w_i^l w_i^m \varphi_l(\mathbf{r}) \varphi_m(\mathbf{r})\end{aligned}$$

where  $\varphi$  denotes MO. "loc" and "cross" stand for the contribution of local term and cross term to the hole/electron distribution. Note that what we are discussing is distribution rather than wavefunction of hole and electron, so  $\rho^{\text{hole}}$  and  $\rho^{\text{ele}}$  do not have phase.

Due to the orthonormality of MOs, and the fact that the sum of the square of all configuration coefficients is 1, it is clear that

$$\int \rho^{\text{hole}}(\mathbf{r}) d\mathbf{r} = 1 \quad \int \rho^{\text{ele}}(\mathbf{r}) d\mathbf{r} = 1$$

This is an important expected property of the definition of hole and electron distribution.

The overlap between hole and electron distribution is defined as  $\min[\rho^{\text{hole}}(\mathbf{r}), \rho^{\text{ele}}(\mathbf{r})]$ , namely taking the minimal value of  $\rho^{\text{hole}}$  and  $\rho^{\text{ele}}$  everywhere.

The charge density difference between excited state and ground state can be exactly evaluated as

$$\Delta\rho(\mathbf{r}) = \rho^{\text{ele}}(\mathbf{r}) - \rho^{\text{hole}}(\mathbf{r})$$

Beware that if you are a Gaussian user, the  $\Delta\rho$  calculated in this way is obviously different to the  $\Delta\rho$  produced by minusing ground state density from excited state density unless you specified the keyword "density=rhocci" when generating excited state wavefunction, because by default the excited state density outputted by Gaussian is the relaxed one, rather the unrelaxed one (directly constructed by CIS excited state wavefunction)

After generalization, above definitions can also be applied to TDHF and TDDFT cases, where de-excitations occur. The generalized local terms are

$$\begin{aligned}\rho_{\text{(loc)}}^{\text{hole}} &= \sum_{i \rightarrow l} (w_i^l)^2 \rho_i - \sum_{i \leftarrow l} (w_i^l)^2 \rho_i \\ \rho_{\text{(loc)}}^{\text{ele}} &= \sum_{i \rightarrow l} (w_i^l)^2 \rho_l - \sum_{i \leftarrow l} (w_i^l)^2 \rho_l\end{aligned}$$

The generalized cross terms are

$$\begin{aligned}\rho_{\text{(cross)}}^{\text{hole}} &= \sum_{i \rightarrow l} \sum_{j \neq i \rightarrow l} w_i^l w_j^l \varphi_i \varphi_j - \sum_{i \leftarrow l} \sum_{j \neq i \leftarrow l} w_i^l w_j^l \varphi_i \varphi_j \\ \rho_{\text{(cross)}}^{\text{ele}} &= \sum_{i \rightarrow l} \sum_{i \rightarrow m \neq l} w_i^l w_i^m \varphi_l \varphi_m - \sum_{i \leftarrow l} \sum_{i \leftarrow m \neq l} w_i^l w_i^m \varphi_l \varphi_m\end{aligned}$$

In order to investigate which MOs have significant contribution to hole and electron, I defined the contribution of occupied MO to hole and virtual MO to electron as follows

$$\Theta_i^{\text{hole}} = \sum_{i \rightarrow l} (w_i^l)^2 - \sum_{i \leftarrow l} (w_i^l)^2 \quad \Theta_l^{\text{ele}} = \sum_{i \rightarrow l} (w_i^l)^2 - \sum_{i \leftarrow l} (w_i^l)^2$$

The normalization conditions are held evidently

$$\sum_i \Theta_i^{\text{hole}} = 1 \quad \sum_l \Theta_l^{\text{ele}} = 1$$

#### Theory 2: Quantitative representation of hole and electron distribution

### 3 Functions

The distribution of hole and electron can be quantitatively represented in following ways.

$S = \int \min(\rho^{\text{hole}}(\mathbf{r}), \rho^{\text{ele}}(\mathbf{r})) d\mathbf{r}$  is used to characterize the overlapping extent of hole and electron.

Centroid of hole and electron can be calculated. For example, X coordinate of centroid of electron is

$$X_{\text{ele}} = \int x \rho^{\text{ele}}(\mathbf{r}) d\mathbf{r}$$

where  $x$  is X component of  $\mathbf{r}$ .

The distance between the two centroids measures the CT length

$$D_{\text{CT},x} = |X_{\text{ele}} - X_{\text{hole}}| \quad D_{\text{CT},y} = |Y_{\text{ele}} - Y_{\text{hole}}| \quad D_{\text{CT},z} = |Z_{\text{ele}} - Z_{\text{hole}}|$$

$$D_{\text{CT}} = \sqrt{(D_{\text{CT},x})^2 + (D_{\text{CT},y})^2 + (D_{\text{CT},z})^2}$$

It is noteworthy that the variations of dipole moment of excited state with respect to ground state in X, Y and Z can be simply calculated as (not true if relaxed density of excited state is used)

$$\Delta\mu_x = -(X_{\text{ele}} - X_{\text{hole}}) \quad \Delta\mu_y = -(Y_{\text{ele}} - Y_{\text{hole}}) \quad \Delta\mu_z = -(Z_{\text{ele}} - Z_{\text{hole}})$$

The RMSDs of hole and electron are used to characterize their distribution breadths. For example, Y component of RMSD of hole

$$\sigma_{\text{hole},y} = \sqrt{\int (y - Y_{\text{hole}})^2 \rho^{\text{hole}}(\mathbf{r}) d\mathbf{r}}$$

There are often many nodes or fluctuations in hole and electron distributions. In order to study them more easily,  $C_{\text{hole}}$  and  $C_{\text{ele}}$  functions are defined, whose structures are similar to Gauss function, and the value asymptotically approaches zero.

$$C_{\text{ele}}(\mathbf{r}) = A_{\text{ele}} \exp\left(-\frac{(x - X_{\text{ele}})^2}{2\sigma_{\text{ele},x}^2} - \frac{(y - Y_{\text{ele}})^2}{2\sigma_{\text{ele},y}^2} - \frac{(z - Z_{\text{ele}})^2}{2\sigma_{\text{ele},z}^2}\right)$$

$$C_{\text{hole}}(\mathbf{r}) = A_{\text{hole}} \exp\left(-\frac{(x - X_{\text{hole}})^2}{2\sigma_{\text{hole},x}^2} - \frac{(y - Y_{\text{hole}})^2}{2\sigma_{\text{hole},y}^2} - \frac{(z - Z_{\text{hole}})^2}{2\sigma_{\text{hole},z}^2}\right)$$

The factor  $A$  is introduced so that  $C_{\text{hole}}$  and  $C_{\text{ele}}$  are normalized.

$H$  and  $t$  indices are defined as

$$H_\lambda = (\sigma_{\text{ele},\lambda} + \sigma_{\text{hole},\lambda})/2$$

$$t_\lambda = D_{\text{CT},\lambda} - H_\lambda$$

where  $\lambda$  corresponds to the direction in which CT occurred.  $t$  may be regarded as the separation degree of hole and electron. If  $t < 0$ , an evident overlap between hole and electron is expected. Clear separation of hole and electron distributions must correspond to a larger positive value of  $t$ .

#### Theory 3: Transition density matrix and transition density

(One-electron, spinless) transition density matrix between excited state and ground state of an  $N$ -electron system in real space representation is defined as follows (I assume that all wavefunctions are real type, so complex conjugation sign is omitted)

### 3 Functions

$$T(\mathbf{r}; \mathbf{r}') \equiv T(\mathbf{r}_1; \mathbf{r}'_1) = \int \Phi^0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^{\text{exc}}(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\sigma_1 d\mathbf{x}_2 d\mathbf{x}_3 \dots d\mathbf{x}_N$$

where  $\Phi^0$  is the Slater-determinant of ground state wavefunction.  $\mathbf{x}$  is spin-space coordinate,  $\sigma$  stands for spin coordinate.

For CIS/TDHF/TDDFT excited state wavefunction, after we expanded  $\Psi^{\text{exc}}$  and applied Slater-Condon rule, it can be easily shown that  $T$  can be explicitly written as

$$T(\mathbf{r}; \mathbf{r}') = \sum_i \sum_l w_i^l \varphi_i(\mathbf{r}) \varphi_l(\mathbf{r}')$$

If we only take the diagonal terms of the transition density matrix, then we obtain transition density

$$T(\mathbf{r}) = \sum_i \sum_l w_i^l \varphi_i(\mathbf{r}) \varphi_l(\mathbf{r})$$

$T(\mathbf{r})$  can be studied as a normal real space function, for example, visualized in terms of isosurface.

Note that due to the orthonormality of MOs, integration of  $T(\mathbf{r})$  over the whole space is exactly zero. If the excited state and ground state correspond to different spin states, due to the orthonormality of spin coordinate,  $T(\mathbf{r}; \mathbf{r}')$  must be a zero matrix, and  $T(\mathbf{r})$  is zero everywhere.

In basis function representation, transition density matrix can be written as

$$P_{\mu\nu}^{\text{tran}} = \sum_i \sum_l w_i^l C_{\mu i} C_{\nu l}$$

where  $C_{\mu i}$  denotes the expansion coefficient of basis function  $\mu$  in MO  $i$ .

Transition density matrix in real space and in basis function representations are correlated as

$$T(\mathbf{r}; \mathbf{r}') = \sum_{\mu} \sum_{\nu} P_{\mu\nu}^{\text{tran}} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}')$$

Notice that transition density matrix in general is not a symmetric matrix (though the deviation is often very small), however it can be symmetrized as follows (the case  $\mu=\nu$  is also included)

$$\bar{P}_{\mu\nu}^{\text{tran}} = \frac{(P_{\mu\nu}^{\text{tran}} + P_{\nu\mu}^{\text{tran}})}{\sqrt{2}} = \frac{1}{\sqrt{2}} \sum_i \sum_l w_i^l (C_{\mu i} C_{\nu l} + C_{\nu i} C_{\mu l})$$

#### Theory 4: Transition dipole moment and oscillator strength

X, Y and Z components of transition dipole moment density can be defined as are the negative value of product of X, Y and Z coordinate variables and transition density

$$T_x(\mathbf{r}) = -x T(\mathbf{r}) \quad T_y(\mathbf{r}) = -y T(\mathbf{r}) \quad T_z(\mathbf{r}) = -z T(\mathbf{r})$$

Integrating transition dipole moment density over the whole space yields transition dipole moment  $\mathbf{D}$

$$D_x = \int T_x(\mathbf{r}) d\mathbf{r} \quad D_y = \int T_y(\mathbf{r}) d\mathbf{r} \quad D_z = \int T_z(\mathbf{r}) d\mathbf{r}$$

Obviously, one can conveniently study the contribution to transition dipole moment from different molecular regions by visualizing transition dipole moment density.

Alternatively, transition dipole moment can be calculated based on dipole moment integral between occupied and virtual MOs

### 3 Functions

$$D_x = -\sum_i \sum_l w_i^l \langle \varphi_i | x | \varphi_l \rangle \quad D_y = -\sum_i \sum_l w_i^l \langle \varphi_i | y | \varphi_l \rangle \quad D_z = -\sum_i \sum_l w_i^l \langle \varphi_i | z | \varphi_l \rangle$$

The contribution from each MO pair to transition dipole moment can be straightforwardly evaluated (namely the term in the summation notation).

Oscillator strength of a transition mode directly relates to the integral area of the corresponding absorption peak. The relationship between oscillator strength  $f$  and transition dipole moment  $\mathbf{D}$  is (in atomic unit)

$$f = \frac{2}{3} \Delta E \times (D_x^2 + D_y^2 + D_z^2)$$

where  $\Delta E$  denotes the transition energy between the two states.

#### Theory 5: Transition magnetic dipole moment and the corresponding density

The transition dipole moments involved in all of above discussions are transition *electric* dipole moment, while the other kind of transition dipole moment, namely transition *magnetic* dipole moment, is also an important property for some special systems.

The operator for magnetic dipole moment due to movement of electrons is the angular momentum operator  $\mathbf{L}$  (see e.g. *Theoret. Chim. Acta*, **6**, 341)

$$\begin{aligned} \mathbf{L} &= -i(\mathbf{r} \times \nabla) = \hat{\mathbf{i}} L_x + \hat{\mathbf{j}} L_y + \hat{\mathbf{k}} L_z \\ &= -i \left[ \hat{\mathbf{i}} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) + \hat{\mathbf{j}} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) + \hat{\mathbf{k}} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right] \end{aligned}$$

where  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  are unity vectors in X, Y and Z directions, respectively. Therefore, the X component of transition magnetic dipole moment is defined as below. Noticed that in order to provide a real value I ignored the imaginary and negative signs simultaneously; the symbol " $\leftarrow$ " denotes de-excitation MO pairs in TDHF/TDDFT formalism.

$$M_x = \left\langle \Phi^0 \left| y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right| \Psi^{\text{exc}} \right\rangle = \sum_{i \rightarrow l} w_i^l \langle \varphi_i | y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} | \varphi_l \rangle - \sum_{j \leftarrow m} w_j^m \langle \varphi_j | y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} | \varphi_m \rangle$$

Clearly, it is straightforward to define the X component of transition magnetic dipole moment density  $m_x(\mathbf{r})$  as follows to satisfy the condition  $M_x = \int m_x(\mathbf{r}) d\mathbf{r}$ , so that the distribution of transition magnetic dipole moment can be visualized as isosurface or plane map

$$m_x(\mathbf{r}) = \sum_{i \rightarrow l} w_i^l \varphi_i(\mathbf{r}) \left[ y \frac{\partial \varphi_l}{\partial z}(\mathbf{r}) - z \frac{\partial \varphi_l}{\partial y}(\mathbf{r}) \right] - \sum_{j \leftarrow m} w_j^m \varphi_j(\mathbf{r}) \left[ y \frac{\partial \varphi_m}{\partial z}(\mathbf{r}) - z \frac{\partial \varphi_m}{\partial y}(\mathbf{r}) \right]$$

Y and Z components are defined similarly.

#### Theory 6: Coulomb attraction between hole and electron

The "electron" of course carries negative charge, while "hole" can be regarded as carrying positive charge, therefore formally there is Coulomb attractive energy between them, which can be calculated as simple Coulomb formula:

$$E_C = - \int \int \frac{\rho^{\text{hole}}(\mathbf{r}_1) \rho^{\text{ele}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

In Multiwfn, above integral is directly calculated based on evenly distributed grid data of hole and electron. Notice that although the code has been substantially optimized and parallelized, the computational cost is still high, so you need to wait patiently during calculation. The cost is formally proportionally to square of the number of grids; therefore, the cost of medium quality grid will be higher than low quality grid by one order of magnitude.

### 3.21.1.2 Input file

This module requests two types of files as input.

**(1) A file containing molecular orbitals of ground states.** .fch/.molden/.gms file produced by excited state calculation (CIS, TDHF or TDDFT method) can be used. This file should be loaded when Multiwfn boots up. Multiwfn will utilize the molecular orbitals and basis function information recorded in it during the electron excitation analysis.

**(2) A file containing configuration coefficients of excited states.** There are three cases, as shown below. The path of this kind of file should be inputted when you enter present module.

(a) Gaussian user: Output file of excited state calculation (CIS, TDHF or TDDFT method) can be used. Since by default Gaussian only outputs the configuration coefficients larger than 0.1, in order to gain acceptable results, you must add *IOP(9/40=4)* keyword in the route section so that all configuration coefficients whose magnitude larger than 0.0001 will be printed. Using *IOP(9/40=5)* instead will result in marginally better accuracy, however the Gaussian output file will become larger and computational cost of present module will be higher.

Note: DO NOT use the Gaussian output file of excited state optimization or frequency analysis task as input file! Multiwfn cannot properly parse this kind of output file!

(b) ORCA user: Output file of excited state calculation by CIS or TDA-DFT method can be used. At least for ORCA 4.0, output file corresponding to standard TDDFT task should not be used, since configuration coefficients are not printed in this case. In addition, beware that current version of ORCA can only output configuration coefficients whose magnitude is larger than 0.01, therefore the analysis result is obviously not quite accurate.

(c) If you are neither a Gaussian user nor an ORCA user, you can also use plain text file as the input file, the format of transition information should be completely identical to Gaussian output, for instance:

```
1 11.4194
 3 -> 10      -0.00361
 5 -> 7       0.69644
 5 -> 8       0.07291
 5 -> 12      0.09814
 5 -> 18      -0.00375
```

where the 1 and 11.4194 in the first line are spin multiplicity of the excited state and transition energy (eV), respectively. (For de-excitation transitions,  $\rightarrow$  should be written as  $\leftarrow$ ).

Both close-shell and open-shell calculations are fully supported.

### 3.21.1.3 Functions

Present module has many functions, they will be described below in turn

**Function 1: Visualize and analyze hole, electron and transition density and so on**

After you enter this function, you are requested to select a way to define grid data, then grid data will be calculated for hole distribution, electron distribution, overlap of hole and electron distribution, transition density, transition electric/magnetic dipole moment density, charge density difference and  $C_{\text{ele}}/C_{\text{hole}}$  functions. Then these grid data can be directly visualized as isosurface, or exported as cube file in current folder by corresponding options. In the post-process menu, you can also choose to calculate Coulomb attractive energy between hole and electron distribution, notice that this calculation is expensive even if you are using low quality grid.

After the calculation of the grid data have been finished, some statistic data will be shown. The ideal value of the integral of hole or electron distribution is 1, while for transition density the ideal value is 0. The transition electric/magnetic dipole moment is calculated by integrating the grid data of transition dipole moment density, the value should be very close to the one directly outputted by quantum chemistry program. RMSDs of hole and electron exhibit their distribution breadth in each direction. Integral of overlap of hole-electron distribution can be used to identify if a transition mode is local excitation, and the distance between centroid of hole and electron is a good indicative of charge-transfer length of present electron transition mode.  $t$  index reveals if hole and electron distributions are separated clearly.

When you choose to visualize/export hole and electron distribution, you can visualize/export their local term, cross term or total distribution (local term + cross term) separately. The hole and electron distributions involved in other options corresponds to their total distributions.

By default the transition magnetic dipole moment density is not evaluated because it is less important than the transition electric dipole moment density. If you want to calculate it, select option -1 before using this function. An example of analyzing transition magnetic dipole moment density can be found in Section 4.18.1.

#### **Function 2: Show contribution of MO pairs to transition dipole moment**

The transition dipole moment in X/Y/Z can be decomposed into MO pair contributions (in other words, configuration contribution) by this function. Since there may be very large number of MO pairs recorded in the input file, you need to input the threshold for printing the result. For very large system, calculating contributions from all MO pairs is quite expensive, therefore Multiwfn enables the user to set a threshold, if absolute value of coefficient of a configuration is lower than this threshold, then contribution to transition dipole moment from the corresponding MO pair will not be computed but simply regarded as zero. Evidently, the lower the threshold, the higher the computational cost. If you set threshold to 0, then all configurations will be evaluated.

You can also choose to print the contributions from all MO pairs to transdip.txt in current folder. This function is very useful for figuring out which MO pairs have large contribution to transition dipole moment and thus oscillator strength.

Finally, the norm of transition dipole moment and the corresponding oscillator strength are also outputted (The threshold you set for considering MO pairs evidently affects there values).

#### **Function 3: Show contribution of each MO to hole and electron distribution**

You only need to input printing threshold, then contribution of MO to hole and electron distribution will be shown. This function is very useful to identify which MOs significantly constitute the hole and electron.

#### **Function 4: Generate and export transition density matrix**

According to MO expansion coefficients and configuration coefficients, transition density matrix in basis function representation can be constructed by this function. You can choose if

symmetrizing the matrix according to the formula shown above. The generated matrix will be outputted to tpmat.txt in current folder, which can be plotted as color-filled map by function 2 of main function 18, see Section 3.21.2 for detail.

Note that when ground state and excited state have different spin multiplicities, due to the orthonormality of spin coordinate, although in principle the transition density matrix should be zero, the outputted matrix is not, because Multiwfn only takes space part of the MOs into account during constructing the matrix.

#### **Function 5: Decompose transition dipole moment to basis function and atom contributions**

This function is used to decompose the total transition electric or magnetic dipole moment into contributions from each basis function and atom. As there is no unique way to derive population number, there are also many possible ways to realize the decomposition. In this function Mulliken partition is employed. For example, the contribution from basis function  $\mu$  to Z component of transition electric dipole moment is evaluated as follows

$$D_z^{(\mu)} = P_{\mu\mu}^{\text{tran}} \langle \chi_\mu | -z | \chi_\mu \rangle + \sum_{v \neq \mu} [P_{\mu v}^{\text{tran}} \langle \chi_\mu | -z | \chi_v \rangle + P_{v\mu}^{\text{tran}} \langle \chi_v | -z | \chi_\mu \rangle] / 2$$

and the contribution from basis function  $\mu$  to Z component of transition magnetic dipole moment

$$M_z^{(\mu)} = P_{\mu\mu}^{\text{tran}} \left\langle \chi_\mu \left| x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right| \chi_\mu \right\rangle + \sum_{v \neq \mu} [P_{\mu v}^{\text{tran}} \left\langle \chi_\mu \left| x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right| \chi_v \right\rangle + P_{v\mu}^{\text{tran}} \left\langle \chi_v \left| x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right| \chi_\mu \right\rangle] / 2$$

Then the contribution from an atom is simply the sum of the contribution from the basis functions belonging to it.

The result is unreliable if diffuse functions are presented in your calculation. In this case, the best way to study the contribution from atoms is visualizing the aforementioned transition dipole moment density.

You can select decomposing which type of transition dipole moment when enter this function. Notice that in order to decompose transition electric (magnetic) dipole moment, before booting up Multiwfn, you must set "igenDbas" ("igenMagbas") parameter in settings.ini to 1, so that electric (magnetic) dipole moment integral matrix, which is required in present function, can be generated when loading input file.

#### **Function 6: Calculate Mulliken atomic transition charges**

This function is used to calculate atomic transition charges, which is useful for studying Coulomb coupling between ground state and excited state of two molecules (see e.g. *J. Phys. Chem. B*, **110**, 17268).

Transition population of a basis function  $\mu$  derived by Mulliken method is

$$\Theta_\mu^{\text{tran}} = P_{\mu\mu}^{\text{tran}} + \sum_{v \neq \mu} (P_{\mu v}^{\text{tran}} + P_{v\mu}^{\text{tran}}) S_{\mu v} / 2$$

So, the Mulliken atomic transition charge of atom  $A$  should be  $\sum_{\mu \in A} \Theta_\mu^{\text{tran}}$ . The sum of all atomic transition charges must be equal to zero.

The result will be outputted to .chg file in current folder, the format of this kind of file has been introduced in Section 2.5. You can use your text editor to open it, the last column is what you

need.

#### **Function 7: Decompose transition magnetic dipole moment as basis function and atom contributions**

Very similar to function 5, but the transition dipole moment to be decomposed is the magnetic one rather than the electric one. You must set "igenMagbas" in settings.ini to 1.

#### **Function 10: Modify or check excitation coefficients**

This function allows one to modify or check coefficient of MO pairs (or say configuration coefficient). If you have modified the coefficients, then during the calculation of hole-electron distribution, transition dipole moment density, oscillator strength and so on, the modified coefficients will be used. Obviously, if you set the coefficient of some MO pairs to zero, then their contributions to the quantities you calculated will be ignored; while if you clean all coefficients but for a specific MO pair (this can be directly realized via suboption 3), then the resultant quantities will only characterize this MO transition.

An very detailed example is given in Section 4.18.1

**Information needed:** GTF and basis function (for all MOs, so use .fch/.molden/.gms), Gaussian output file or plain text file which describes electron transition information

### **3.21.2 Plot transition density matrix as color-filled map (2)**

#### **Theory**

Transition density matrix (TDM) between electronic state  $K$  and state  $L$  is denoted by  $P^{KL}$ , during excited state calculation in many quantum chemistry programs this matrix can be outputted in the form of expansion by atomic-center basis functions. We can further contract such matrix by following equation to make it represented by atom centers:

$$\tilde{P}_{A,B}^{KL} = \sum_{\mu \in A} \sum_{\nu \in B} (P_{\mu\nu}^{KL})^2$$

where  $\mu$  and  $\nu$  denote the basis functions centered at atom A and on B respectively.

Diagonal terms, e.g.  $\tilde{P}_{A,A}^{KL}$ , represents the magnitude of induced charge on atom A when the system undergoes electron transition from state  $K$  to  $L$ . While off-diagonal terms, e.g.  $\tilde{P}_{A,B}^{KL}$ , displays the strength of hole-electron coherence between atom A and B when electron transits. If this matrix is plotted as a color-filled map, then the primary atoms involved in specific electron transition mode, and the spatial span of the electron transition can be clearly and visually studied, this is especially useful for analyzing large-size and conjugated molecules. Commonly hydrogens can be omitted when plotting.

#### **Input file**

This function requires two files as input. The first one is the .fch/.molden/.gms file corresponding to current system. This file can be obtained by any type of calculation, since only the elements and the correspondence between basis functions and the atoms will be loaded from this file.

The second one must be an ASCII type file containing TDM. There are two circumstances:

(1) If you are a Gaussian user, you can directly let Gaussian to write TDM in the output file. However, by default, TDM is not printed in output file, thus you have to specify `density=transition=X IOp(6/8=3)` in route section of Gaussian input file, so that TDM between ground state and excited state X can be written in Gaussian output file by Link 601 module.

Note that in fact, TDM is not exactly symmetrical, but commonly very close to a symmetry matrix. In Gaussian, the outputted TDM is artificially symmetrized; that is the elements of the outputted TDM (referred to as  $P'$ ) are generated as  $P'_{\mu\nu}=P'_{v\mu}=(P_{\mu\nu}+P_{v\mu})/\sqrt{2}$ , including both cases  $\mu=v$  and  $\mu\neq v$ . If you want to plot original TDM, you can use option 4 in subfunction 1 of main function 18 to generate the TDM and use resulting `tdmat.txt` as input file.

(2) If you are not a Gaussian user but the program you used can output `.molden` or `.gms` file, you can make use of option 4 in subfunction 1 of main function 18 to generate the `tdmat.txt` file, which contains TDM and can be directly used as input file for present function, see corresponding section of the manual for detail. Alternatively, you can try to use proper keywords in your quantum chemistry program to let it output TDM, and then write a small program by yourself to make the format of the TDM completely consistent with `examples\tdmat.txt` file, then the file could be used as input file.

### Usage

After you boot up Multiwfn, first you should input the path of `.fch/.molden/.gms` file corresponding to current system, and then choose main function 18 and subfunction 2 to enter TDM plotting module, then input the path of the Gaussian output file or the plain text file containing TDM. After that you will see several options, you can choose 0 to show  $\tilde{P}^{KL}$  graph on screen immediately, or choose 1 to save the TDM plot to graphical file in current folder with `DISLIN` prefix. Labels in abscissa and ordinate of the plot correspond to indices of atom (notice that only if hydrogens are taken into account, then the indices in the plot will be consistent with actual atom indices in present system). By option 3 the data point can be exported to external file, so that the  $\tilde{P}^{KL}$  can be conveniently replotted by some third-party plotting tools such as Origin and SigmaPlot. By option 4 you can choose if hydrogens will be taken into account in the  $\tilde{P}^{KL}$  graph. Upper and lower range of color scale can be changed by option 5, by default these two values are set automatically to maximal and minimal values of  $\tilde{P}^{KL}$ . Through option 6 you can change the number of interpolation steps between grid data, if you want to make the graph looks more smooth then set it to a larger value, if the value is set to 1 then interpolation will not be performed. Steps between labels in abscissa and ordinate can be set by option 7. Option 8 determine if performing normalization for  $\tilde{P}^{KL}$ , if perform, then the sum of all elements of the normalized  $\tilde{P}^{KL}$  will be equal to unity.

Please note that, if the basis-set you used contains diffuse basis functions, in rare cases, the transition density outputted by Gaussian may be incorrect, and thus the TDM map will be useless.

**Hint:** Aside from plotting TDM, it is also possible to use present function to plot density matrix (DM) for a given state, then how the atoms are correlated to each other can be clearly seen, since the off-diagonal elements can be approximately regarded as the bond orders between the corresponding atoms. The steps of plotting DM in Multiwfn is completely identical to plotting TDM. The only difference comes from Gaussian input files. If you intend to plot DM for ground state, simply use the keyword `IOp(6/8=3)` in the ground state calculation, then the DM will be printed in the Gaussian output file. If you wish to plot DM for the  $i$ th excited state, then you

should specify the keyword *density IOp(6/8=3)*, and meantime set the *root* keyword in CIS/ZINDO/TD to *i*. For example *#P cis(root=5, nstates=10)/6-31g(d) density iop(6/8=3)*.

An example of plotting TDM is given in Section 4.18.2.

**Information needed:** Basis functions, Gaussian output file or plain text file containing TDM

### 3.21.3 Analyze charge-transfer based on density difference grid data (3)

#### Theory

In the paper *J. Chem. Theory Comput.*, **7**, 2498 (2011), the authors proposed a method for analyzing charge-transfer (CT) during electron transition. It is also probable that this method can be used to study CT in other processes, such as formation of complex. In the original paper, the author only discussed the cases when charge-transfer is in one-dimension, while in Multiwfn this scheme is generalized in three-dimension cases.

The electron density variation between excited state (EX) and ground state (GS) is

$$\Delta\rho(\mathbf{r}) = \rho_{EX}(\mathbf{r}) - \rho_{GS}(\mathbf{r})$$

Notice that the geometry used in calculating  $\rho_{EX}(\mathbf{r})$  and  $\rho_{GS}(\mathbf{r})$  must be identical, otherwise the resulting  $\Delta\rho(\mathbf{r})$  is meaningless.  $\Delta\rho(\mathbf{r})$  can be divided into positive and negative parts, namely  $\rho_+(\mathbf{r})$  and  $\rho_-(\mathbf{r})$ . Of course, the integral of  $\rho_+(\mathbf{r})$  and  $-\rho_-(\mathbf{r})$  over the whole space should be equal, if evident inequality is observed, that means the error in numerical integral is unnegelectable, and denser grid is required. Even though what you analyzed is single-electron excitation, the magnitude of  $\rho_+(\mathbf{r})$  and  $\rho_-(\mathbf{r})$  as well as their integrals can also be larger than 1.0 theoretically, this is because the excitation of an electron leads to reorganization of distribution of the rest of electrons, which also make contribution to  $\Delta\rho(\mathbf{r})$ .

The transferred charge  $q_{CT}$  is the magnitude of the integral of  $\rho_+(\mathbf{r})$  or  $\rho_-(\mathbf{r})$ .

The barycenters of positive and negative parts can be computed as

$$\begin{aligned}\mathbf{R}_+ &= \int \mathbf{r} \rho_+(\mathbf{r}) d\mathbf{r} / \int \rho_+(\mathbf{r}) d\mathbf{r} \\ \mathbf{R}_- &= \int \mathbf{r} \rho_-(\mathbf{r}) d\mathbf{r} / \int \rho_-(\mathbf{r}) d\mathbf{r}\end{aligned}$$

The component coordinates of  $\mathbf{R}_+$  will be referred to as  $X_+, Y_+, Z_+$ , of  $\mathbf{R}_-$  will be referred to as  $X_-, Y_-, Z_-$ .

The distance between the two barycenters measures the CT length

### 3 Functions

$$D_{CT,X} = |X_+ - X_-|, \quad D_{CT,Y} = |Y_+ - Y_-|, \quad D_{CT,Z} = |Z_+ - Z_-|$$

The dipole moment variation caused by CT is evaluated as

$$\mu_{CT,X} = (X_+ - X_-)q_{CT}, \quad \mu_{CT,Y} = (Y_+ - Y_-)q_{CT}, \quad \mu_{CT,Z} = (Z_+ - Z_-)q_{CT}$$

Notice that the Eq. 7 in the original paper is  $\|\mu_{CT}\| = D_{CT}^* q_{CT} = |\mathbf{R}_+ - \mathbf{R}_-| * q_{CT}$ , this relationship is not rigorously and evidently only holds for one-dimension transfer cases (namely only one of  $D_{CT,X}, D_{CT,Y}, D_{CT,Z}$  is not zero). Only the equations shown above, which are used by Multiwfn, are correct for all cases! So DO NOT suspect whether Multiwfn is reliable or buggy due to the results often seemingly violates Eq. 7 of the original paper!

The RMSDs of the distribution of  $\rho_+(\mathbf{r})$  and  $\rho_-(\mathbf{r})$  in each direction are defined as

$$\sigma_{a,\lambda} = \sqrt{\frac{\int \rho_a(\mathbf{r})(\lambda' - \lambda_a)^2 d\mathbf{r}}{\int \rho_a(\mathbf{r}) d\mathbf{r}}}$$

where  $a=\{+,-\}$ ,  $\lambda'=\{x,y,z\}$ ,  $\lambda=\{X, Y, Z\}$ .  $x$ ,  $y$  and  $z$  are components of integral variable  $\mathbf{r}$ . For example

$$\sigma_{+,y} = \sqrt{\frac{\int \rho_+(\mathbf{r})(y - Y_+)^2 d\mathbf{r}}{\int \rho_+(\mathbf{r}) d\mathbf{r}}}$$

$C_+(\mathbf{r})$  and  $C_-(\mathbf{r})$  functions are defined aiming for visualizing CT more clearly than  $\Delta\rho(\mathbf{r})$ , their structure are similar to Gauss function, the value asymptotically approaches zero.

$$C_+(\mathbf{r}) = A_+ \exp\left(-\frac{(x - X_+)^2}{2\sigma_{+,x}^2} - \frac{(y - Y_+)^2}{2\sigma_{+,y}^2} - \frac{(z - Z_+)^2}{2\sigma_{+,z}^2}\right)$$

$$C_-(\mathbf{r}) = A_- \exp\left(-\frac{(x - X_-)^2}{2\sigma_{-,x}^2} - \frac{(y - Y_-)^2}{2\sigma_{-,y}^2} - \frac{(z - Z_-)^2}{2\sigma_{-,z}^2}\right)$$

The normalization factor  $A$  are introduced so that the integrals of  $C_+(\mathbf{r})$  and  $C_-(\mathbf{r})$  are equal to the integrals of  $\rho_+(\mathbf{r})$  and  $\rho_-(\mathbf{r})$ , respectively.

$H$  and  $t$  indices are defined as

$$H_\lambda = (\sigma_{+,\lambda} + \sigma_{-,\lambda})/2$$

$$t_\lambda = D_{CT,\lambda} - H_\lambda$$

where  $\lambda$  corresponds to the direction in which CT occurred.  $t$  may be regarded as the separation degree of  $\rho_+(\mathbf{r})$  and  $\rho_-(\mathbf{r})$ . If  $t < 0$ , an overlap between the distribution of  $\rho_+(\mathbf{r})$  and  $\rho_-(\mathbf{r})$  is expected. If  $t$  is evidently less than 0, then the excitation must not be a charge-transfer

excitation.

I defined another quantity to measure overlapping extent between  $C_+(\mathbf{r})$  and  $C_-(\mathbf{r})$

$$\int \sqrt{C_+(\mathbf{r})/A_+} \sqrt{C_-(\mathbf{r})/A_-} d\mathbf{r}$$

If the value equals to 1, that means the two functions are completely superposed, else if the value equals to zero, it indicates that the distribution of them are completely separated.

### Implementation

Because all numerical integrals mentioned above are computed based on cubic grid data, user needs to generate grid data for  $\Delta\rho(\mathbf{r})$  by using custom operation, see Section 3.7.1. After that, return to main menu, and go into subfunction 3 in main function 18. The results will be shown up immediately, user can choose to visualize  $C_+(\mathbf{r})$  and  $C_-(\mathbf{r})$ , or export the grid data of the two functions to Gaussian cube file in current folder.

The outputs are self-explained. The “Overlap integral between C+ and C-“ term is the last quantity defined above.

An example is given in Section 4.18.3.

**Information needed:** GTFs, atom coordinates

### 3.21.4 Calculate $\Delta r$ index to measure charge-transfer length (4)

#### Theory

In the paper *J. Chem. Theory Comput.*, **9**, 3118 (2013),  $\Delta r$  index was proposed to measure charge-transfer length during electron excitation. However, I found this argument is wrong. One only can say that the smaller the  $\Delta r$  is, the more likely the transition is local excitation (LE) rather than charge-transfer excitation (CT) or Rydberg excitation.

The definition of  $\Delta r$  is

$$\Delta r = \frac{\sum_{i,l} (K_i^l)^2 |\langle \varphi_l | \mathbf{r} | \varphi_i \rangle - \langle \varphi_i | \mathbf{r} | \varphi_i \rangle|}{\sum_{i,l} (K_i^l)^2}$$

where index  $i$  and  $l$  run over all occupied and virtual MOs, respectively.  $\varphi$  is orbital wavefunction. Assume that the method you used to calculate electron excitation is CIS or the TDDFT under Tamm-Dancoff approximation, then  $K_i^l$  is simply the configuration coefficient corresponding to the excitation  $i \rightarrow l$ . If the method you used is TDHF or full TDDFT, then  $K_i^l = X_i^l + Y_i^l$ , where  $X_i^l$  and  $Y_i^l$  denote the configuration coefficient corresponding to the excitation  $i \rightarrow l$  and de-

excitation  $i \leftarrow l$ . These coefficients are directly outputted by commonly used quantum chemistry program such as Gaussian.

$\Delta r$  is especially useful for diagnosing when conventional DFT functional is failure for TDDFT purpose, that is when  $\Delta r$  is large, such as B3LYP, BPW91 and PBE1PBE will not work well, and long-range corrected functionals should be employed, for instance, CAM-B3LYP, LC-PBE and  $\omega$ B97X.

### Usage

Two files are needed to calculate  $\Delta r$ , the first one is the .fch/.molden/.gms file produced by ground state calculation and should be loaded when Multiwfn boots up. Multiwfn will utilize the orbital wavefunctions ( $\varphi$ ) recorded in this file. The second one is the Gaussian output file of excitation state calculation (must be CIS, TDHF or TDDFT), and it is recommended to use the keyword  $IOp(9/40=4)$  to print more configuration coefficients. Also you can use the plain text file containing electron transition information. See Section 3.21.1.2 for detail. The path of the second file should be inputted when you enter present function.

After the  $\Delta r$  is calculated, Multiwfn will ask you to choose if decompose  $\Delta r$  into orbital pair contributions. If you input for example 0.01, then below term will be outputted for all  $i-l$  orbital pairs with  $K_i^l$  larger than 0.01

$$\Delta r_i^l = \frac{|\langle \varphi_l | \mathbf{r} | \varphi_l \rangle - \langle \varphi_i | \mathbf{r} | \varphi_i \rangle|}{\sum_{i,l} (K_i^l)^2}$$

Therefore, from the output, you can easily identify which orbital pairs markedly participated the electron transfer.

The example in Section 4.18.1 involves present function.

**Information needed:** GTF (for all MOs, so use .fch/.molden/.gms), Gaussian output file or plain text file which describes electron transition information

### 3.21.5 Calculate transition dipole moments between all excited states

This function is used to calculate transition dipole moment between all excited states, which cannot be directly outputted by TD task of Gaussian.

The requirement of input file of this function is exactly identical to the one in Section 3.21.1, namely .fch file and corresponding Gaussian output file of CIS/TDHF/TDDFT task; the former should be loaded when Multiwfn boots up, and the latter should be loaded when enter this function, please check "Input file" entry in Section 3.21.1 for more detail. I strongly suggest you use  $IOp(9/40=5)$  keyword to make Gaussian print as more configurations as possible, so that accurate transition dipole moment can be obtained by Multiwfn.

This function first prints summary of all excited states. "Multi." denotes multiplicity of the excited state; "N\_pairs" is the number of configurations involved in the state, which is directly associated to  $N$ . "Sum coeff.^2" should as close to expected value as possible (0.5 and 1.0 for

close- and open-shell cases, respectively), evident deviation implies that the result will be inaccurate and  $N$  must be set larger. Multiwfn then let you select the destination of the output (you can also choose to generate input file of SOS module of Multiwfn, as introduced in Section 3.200.8), and calculates transition dipole moments between all excited states. Finally the X, Y, Z components of transition dipole moments, energy differences and corresponding oscillator strengths of each pair of excited states will be printed. Note that in the case that the index of the two excited states are identical, the transition dipole moment simply corresponds to the electric dipole moment of this excited state.

Fortunately, if you are not a Gaussian user it is also possible to use this function. You can use .molden or .gms file instead of .fch file, and use a plain text file instead of Gaussian output file. The plain text file should record all excited states, the MO transitions should be organized in exact Gaussian format. An example is given below

```

Excited State 1 1 5.7945      // Excited index, multiplicity and excitation energy(eV)
      5 -> 6       0.70642    // MO transitions and transition coefficient
                                // Use a blank line to separate each excited state

Excited State 2 1 7.8943
      5 -> 7       0.63860
      5 -> 8       0.30006

Excited State 3 1 7.8943
      5 -> 7       -0.30006
      5 -> 8       0.63860

```

### 3.21.6 Generate natural transition orbitals (NTOs)

This function is used to generate natural transition orbitals (NTOs) based on excited state task of quantum chemistry packages. NTO was proposed in *J. Chem. Phys.*, **118**, 4775 (2003), it is a very popular and useful way to analyze the electronic excitation result of CIS or TDDFT calculation.

Transition of electronic state is often not predominated by only one pair of MO transition, in most cases many different MO transitions simultaneously have non-negligible contributions, which can be evaluated as square of corresponding configuration coefficient. This fact brings great hindrance of analyzing transition character by means of visualizing related MOs. The NTO method aims to relieve this difficulty, it separately performs unitary transformation for occupied MOs and virtual MOs, so that only one or very few number of orbital pairs have dominant contributions, which makes orbital inspection much easier.

The basic procedure of yielding NTOs are outlined below:

(1) Generating transition density matrix in MO basis ( $\mathbf{T}$ ). Assume that the system has  $n_{\text{occ}}$  occupied MOs and  $n_{\text{vir}}$  virtual MOs, then  $\mathbf{T}$  has dimension of  $(n_{\text{occ}}, n_{\text{vir}})$ , its  $(i,l)$  element is simply calculated as

$$T_{i,l} = \sum_{i \rightarrow l} w_i^l$$

where  $w$  stands for configuration coefficient outputted by CIS/TDDFT calculation. Note that for

### 3 Functions

TD formalism, there may be some de-excitations, their corresponding configuration coefficients are simply ignored in the summation.

(2) Generating temporary matrix for occupied and unoccupied orbitals, respectively

$$\mathbf{T}_{\text{occ}} = \mathbf{T}\mathbf{T}^T \quad \mathbf{T}_{\text{vir}} = \mathbf{T}^T\mathbf{T}$$

Evidently, both  $\mathbf{T}_{\text{occ}}$  and  $\mathbf{T}_{\text{vir}}$  are square matrices, their dimension are  $n_{\text{occ}}$  and  $n_{\text{vir}}$ , respectively.

(3) Diagonalizing  $\mathbf{T}_{\text{occ}}$  and  $\mathbf{T}_{\text{vir}}$  to obtain eigenvalues and eigenvectors

$$\mathbf{U}_{\text{occ}}^{-1} \mathbf{T}_{\text{occ}} \mathbf{U}_{\text{occ}} = \mathbf{\Lambda}_{\text{occ}} \quad \mathbf{U}_{\text{vir}}^{-1} \mathbf{T}_{\text{vir}} \mathbf{U}_{\text{vir}} = \mathbf{\Lambda}_{\text{vir}}$$

(4) The diagonal terms of  $\mathbf{\Lambda}_{\text{occ}}$  and  $\mathbf{\Lambda}_{\text{vir}}$  are eigenvalues of occupied and virtual NTOs, respectively. For the former, the eigenvalues are commonly sorted from low to high, while for the latter, the eigenvalues are commonly sorted from high to low. A NTO pair consists of an occupied NTO and a virtual NTO sharing the same eigenvalue. Eigenvalue of a NTO pair multiplied by 100 is just its percentage contribution to the electronic excitation.

(5) MOs are transformed to NTOs according to unitary transformation matrix  $\mathbf{U}$

$$\mathbf{C}_{\text{occ}}^{\text{NTO}} = \mathbf{C}_{\text{occ}}^{\text{MO}} \mathbf{U}_{\text{occ}} \quad \mathbf{C}_{\text{vir}}^{\text{NTO}} = \mathbf{C}_{\text{vir}}^{\text{MO}} \mathbf{U}_{\text{vir}}$$

where  $\mathbf{C}_{\text{occ}}^{\text{MO}}$  and  $\mathbf{C}_{\text{vir}}^{\text{MO}}$  are coefficient matrix of occupied MOs and virtual MOs in original basis functions, respectively; their columns correspond to different MOs. The counterpart matrices with NTO superscript denote coefficient matrix of occupied and virtual NTOs, by utilizing which the NTOs can be visualized or subject to further analysis.

The input files needed for generating NTOs are exactly the same as the ones mentioned in Section 3.21.1.2, namely a file containing basis function information (such as .fch file. Loaded firstly when Multiwfns boots up), and a file containing electronic transition information (such as Gaussian output file of CIS/TDDFT task with *IOp(9/40=4)* keyword. Loaded when you enter present function).

After you enter present function, you should select the index of the electronic excitation to be studied, then Multiwfns will load corresponding configuration coefficients and generate NTOs according to the equations shown above, and then output eigenvalues of occupied and virtual NTOs. At the meantime, the MOs stored in memory are transformed to NTOs, and the orbital energies are filled by corresponding NTO eigenvalues. Next, you can choose if output the NTOs to .fch or .molden file, if you choose to output, then you can use Multiwfns to load the newly generated .fch or .molden file to visualize the NTOs, analyze NTO orbital composition, and so on.

Present function works for both restricted and unrestricted wavefunction as reference state, for the latter, the result of Alpha part and Beta part are printed separately, you only need to pay attention to the NTO pairs having largest eigenvalues (e.g. the largest eigenvalue of Alpha part is 0.03, while the largest eigenvalue of Beta part of 0.95, that means this electronic excitation is dominated by transition of that Beta NTO pair)

According to my experiences, NTO analysis often works equally well as the hole-electron analysis introduced in Section 3.21.1, namely both of them are able to avoid inspecting many orbitals when discussing electronic excitation, and an additional advantage of NTO analysis is that the orbital phase character is reserved; however, in some cases NTO analysis completely fails, that is even after transformation to NTO representation, there is still no dominant pair of orbital

transition can be found, and you have to resort to hole-electron analysis.

An example of generating and analyzing NTOs is provided in Section 4.18.4.

**Information needed:** Basis function, Gaussian output file or plain text file which describes electron transition information

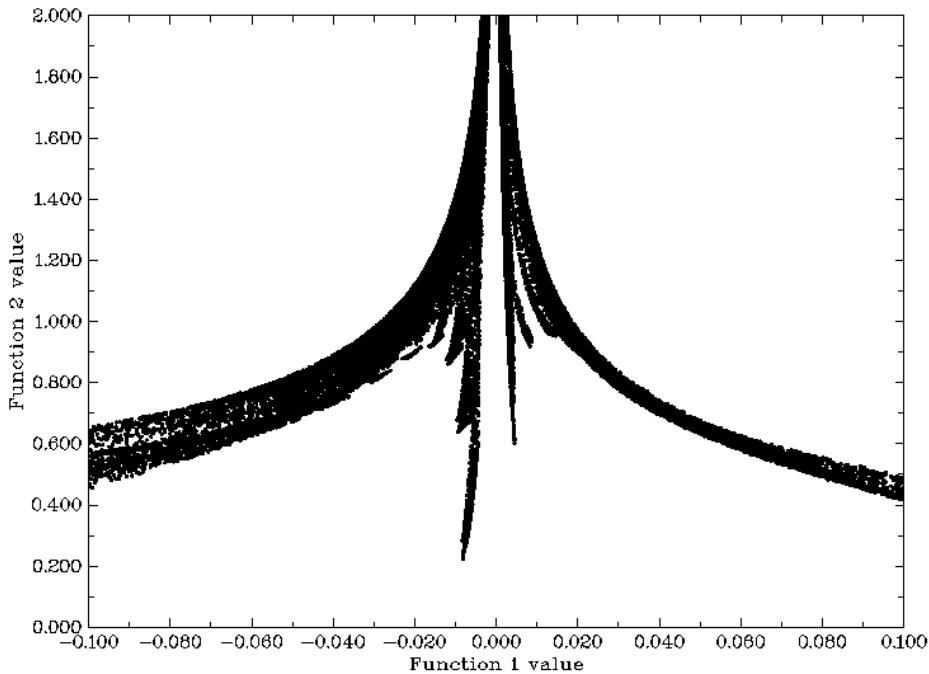
## 3.100 Other functions part 1 (100)

Since Multiwfn has too many functions, some of the functions are relatively "small" compared to main functions, and some functions are not closely related to wavefunctions analysis, these functions are classified as "other functions". Because the number of subfunctions in "other functions" are huge, "other functions" are splitted as part1 (main function 100) and part 2 (main function 200). Part 1 will be described below, and part 2 will be introduced in Section 3.200.

### 3.100.1 Draw scatter graph between two functions and generate their cube files

This function allows grid data of two functions to be generated at the same time with sharing grid setting, you can choose to export their cube files, view their isosurfaces and plot scatter graph between them. It is extremely useful for correlation analysis of two functions in specific spatial scope and visual research of noncovalent interaction (also known as NCI analysis, see *J. Am. Chem. Soc.*, **132**, 6498 for details).

After you entered this function, select two real space functions that you are interested in, for example you want to analyze real space function 16 and 14, you should input *16,14* (the first and the second function will be referred to as functions 1 and 2 respectively below). Then select a mode to set up grid points. After that Multiwfn starts the calculation of grid data for them (computing time is identical to calculate grid data for the two real space functions in turn by using main function 5, except special case, see below), once the calculation is finished, Pearson correlation coefficient of the two functions in all grid points is printed and a menu appears on screen, all options are self-explained. If you choose -1 to draw scatter graph, a graph like this will pop up immediately:



Each scatter point corresponds to each grid point, the position in X-axis and Y-axis corresponds to the value of function 1 and function 2 at this point respectively. Multiwfn determines the range of axes automatically according to the minimum and maximum value, sometimes you have to use option 4 and 5 to reset the range by yourself, otherwise barely points can be seen in the graph. The size of points can be adjusted by “symbolsize” in settings.ini. The graph can be saved to current directory by option 1. The X-Y data set of the points can be exported to output.txt in current directory by option 2.

Option -2 and -3 set the value of function 2 where the value of function 1 is within or without of a specific range respectively. Notice that the data once modified cannot be retrieved again, for example you set the value of function 2 to 0.0 where function 1 is in the range of 1.4 to 3.5, then you reuse option -2 to set the value of function 2 to 0.1 where function 1 is in the range of 2.5 to 3.5, now the value of function 2 is 0.0 rather than original data where function 1 is within 1.4 to 2.5.

Since the combination of real space function 15 and 13 (as well as 16 and 14 for promolecule approximation) is frequently used in weak interaction analysis, for improving calculation speed, a special routine will be invoked to evaluate grid data for them simultaneously, hence the computational cost is obviously lower than evaluating the two real space functions separately.

**Special usage:** If you already have cube files of the two functions to be studied (referred to as func1.cub and func2.cub, respectively) and you want to directly use the functions in post-process menu (e.g. plotting scatter map, modifying values), you should follow these steps: Input the path of func1.cub after booting up Multiwfn, then enter main function 100 and select subfunction 1, then input 0,0 when selecting real space functions, then input the path of func2.cub, after that the grid data of the two cube files will be directly taken as function 1 and function 2. Notice that, of course, the grid setting of func1.cub and func2.cub must be exactly identical.

### 3.100.2 Export .pdb, .xyz, .wfn, .wfx, .molden, .fch, NBO .47 or Gaussian/GAMESS-US input file

This function is used to output current structure to .pdb, .xyz, Gaussian or GAMESS-US input file. Wavefunction information can be exported as .wfn or .wfx file when GTF information is available, and can be exported as .molden, .fch or GENNBO input file (.47) when basis function information is presented. By this function Multiwfn can be used as file format converter, e.g. .wfn/.wfx/.fch/.molden/.gms ... → .pdb/.xyz/.gjf/.wfn/.wfx/.molden/.fch/.47 ...

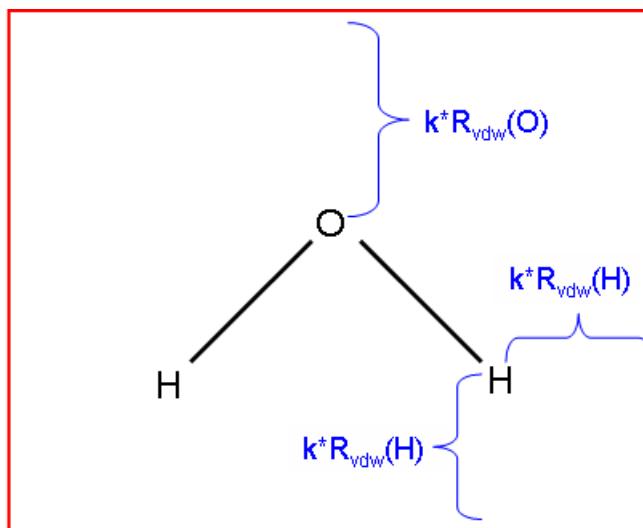
The generated GAMESS-US input file corresponds to single point at B3LYP-D3/6-31G\*. If basis function information is also presented, then you can select if writing the orbital coefficients as \$VEC field so that they can be used as initial guess.

**Information needed:** Atom coordinates, GTFs (for exporting .wfn/.wfx), basis functions (for exporting .fch/.molden/.47)

### 3.100.3 Calculate molecular van der Waals volume

In this function Monte Carlo method is used for evaluating van der Waals (vdW) volume of present system, two definitions of vdW region are provided: (1) The superposition of vdW sphere of atoms. This definition is not very accurate, because electron effect is not taken into consideration, but the speed of evaluation is very fast and wavefunction information is not required. (2) The region encompassed by certain isosurface of electron density, the isovalue of 0.001 is suitable for isolated system, while 0.002 is more suitable for molecules in condensed phase. One can choose the definition by "MCvommethd" in settings.ini.

The principle of the Monte Carlo procedure is very simple: If we define a box (volume is  $L$ ) which is able to hold the entire system, and let  $N$  particles randomly distributed in the box, if  $n$  particles are presented in the vdW region, then the vdW volume of present system is  $n/N*L$ . Of course, the result improves with the increase of  $N$ . In Multiwfn, you need to define  $N$  by input a number  $i$ , the relationship is  $N=100*2^i$ , for small molecular when  $i=9$  the accuracy is generally acceptable, for large system you may need to increase  $i$  gradually until the result variation between  $i$  and  $i+1$  is small enough to be acceptable as converged. For definition 2 of vdW region, you also need to input the isovalue of density, and the factor  $k$  used to define the box, see below illustration, where  $R_{vdw}$  is vdW radius. If  $k$  is too small, then the vdW region may be truncated, however if  $k$  is too large, more points are needed to maintain enough accuracy. For isovalue of 0.001,  $k=1.7$  is recommended.



The box used in Monte Carlo procedure

**Information needed:** atom coordinates (for definition 1), GTFs (for definition 2)

### 3.100.4 Integrate a function in whole space

This is a very useful and powerful function for integrating selected real space function in the whole space. The numerical integration method used here is based on the one proposed by Becke in the paper *J. Chem. Phys.*, **88**, 2547 for integrating DFT functional, which is also suitable for any real space function, but notice that the function must be smooth and converges to zero at infinite asymptotically. The accuracy is determined by the number of integration points, you can adjust the number of radial and angular integration points by “radpot” and “sphpot” parameters in settings.ini, respectively. The integrand can be selected from built-in functions, and you can also write new function by yourself as user-defined function, see Sections 2.6 and 2.7.

**Information needed:** Atom coordinates, GTFs.

### 3.100.5 Show overlap integral between alpha and beta orbitals

For unrestricted wavefunctions, orthonormalization condition does not in general hold between alpha and beta orbitals. This function computes the overlap matrix between alpha and beta orbitals

$$S_{i,j}^{\alpha\beta} = \int \varphi_i^\alpha(\mathbf{r}) \varphi_j^\beta(\mathbf{r}) d\mathbf{r}$$

The diagonal elements are useful for evaluating the matching degree of corresponding spin orbital pairs, evident deviation to 1 indicates that spin polarization is remarkable.

In present function, there are two options, option 1 calculates the full overlap matrix, the diagonal elements will be printed on screen and the whole overlap matrix can be selected to output to *ovlpmat.txt* in current folder; in addition, the maximum pairing between Alpha and Beta orbitals

### 3 Functions

are shown. This calculation may be time-consuming for large system. Option 2 only calculates and prints the diagonal elements, this is always fast.

Since the expectation of  $S^2$  operator for single determinant (SD) wavefunction can be easily derived from the overlap matrix, if option 1 is selected, Multiwfn also outputs this quantity:

$$\langle S^2 \rangle_{\text{SD}} = S^2_{\text{Exact}} + N^\beta - \sum_i^{N^\alpha} \sum_j^{N^\beta} |S_{i,j}^{\alpha\beta}|^2$$

where  $N^\alpha$  and  $N^\beta$  are the number of alpha and beta electrons.  $\langle S^2 \rangle_{\text{Exact}}$  is the exact value of square of total spin angular momentum

$$S^2_{\text{Exact}} = S(S+1) = \frac{N^\alpha - N^\beta}{2} \left( \frac{N^\alpha - N^\beta}{2} + 1 \right)$$

**Information needed:** GTFs

#### 3.100.6 Monitor SCF convergence process of Gaussian

Difficulty in SCF convergence is an annoying problem that always encountered in daily work, monitoring the convergence is important for finding solutions. Multiwfn can monitor SCF process by using the output file of Gaussian as input, notice that “#P” has to be specified in the route section, otherwise no intermediate information of SCF process will be recorded in output file.

When you entered this function, all information of previous steps and the thresholds of convergence are printed on screen, such as

Step#	RMSDP	Conv?	MaxDP	Conv?	DE	Conv?
8	3.51D-06	NO	5.15D-05	NO	-8.43D-08	YES
9	1.37D-06	NO	9.11D-06	NO	-2.17D-09	YES
10	3.03D-07	NO	2.91D-06	NO	-3.75D-10	YES
11	3.12D-08	NO	4.76D-07	YES	-1.07D-11	YES
12	7.69D-09	YES	5.72D-08	YES	-1.56D-13	YES
Goal	1.00D-08		1.00D-06		1.00D-06	

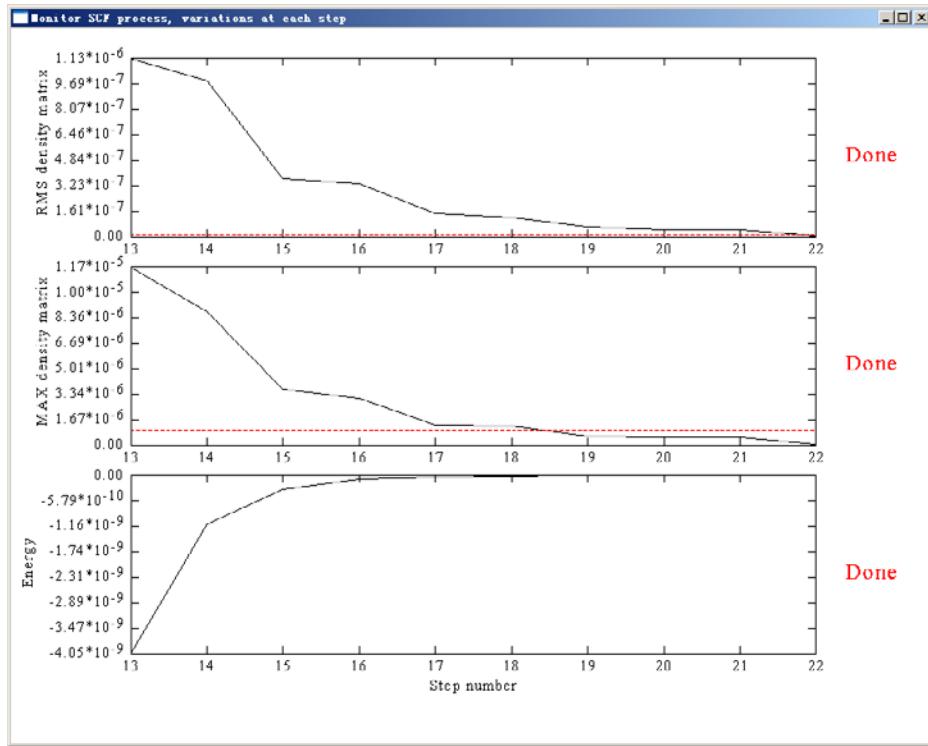
SCF done!

Meanwhile a window pops up, which contains curves that corresponding to convergence process of energy, maximum value and RMS variation of density matrix. After you close the window, you can print the information and draw the curve graphs again in specific step range by choosing corresponding options, the Y-axis is adjusted automatically according to the data range.

If the SCF task is work in progress, that is output file is updated constantly, every time you choose to print and draw the convergence process, the Gaussian output file will be reloaded, so what you see is always the newest information. For monitoring a time-consuming SCF process, I suggest you keep the interface on until the SCF task is finished, during this period you choose option 2 every so often to show the latest 5 steps and analyze convergence trend.

In the graph, gray dash line shows the zero position of Y-axis, the red dash line shows the threshold of convergence. The picture below shows the last 10 SCF steps of a system. If “Done” appears in the rightmost, that means corresponding property has already converged, here all three

terms are marked by “Done”, so the entire SCF process has finished.



This function is also compatible with keyword “SCF=QC” and “SCF=XQC”, but not with “SCF=DM”.

### 3.100.7 Generate Gaussian input file with initial guess from converged wavefunction

In Gaussian, the keyword “guess=read” tells the program to read guess wavefunction from checkpoint file, unfortunately sometimes the checkpoint file is missing. If you still have the output file of last task and in which “pop=full” keyword is used, you can load that file into Multiwfn, and then select this function, a new input file named “new.gjf” will be generated in current directory, in which the converged wavefunction is presented. If the keyword “guess=card” is specified in route section, these wavefunction information will be used as initial guess.

### 3.100.8 Generate Gaussian input file with initial guess from fragment wavefunctions

This function is used to combine several fragment wavefunctions to an initial guess wavefunction, there are three main uses:

**1 Generate high quality initial guess wavefunction for complex:** If you already have converged wavefunctions for each fragment, and the interaction between fragments is not very strong, by using the combined wavefunction as initial guess the SCF process of complex will converge faster.

### 3 Functions

**2 Perform simple energy decomposition:** The total energy variation of forming a complex can be decomposed as

$$\Delta E_{\text{tot}} = E^{\text{complex}} - \sum_i E_i^{\text{frag}} = (\Delta E_{\text{els}} + \Delta E_{\text{Ex}}) + \Delta E_{\text{orb}} = \Delta E_{\text{steric}} + \Delta E_{\text{polar}}$$

where  $E_{\text{els}}$  is electrostatic interaction term, normally negative if the two fragments are neutral;  $E_{\text{Ex}}$  is exchange repulsion term, which comes from the Pauli repulsion effect and is invariably positive. For convenience, it is customary to combine these two terms as steric term ( $E_{\text{steric}}$ ).

$E_{\text{orb}}$  in above formula is orbital interaction term, and sometimes also known as induction term or polarization term.  $E_{\text{orb}}$  arises from the mix of occupied MOs and virtual MOs. If the combined wavefunction is used as initial guess for complex, then  $E_{\text{orb}}$  can be evaluated by subtracting the first SCF iteration energy from the last SCF iteration energy.

$$\Delta E_{\text{orb}} = E_{\text{SCF, last}} - E_{\text{SCF, 1st}}$$

Note that  $E_{\text{SCF, last}} = E^{\text{complex}}$ , obviously we can write out below relationship

$$\Delta E_{\text{steric}} = \Delta E_{\text{els}} + \Delta E_{\text{Ex}} = \Delta E_{\text{tot}} - \Delta E_{\text{orb}} = E_{\text{SCF, 1st}} - \sum_i E_i^{\text{frag}}$$

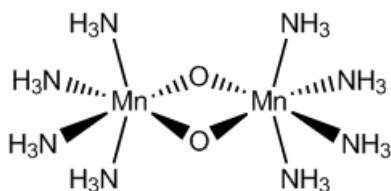
By the way, if the complex you studied concerns evident dispersion interaction (vdW interaction), there are two possible ways to evaluate the dispersion energy component:

(1) Use Hartree-Fock to calculate interaction energy first ( $\Delta E_{\text{tot}}^{\text{HF}}$ ), then use MP2 (or better post-HF method) to calculate interaction energy again ( $\Delta E_{\text{tot}}^{\text{MP2}}$ ), then  $\Delta E_{\text{disp}} = \Delta E_{\text{tot}}^{\text{MP2}} - \Delta E_{\text{tot}}^{\text{HF}}$ .

This relationship comes from the fact that dispersion energy is completely missing in HF energy.

(2) Use HF or the DFT functionals that completely failed to represent dispersion energy to calculate interaction energy (e.g. B3LYP and BLYP), then use Grimme's DFT-D3 program (<http://www.thch.uni-bonn.de/tc/index.php?section=downloads&>) with corresponding parameter to evaluate DFT-D3 dispersion correlation to interaction energy, which can be simply regarded as the dispersion component in total interaction energy. If you do not know how to do this and you can read Chinese, you may consult the post in my blog: <http://sobereva.com/210>

**3 Modelling antiferromagnetic coupling system:** I exemplify this concept and show you how to use the function by a representative antiferromagnetic coupling system --  $\text{Mn}_2\text{O}_2(\text{NH}_3)_8$ ,



The ground state is singlet, while the two Mn atoms have opposite spin and each Mn atom has high spin. Obviously, restricted close-shell calculation is not suitable for this system, unrestricted calculation is required, however, the default initial guess is non symmetry-broken state, therefore the converged unrestricted wavefunction returns to restricted close-shell wavefunction. In order to

make the wavefunction converges to expected state, we have to compute wavefunction for four fragments separately and then combine them by Multiwfn to construct a proper symmetry-broken initial guess. The four fragments should be defined as

- Fragment 1: Mn(NH<sub>3</sub>)<sub>4</sub> at left side. Charge=+2, sextet.
- Fragment 2: Mn(NH<sub>3</sub>)<sub>4</sub> at right side. Charge=+2, sextet.
- Fragment 3: One of bridge oxygen atoms. Charge=-2, singlet.
- Fragment 4: Another bridge oxygen atom. Charge=-2, singlet.

Notice that “nosymm” and “pop=full” keywords must be specified in the calculation of each fragment. Assuming the output files are “frag1.out”, “frag2.out”, “frag3.out” and “frag4.out” respectively, let Multiwfn load “frag1.out” first after boot up, then select function 100 and subfunction 8 to enter present function, input 4 to tell Multiwfn there are four fragments in total; since “frag1.out” has already been loaded, you only need to input the path (including filename) of “frag2.out”, “frag3.out” and “frag4.out” in turn. After that a Gaussian input file named “new.gjf” will be outputted in current directory. Notice that everytime you input a fragment, Multiwfn asks you if flip its spin, only for fragment 2 you should choose “y”, that is make the spin direction of unpaired electrons down (by default the spin is in up direction) to exactly counteract the opposite spin in fragment 1, so that multiplicity of complex is 1.

From the comment of “new.gjf” (the texts behind exclamation mark), you can know clearly how the MOs of complex are combined from MOs of fragments. For example, a two-fragment system, one of complex MOs in “new.gjf” is

```
! Al pha orbi tal : 12 0cc: 1. 000000 from fragment 2
      0. 00000E+00  0. 00000E+00  0. 00000E+00  0. 00000E+00  0. 00000E+00
      0. 00000E+00  0. 00000E+00  0. 00000E+00   0. 18850E-01 -0. 53690E-01
     -0. 74180E-01   0. 48861E+00   0. 16080E+00  -0. 12897E+00  -0. 12897E+00
      0. 47150E-01  -0. 25269E+00   0. 39361E+00  -0. 48811E+00   0. 36123E+00
```

We already know there are 8 basis functions in fragment 1 and 12 basis functions in fragment 2, and this complex MO comes from fragment 2, so the first 8 data (highlighted) are zero and only the last 12 data have values (the same as corresponding MO coefficients in Gaussian output file of fragment 2).

### 3.100.9 Evaluate coordination number for all atoms

The method come from the original paper of DFT-D3 (*J. Chem. Phys.*, **132**, 154104). The coordination number of atom A can be approximately expressed as

$$\text{CN}_A = \sum_{B \neq A} \frac{1}{1 + \exp\{-16 \times [(4/3)(R_A + R_B)/r - 1]\}}$$

where R is covalent radius from *Chem. Eur. J.*, **15**, 186.

Although the formula is very simple, however the result is surprisingly good, for example, the Multiwfn output of formamide in equilibrium structure:

```
1 N  Coordination number  3. 0268
2 H  Coordination number  1. 0039
```

```

3 H Coordination number 1.0049
4 C Coordination number 3.0027
5 H Coordination number 0.9973
6 O Coordination number 1.0315

```

We can see that the result is very close to empirical coordination number, which is integer. By using this function, atoms in different chemical environment could be readily distinguished.

The so-called "Coordination matrix" is also outputted. The  $A,B$  element is the coordination number between atom  $A$  and atom  $B$ . The sum of row or column  $A$  is  $CN_A$  value.

**Information needed:** atom coordinates

### 3.100.11 Calculate overlap and centroid distance between two orbitals

This function is used to calculate overlap and centroid distance between two orbitals, this is useful for many purposes, e.g. analyzing charge transfer during electronic excitation. You need to input index of two orbitals, then X, Y, Z of centroid of the orbitals will be calculated as follows

$$X_i = \int |\varphi_i(\mathbf{r})|^2 x d\mathbf{r} \quad Y_i = \int |\varphi_i(\mathbf{r})|^2 y d\mathbf{r} \quad Z_i = \int |\varphi_i(\mathbf{r})|^2 z d\mathbf{r}$$

then the centroid distance between orbital  $i$  and  $j$  is calculated as

$$D_{ij} = \sqrt{(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2}$$

Present function also calculates overlap degree of the two orbitals, below two quantities are calculated respectively (while directly calculating overlap integral of two orbital wavefunctions is clearly meaningless, since it must be zero due to orthonormalization condition):

$$\int |\varphi_i(\mathbf{r})| |\varphi_j(\mathbf{r})| d\mathbf{r} \quad \int |\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r})|^2 d\mathbf{r}$$

The integrals shown above are not calculated analytically but numerically via Becke's grid-based integration approach. The integration grid can be set by "radpot" and "sphpot" in settings.ini, the default values are high enough, and you may want to somewhat decrease them to reduced computational cost for large system, especially when you want to study many orbital pairs.

When the calculation is finished, Multiwfn will ask you whether or not add the two centroids as two additional dummy atoms (the symbol is Bq). If you choose y, then you can go to main function 0 to visualize corresponding orbital isosurfaces by transparent or mesh style to examine correspondence between centroid position and orbital shape.

**Information needed:** GTFs, atom coordinates

### 3.100.13 Calculate HOMA and Bird aromaticity index

HOMA is one of the most popular indexes for measuring aromaticity. This quantity was originally proposed in *Tetrahedron Lett.*, **36**, 3839, and then the generalized form was given in *J. Chem. Inf. Comput. Sci.*, **33**, 70. The generalized HOMA can be written as (notice that the HOMA formula has been incorrectly cited by numerous literatures)

### 3 Functions

$$\text{HOMA} = 1 - \sum_i \frac{\alpha_{i,j}}{N} (\mathbf{R}_{\text{Ref}} - \mathbf{R}_{i,j})^2$$

where  $N$  is the total number of the atoms considered,  $j$  denotes the atom next to atom  $i$ ,  $\alpha$  and  $\mathbf{R}_{\text{Ref}}$  are pre-calculated constants given in original paper for each type of atom pair. If HOMA equals to 1, that means length of each bond is identical to optimal value  $\mathbf{R}_{\text{Ref}}$  and thus the ring is fully aromatic. While if HOMA equals to 0, that means the ring is completely nonaromatic. If HOMA is significant negative value, then the ring shows anti-aromaticity characteristic.

HOMA can be calculated by subfunction 13 in main function 100. The built-in  $\alpha$  and  $\mathbf{R}_{\text{Ref}}$  parameters are directly taken from *Chem. Inf. Comput. Sci.*, 33, 70, they can be adjusted customly by option 1. When you choose option 0, Multiwfn will prompt you to input the indices of the atoms in the local system, for example, 2,3,4,5,6,7 (assume that there are six atoms in the ring. The input order must be consistent with atom connectivity), then HOMA value and contributions from each atom pair will be immediately outputted on the screen. For example, thiophene optimized under MP2/6-311+G\*\*, the output is

Atom pair		Contribution	Bond Length(Angstrom)
1(C )	--	2(C ):	-0. 001852      1. 382006
2(C )	--	3(C ):	-0. 056708      1. 421170
3(C )	--	4(C ):	-0. 001852      1. 382006
4(C )	--	5(S ):	-0. 023886      1. 712627
5(S )	--	1(C ):	-0. 023886      1. 712627

HOMA value is 0.891817

Since 0.891817 is close to 1, the HOMA analysis suggests that thiophene has relatively strong aromaticity.

Bird index (*Tetrahedron*, **41**, 1409) is another geometry-based quantity aimed at measuring aromaticity, and can be calculated by option 2 of subfunction 13 in main function 100. The formula is

$$I = 100[1 - (V / V_K)]$$

where

$$V = \frac{100}{\bar{N}} \sqrt{\frac{\sum_i (N_{i,j} - \bar{N})^2}{n}} \quad N_{i,j} = \frac{a}{R_{i,j}} - b$$

In the formula,  $i$  cycles all of the bonds in the ring,  $j$  denotes the atom next to atom  $i$ .  $n$  is the total number of the bonds considered.  $N$  denotes Gordy bond order,  $\bar{N}$  is the average value of the  $N$  values.  $R_{i,j}$  is bond length.  $a$  and  $b$  are predefined parameters respectively for each type of bonds.  $V_K$  is pre-determined reference  $V$ , for five and six-membered rings the value is 35 and 33.2, respectively. The more the Bird index close to 100, the stronger the aromaticity is.

Available  $a$  and  $b$  include C-C, C-N, C-O, C-S, N-O and N-N; for other type of bonds user should set corresponding parameter by option 3. By option 4 user can adjust or add  $V_K$  parameter.

**Information needed:** Atom coordinates

### 3.100.14 Calculate LOLIPOP (LOL Integrated Pi Over Plane)

In the paper *Chem. Commun.*, **48**, 9239, the authors proposed a quantity named LOLIPOP (Localized Orbital Locator Integrated Pi Over Plane) to measure  $\pi$ -stacking ability of aromatic systems, they argued that a ring with smaller LOLIPOP value has stronger  $\pi$ -depletion (namely lower  $\pi$ -delocalization), and hence shows stronger  $\pi$ -stacking ability.

LOLIPOP is defined as definite integral of LOL- $\pi$  (the LOL purely contributed by  $\pi$ -orbitals) from a distance of 0.5Å away from the molecular plane. Only points with LOL- $\pi$ >0.55 are taken into account. The integration is made in a cylindrical region perpendicular to the molecular plane, with a radius of 1.94Å corresponding to the average between the C and H ring radii in benzene.

In Multiwfn, function 14 in main function 100 is designed for calculating LOLIPOP, the default value 0.5Å and 1.94Å mentioned above can be changed by option 4 and 3 respectively. Before starting the calculation, you have to choose which orbitals are  $\pi$  orbitals by option 3, you can find out  $\pi$  orbitals by visualizing orbital isosurfaces via main function 0. The calculation can be triggered by option 0, you need to input the indices of the atoms in the ring in accordance with the atom connectivity, then grid data of LOL around the ring will be evaluated, then the LOLIPOP value is computed by numerical integration. Of course, smaller grid spacing gives rise to higher integration accuracy, but brings severer computational requirement on evaluating LOL. The default spacing of grid data is 0.08 Bohr, this value is fine enough in general.

**Information needed:** GTFs, atom coordinates

### 3.100.15 Calculate intermolecular orbital overlap

This function is used to calculate orbital overlap integral between two molecules, namely

$$S_{i,l}^{\text{Int mol}} = \int \varphi_i^{\text{Monomer 1}}(\mathbf{r}) \varphi_l^{\text{Monomer 2}}(\mathbf{r}) d\mathbf{r}$$

where  $i$  and  $l$  are molecular orbital indices of monomer 1 and monomer 2, respectively. This integral is useful in discussions of intermolecular charge transfer, e.g. *J. Phys. Chem. B*, **106**, 2093.

Three files are required for evaluating the integral:

- (1) Gaussian output file of dimer, "iop(3/33=1) nosymm guess(only)" should be specified in route section. Multiwfn will read overlap matrix from this file.
- (2) Gaussian output file of monomer 1, "nosymm pop=full" should be specified in route section. Multiwfn will read orbital coefficients of monomer 1 from this file.
- (3) Gaussian output file of monomer 2, "nosymm pop=full" should be specified in route section. Multiwfn will read orbital coefficients of monomer 2 from this file.

Notice that, the atomic coordinates in file (2) and (3) must be in accordance with the one in file (1). The basis-set used should be the same for the three calculations. The atomic sequence should be identical. Molecular geometry must be given in Cartesian coordinate.

To calculate the intermolecular orbital overlap integral, after booting up Multiwfn, the file (1) should be loaded first. After entering present module, the paths of file (2) and (3) should be

inputted in turn. Then one can input such as 8,15 to obtain  $S_{8,15}^{\text{Intmol}}$ . If user input the letter *o*, then the entire  $S^{\text{Intmol}}$  matrix will be outputted to "ovlpint.txt" in current folder.

**Information needed:** Gaussian output files

### 3.100.18 Yoshizawa's electron transport route analysis

#### Theory

This function is used to analyze electron transport route and is mainly based on Yoshizawa's formula (*Acc. Chem. Res.*, **45**, 1612). At the Fermi energy, the matrix elements of the zeroth Green's function,  $G_{rs}^{(0)\text{R/A}}$ , which describes the propagation of a tunneling electron from site *r* to site *s* through the orbitals in a molecular part, can be written as follows:

$$G_{rs}^{(0)\text{R/A}}(E_F) = \sum_k \frac{C_{rk} C_{sk}^*}{E_F - \varepsilon_k \pm i\eta}$$

where  $C_{rk}$  is the *k*th MO coefficient at site *r*, asterisk on the MO coefficient indicates a complex conjugate,  $\varepsilon_k$  is the *k*th MO energy, and  $\eta$  is an infinitesimal number determined by a relationship between the local density of states and the imaginary part of Green's function. By this formula, if two electrodes are connected to site *r* and *s*, by this formula we can readily predict the transmission probability between the two sites. From the expression of the denominator, it can be seen that HOMO and LUMO have the largest contribution to  $G$ . If only HOMO and LUMO are taken into account, the formula can be explicitly written as

$$G_{rs}^{(0)\text{R/A}}(E_F) = \frac{C_{r\text{HOMO}} C_{s\text{HOMO}}^*}{E_F - \varepsilon_{\text{HOMO}} \pm i\eta} + \frac{C_{r\text{LUMO}} C_{s\text{LUMO}}^*}{E_F - \varepsilon_{\text{LUMO}} \pm i\eta}$$

This formula allows one to visually examine the possibility of electron transmission between site *r* and *s* by means of observing molecular orbital diagram. If both site *r* and *s* have large  $C$  in magnitude, and their relative phase in HOMO and in LUMO is different, then the magnitude of  $G$  will be large, indicating that transmission between *r* and *s* will be favourable. For examples, see *Acc. Chem. Res.*, **45**, 1612. Note that  $G$  may be positive and negative, but only absolute value of  $G$  is meaningful for discussing transmission.

In Multiwfn,  $i\eta$  term in  $G$  is always ignored, since this is an infinitesimal number. The coefficient  $C$  comes from the output of "NAOMO" keyword in NBO program. In almost all organic conductors,  $\sigma$  orbitals have little contribution to conductance, therefore present function only takes  $\pi$  orbitals into account, and the molecular plane must be parallel in XY or YZ or XZ plane.

#### Input file

Gaussian output file is required as input file. In the route section, pop=nboread must be specified, and "\$NBO NAOMO \$END" must be written at the last line, for example:

```
#P b3lyp/6-31g* pop=nboread

b3lyp/6-31g* opted

0 1
[Molecular geometry field]

$NBO NAOMO $END
```

**Usage**

After you enter this function, you need to select which plane is the one your molecular plane parallel to. Then program will load Gaussian output file and find out the atoms having expected  $\pi$  atomic orbital (restrictly speaking, the "Val"-type  $p$  natural atomic orbitals that perpendicular to the chosen plane). The coefficient of these atomic orbitals will be used to compute  $G$ .

Then you will see a menu, the options are explained below:

**-4 Set distance criterion:** Input lower and upper limits. Then in option 2 and 3, the route whose distance exceeds this criterion will not be shown.

**-3 Set value criterion:** In option 1, the MO whose contribution to  $G$  is less than this criterion will not be shown. In option 2 and 3, the route whose  $|G|$  is smaller than this criterion will not be shown.

**-2 Set Fermi energy level:** Namely set  $E_F$  in the Yoshizawa's formula.

**-1 Select the range of MOs to be considered:** Namely set the MO range of the summation in the Yoshizawa's formula.

**0 View molecular structure:** As the title says.

**1 Output detail of electron transport probability between two atoms:** You need to input index for two atoms, they will be regarded as site  $r$  and  $s$ , then  $G_{rs}$  (the value behind "Total value") will be outputted; meanwhile program also outputs the contribution from each MO, the distance between the two atoms, and the calculated  $G_{rs}$  for the case when only HOMO and LUMO are taken into the summation.

**2 Output and rank all electron transport routes in the system:** All routes in current system will be tested, if the route simultaneously fulfills the  $G$  and distance criteria set by -3 and -4, then the involved atoms,  $G$  and distance of the route will be printed. The routes are ranked by absolute value of  $G$ .

**3 Output and rank all electron transport routes for an atom:** Similar to option 2, but only consider the routes involving specific atom.

**Information needed:** Gaussian output files containing NAOMO information

### 3.100.19 Generate promolecular .wfn file from fragment wavefunctions

This function is used to generate promolecular wavefunction in .wfn format based on

fragment wavefunctions. In the promolecular state, the electron distribution simply comes from the superposition of the electron distribution of the related fragments; in other words, in this state the electron transfer and polarization between the fragments have not started. Each promolecular orbital directly corresponds to one of fragment orbitals.

The input file can be in any wavefunction format, such as .wfn, .wfx, .fch, .molden and .gms, any kind of wavefunction is supported. Infinite number of fragments are supported.

Assume that the promolecular wavefunction consists of  $N$  fragments, after boot up Multiwfn, you should make Multiwfn load the first fragment wavefunction file, and then go to this function, input the total number of fragments ( $N$ ), then input the path of the wavefunction files corresponding to the other fragments in turn. The promolecule .wfn file will be generated in current folder as "promol.wfn".

For SCF wavefunctions, the MOs are sorted according to orbital energies from low to high, virtual MOs are not recorded. For post-HF wavefunctions, the natural orbitals are sorted according to orbital occupation from high to low.

If any fragment is unrestricted open-shell, then the promolecular wavefunction will be regarded as unrestricted open-shell type, namely the alpha and beta orbitals will separately occur in the resultant .wfn file. In this case, for each unrestricted open-shell fragment Multiwfn will ask you if flipping the spin of its orbitals; if you choose yes, then the energies and occupations of all alpha and all beta orbitals will be exchanged; this treatment is particularly important if you want to get the promolecular wavefunction combined from free-radical fragments.

Please always carefully check the resultant .wfn file to examine its reasonableness before using it.

Some examples are given in Section 4.100.19.

**Information needed:** GTFs, atom coordinates

### 3.100.20 Calculate Hellmann-Feynman forces

The Hellmann-Feynman (H-F) force is the actual force acting on nuclei in a quantum system, which is exerted by electron density and other nuclei:

$$\mathbf{F}_A = -\left\langle \Psi \left| \frac{\hat{H}}{\partial \mathbf{R}_A} \right| \Psi \right\rangle = \mathbf{F}_A^{\text{ele}} + \mathbf{F}_A^{\text{nuc}} = -Z_A \int \frac{\rho(\mathbf{r})(\mathbf{R}_A - \mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|^3} d\mathbf{r} + Z_A \sum_{B \neq A} \frac{Z_B(\mathbf{R}_A - \mathbf{R}_B)}{|\mathbf{R}_A - \mathbf{R}_B|^3}$$

Present function calculates and prints total H-F force as well as the contribution from electron density and other nuclei respectively.

In practice, notice that the H-F forces calculated as above based on the electronic wavefunction and nuclear information recorded in the wavefunction file are generally not equivalent to the forces computed by quantum chemistry program at current calculation level ( $\mathbf{F}^{\text{QC}}$ ), which may be expressed as:

$$\mathbf{F}_A^{\text{QC}} = -\frac{\partial E}{\partial \mathbf{R}_A} = -\left\langle \Psi \left| \frac{\hat{H}}{\partial \mathbf{R}_A} \right| \Psi \right\rangle - 2 \left\langle \frac{\partial \Psi}{\partial \mathbf{R}_A} \left| \hat{H} \right| \Psi \right\rangle$$

The partial derivative of wavefunction with respect to nuclear coordinate involves partial derivative of orbital coefficients, configuration state coefficients and basis functions with respect

to  $\mathbf{R}_A$ . Therefore, only for the fully variational wavefunctions such as HF, DFT and MCSCF with basis functions independent of nuclear coordinates (e.g. plane wave), the second term on the r.h.s. of above equation is vanishing, and then the H-F forces just equals to the force at current calculation level.

**Information needed:** GTFs, atom coordinates

### 3.100.21 Calculate properties based on geometry information for specific atoms

Input index range of some atoms (or input *all* to select the whole system), then many properties based on geometry information will be calculated for them, including

- (1) Mass
- (2) Geometry center, center of mass, center of nuclear charges
- (3) Radius of gyration
- (4) Sum of nuclear charges and dipole moments from nuclear charges
- (5) The atom having minimum/maximum coordinate in X/Y/Z
- (6) Minimum and maximum distance
- (7) Moments of inertia tensor, principal axes and principal moments of inertia
- (8) Rotational constant
- (9) Electrostatic interaction energy between nuclear charges

Note: If the input file is .chg, then "nuclear charges" mentioned above will stand for atomic charges.

Radius of gyration is computed as  $\sqrt{\frac{\sum_i m_i (\mathbf{r}_i - \mathbf{r}_c)^2}{\sum_j m_j}}$ , where  $\mathbf{r}$  is the coordinate of nucleus,

$\mathbf{r}_c$  is mass center,  $m$  is atomic mass.

The moments of inertia tensor, which is a symmetry matrix, is calculated as

$$\mathbf{I} = \begin{bmatrix} I_{XX} & I_{XY} & I_{XZ} \\ I_{YX} & I_{YY} & I_{YZ} \\ I_{ZX} & I_{ZY} & I_{ZZ} \end{bmatrix} = \begin{bmatrix} \sum_i m_i (y_i^2 + z_i^2) & -\sum_i m_i x_i y_i & -\sum_i m_i x_i z_i \\ -\sum_i m_i y_i x_i & \sum_i m_i (x_i^2 + z_i^2) & -\sum_i m_i y_i z_i \\ -\sum_i m_i z_i x_i & -\sum_i m_i z_i y_i & \sum_i m_i (x_i^2 + y_i^2) \end{bmatrix}$$

In the output, "The moments of inertia relative to X,Y,Z axes" correspond to the three diagonal terms of  $\mathbf{I}$ .

The three eigenvectors of  $\mathbf{I}$  are known as principal axes, they are outputted as the three columns of the matrix with the title "\*\*\*\*\* Principal axes (each column vector) \*\*\*\*\*". The corresponding three eigenvalues of  $\mathbf{I}$  are the moments of inertia relative to principal axes.

If the moments of inertia are given in amu $\cdot$  $\text{\AA}^2$ , then the rotational constants in GHz can be

directly evaluated; for example, the rotational constant relative to Z axis is  $\frac{h}{8\pi^2 I_{zz} \zeta} 10^{11}$ , where

$h$  is Planck constant, and  $\zeta=1.66053878*10^{-27}$  is a factor used to convert amu to kg.

**Information needed:** Atom coordinates

### 3.100.22 Detect $\pi$ orbitals and set occupation numbers

Sometimes one wants to analyze  $\pi$  properties of a conjugated system, e.g. calculating ELF- $\pi$ , hence one must first find out which are  $\pi$  orbitals by visualizing orbital isosurfaces, and then set occupation number of all the other orbitals to zero. Unfortunately, for large system this work is very tedious and time-consuming. To make your life easier, when your system is an **exactly** planar molecule (in the input file all atoms are exactly in the same Cartesian plane XY, YZ or XZ), you can use this function to do the work. First, you need to choose the molecular is in which plane (or you can let Multiwfn detect the plane), then  $\pi$  orbitals will be detected automatically, their indices (due to a special reason the indices will be printed twice), occupation numbers and energies will be shown on screen. Then you can choose option 1 to set the occupation numbers of these  $\pi$  orbitals to zero, or choose option 2 to set the occupation number of all the other orbitals to zero. Option 3 is akin to option 1, but only valence  $\pi$  orbitals are taken into account. Option 4 is used to clean occupation number for all orbitals except for valence  $\pi$  orbitals.

**Information needed:** GTFs, atom coordinates

### 3.100.23 Fit function distribution to atomic value

This function is very similar to the function used to fit ESP charge (see Section 3.9.10 and 3.9.11), but the real space function to be fitted is not limited to ESP, for example you can fit average local ionization energy or even Fukui function distributed on molecular surface to atomic values.

After select option 1, and then select a real space function, the function value will be calculated on the fitting points and then fit to atomic value by least-squares method, namely minimizing below error function

$$F(p_1, p_2 \dots p_N) = \sum_i [V(\mathbf{r}_i) - V'(\mathbf{r}_i)]^2$$

where  $i$  denotes the index of fitting points,  $p$  is atomic value,  $V$  is the value of real space function, while  $V'$  is the function value evaluated by atomic value, which is defined as

$$V'(\mathbf{r}_i) = \sum_A \frac{p_A}{r_{A,i}}$$

where  $A$  denotes atom index,  $r_{A,i}$  corresponds to the distance between nucleus of atom A and the fitting point  $i$ .

The error of fitting are measured by RMSE and RRMSE

$$\text{RMSE} = \sqrt{\frac{\sum_i [V(\mathbf{r}_i) - V'(\mathbf{r}_i)]^2}{N}} \quad \text{RRMSE} = \sqrt{\frac{\sum_i [V(\mathbf{r}_i) - V'(\mathbf{r}_i)]^2}{\sum_i V(\mathbf{r}_i)^2}}$$

where  $N$  denotes the number of fitting points.

By default all fitting centers are placed at nuclei, you can also load additional fitting centers from external file by option -2, see Section 3.9.10 for the format.

The default fitting points are exactly the ones used by Merz-Kollman method (see Section 3.9.11). You can use option 3 to customize the number of layers, use option 2 to adjust the density of the fitting points distributed on the surface, and use option 4 to set the scale factor of the vdW radii used for constructing each layer. (e.g. If you set two layers, and their scale factors are set to 1.0 and 1.2 respectively, then the first and the second layer will be constructed by superposing the vdW radii of all atoms multiplied by 1.0 and 1.2, respectively)

No constraint on the total value (viz.  $\sum_i p_i$ ) is applied by default. However, you can use

option 5 to set a constraint on the total value. Evidently, if the constraint is set to the net charge of your system, and you choose ESP as fitting function, then the result will be identical to MK charges.

The fitting points can be directly defined via external plain text file by option -1 (and thus will not be constructed by superposing vdW spheres), see Section 3.9.10 for the file format. If the file contains calculated function values of all fitting points and meanwhile the first line of this file (the number of points) is set as negative value, then the real space function at each fitting point will not be evaluated by Multiwfn but loaded from this file directly.

**Information needed:** GTFs, atom coordinates

### 3.100.24 Obtain NICS\_ZZ for non-planar system

NICS is a very popular index used to measure aromaticity. In many literatures, such as *Org. Lett.*, **8**, 863, It was shown that NICS(0)<sub>ZZ</sub> or NICS(1)<sub>ZZ</sub> is a better index than the original definition of NICS, which is current known as NICS(0).

For exactly planar systems, if the system plane is parallel to XY plane, then NICS(0)<sub>ZZ</sub> means the ZZ component of magnetic shielding tensor at ring center. The only different from NICS(1)<sub>ZZ</sub> to NICS(0)<sub>ZZ</sub> is that the calculated point is not ring center, but the point above (or below) 1Å of the plane from ring center. Note that the definition of ring center is highly arbitrary, the original definition uses geometry center, while some people use center of mass, and some researchers recommend using ring critical point (RCP) of AIM theory as ring center, for example *WIREs Comput. Mol. Sci.*, **3**, 105. (Personally, I think using RCP is the best choice)

If the ring of interest is skewed or not exactly planar, calculation of NICS<sub>ZZ</sub> is somewhat cumbersome, because one cannot directly acquire the component of magnetic shielding tensor perpendicular to the plane from output file of quantum chemistry programs. Moreover, for NICS(1)<sub>ZZ</sub>, it is difficult to properly set the position to be calculated. Present function is designed to solve these difficulties.

For example, you want to calculate NICS(1)<sub>ZZ</sub> for a non-planar system, you can follow below

steps:

- (1) Use Multiwfn to open a file containing atomic coordinates of your system (e.g. .xyz/.pdb/.wfn/.wfx/.fch/.molden/.gms...)
- (2) Find out ring center. You can use topology analysis module (main function 2) to locate RCP, or use subfunction 21 in main function 100 to obtain geometry center or center of mass. Using which method to define the ring center depends on yourself.
- (3) Enter subfunction 24 of main function 100 (namely the function I am describing), input the ring center you just obtained, and input index of three atoms to define the ring plane. Then the coordinate of the points above and below 1Å of the ring plane from the ring center will be outputted. You can use any one of these two points in quantum chemistry program to calculate magnetic shielding tensor at this position.

Hint: The unit normal vector perpendicular to the ring plane is also outputted by Multiwfn, by which you can easily derive the position used to calculate such as NICS(2), NICS(3.5)...

- (4) Input all components of the magnetic shielding tensor in Multiwfn according to the output of your quantum chemistry program. Then the negative value of "The shielding value normal to the plane" outputted by Multiwfn is just NICS(1)<sub>ZZ</sub>.

For calculating NICS(0)<sub>ZZ</sub>, the process is more simple:

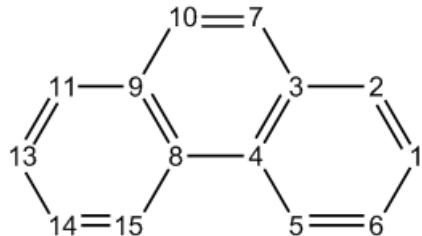
- (1) Identical to the step 1 shown above
- (2) Identical to the step 2 shown above
- (3) Use the ring center you just obtained in your quantum chemistry program to calculate the magnetic shielding tensor at this position.
- (4) Enter subfunction 24 of main function 100, input ring center, and input index of three atoms to define the ring plane. Then input all components of the magnetic shielding tensor according to the output of your quantum chemistry program. Then the negative value of "The shielding value normal to the plane" outputted by Multiwfn is just NICS(0)<sub>ZZ</sub>.

**Information needed:** Atom coordinates

### 3.100.25 Calculate area and perimeter for a ring

This is a utility used to calculate ring area (as well as perimeter), since ring area is sometimes involved in wavefunction analysis. For example, in *J. Org. Chem.*, **72**, 9163 (2007), it is proposed that the aromaticity of an entire polycyclic system can be evaluated as  $\Sigma \text{NICS}(1)_{ZZ}/\text{area}^2$ .

In this function, you need to input the index of the atoms in the ring in clockwise manner, for example, the phenanthrene,



If you would like to calculate the area of the middle ring, you can input for example 3,4,8,9,10,7.

During the calculation, the ring will be partitioned into multiple triangles, whose areas will be calculated separately and then summed up.

The ring can contain arbitrary number of atoms, and the ring may be non-planar; however you should make sure that the ring is convex, otherwise the result could be meaningless. So for a large ring with complex shape (e.g. porphyrin), you'd better to calculate the area of its each part respectively and then sum up the results.

The ring perimeter is outputted along with ring area.

**Information needed:** Atom coordinates

## 3.200 Other functions part 2 (200)

### 3.200.1 Weak interaction analysis for fluctuation environment by RDG method

#### Theory

Reduced density gradient (RDG) method is a very powerful way to analyze weak interaction, if you are not familiar with it, please first check Section 4.100.1 for a brief introduction. In *J. Chem. Theory Comput.*, **9**, 2226, RDG method is extended to analyze fluctuation environment (e.g. molecular dynamics trajectory), resulting in averaged RDG (aRDG) method. Present function aims at realizing aRDG analysis.

The only different between aRDG and the original RDG method is that in the former, the electron density  $\rho$  and its gradient norm  $|\nabla\rho|$  are not calculated for only one geometry, but for multiple frames of a dynamics trajectory and then get average (namely  $\bar{\rho}$  and  $\overline{\nabla\rho}$ ). Therefore, the isosurface of averaged reduced density gradient

$$\text{aRDG}(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\overline{\nabla\rho(\mathbf{r})}|}{\overline{\rho(\mathbf{r})}^{4/3}}$$

can be directly used to reveal the averaged weak interaction regions in the dynamics process.

Similarly, in order to exhibit averaged weak interaction type, in aRDG method, the  $\lambda_2$  term in  $\text{Sign}(\lambda_2)\rho$  function is obtained as the second largest eigenvalue of the averaged electron density Hessian matrix computed through out the dynamical trajectory.

aRDG method also defines a new quantity named thermal fluctuation index (TFI) to reveal the stability of weak interaction

$$\text{TFI}(\mathbf{r}) = \frac{\text{std}[\rho(\mathbf{r})]}{\overline{\rho(\mathbf{r})}}$$

Whose numerator is standard deviation of electron density in the dynamical trajectory, which can be calculated as

$$\text{Std}(\rho(\mathbf{r})) = \sqrt{\frac{\sum_i [\rho_i(\mathbf{r}) - \overline{\rho(\mathbf{r})}]^2}{n}}$$

where  $n$  is the number of frames in consideration,  $\rho_i$  is the density calculated based on the

geometry of frame  $i$ . After mapping TFI on the isosurface of aRDG, the stability of each weak interaction region can be clearly identified by visually examining the color.

Evidently, the quality of aRDG graph directly depends on how many frames are taken into account. Small number of frames, for example 50 frames, only leads to very inaccurate and very unsmooth isosurface graph. In general, at least 500 frames are recommended to be used to generate aRDG graph.

### Usage

First note that since calculating electron density based on wavefunction for large number of geometries is very expensive, promolecular approximation is forced to be used in the aRDG analysis function of Multiwfn. This approximation is highly reasonable and always works well.

The trajectory stored in .xyz file is allowed as input file. You can use such as VMD program to convert other format of trajectory files to .xyz trajectory file.

PS: The structure of a multiple frame .xyz file looks like below

```
[The number of atoms in frame 1]
[Element, x, y and z of atom 1 in frame 1]
[Element, x, y and z of atom 2 in frame 1]
...
[Element, x, y and z of atom n in frame 1]
[The number of atoms in frame 2]
[Element, x, y and z of atom 1 in frame 2]
[Element, x, y and z of atom 2 in frame 2]
...
[Element, x, y and z of atom n in frame 2]
[The number of atoms in frame 3]
...
```

In all of the frames, the coordinate of the interesting molecule should be fixed. For example, if you want to study the weak interaction between solvents and a benzene molecule, then the position of the benzene must be fixed through out the whole trajectory.

After you enter present function, you will be prompted to input the frame range to be analyzed, for example inputting 140,450 means the frame from 140 to 450 will be used in the aRDG analysis. Then you need to set up grid, the spatial range of the box of course should properly enclose the molecule of interest. After that, averaged electron density, averaged density gradient and averaged density Hessian will be calculated for each frame, you should wait patiently. Once the calculation is finished, you can use corresponding options to draw scatter graph between averaged RDG and averaged  $\text{Sign}(\lambda_2)\rho$ , output scatter points, export their cube files, etc. Thermal fluctuation index can also be calculated and export to cube file.

An example is given in Section 4.200.1.

**Information needed:** Multiple frames of atom coordinates

### 3.200.2 Calculate atomic and bond dipole moments in Hilbert space

This function is used to calculate atomic and bond dipole moments directly based on basis functions (viz. in Hilbert space). You can also consult Section 12.3.2 of the book *Ideas of Quantum Chemistry* (L. Piela, 2007).

### 3 Functions

#### Theory

In the formalism of basis functions, the system dipole moment can be expressed as follows

$$\mu = \mu^{\text{nuc}} + \mu^{\text{ele}} = \sum_A Z_A \mathbf{R}_A - \sum_i \sum_j P_{i,j} \langle \chi_i | \mathbf{r} | \chi_j \rangle$$

where  $Z$  and  $\mathbf{R}$  are charge and coordinate of nuclei.  $P$  is density matrix,  $\langle \chi_i | \mathbf{r} | \chi_j \rangle$  is dipole moment integral between basis function  $i$  and  $j$ .

The system dipole moment can be decomposed as the sum of single-atom terms and atom pair terms

$$\mu = \sum_A \mu_A^{\text{tot}} + \sum_{A > B} \sum_B \mu_{AB}^{\text{tot}} = \sum_A (\mu_A^{\text{nuc}} + \mu_A^{\text{pop}} + \mu_A^{\text{dip}}) + \sum_{A > B} \sum_B (\mu_{AB}^{\text{pop}} + \mu_{AB}^{\text{dip}})$$

The expression and physical meaning of the five terms are

$\mu_A^{\text{nuc}}$ : Dipole moment due to nuclear charge

$$\mu_A^{\text{nuc}} = Z_A \mathbf{R}_A$$

$\mu_A^{\text{pop}}$ : Dipole moment due to the electron population number localized on single atom

(Notice that this is different to the electron population number calculated by Mulliken or similar methods, because the overlap population numbers have not been absorbed into respective atoms)

$$\mu_A^{\text{pop}} = -p_A^{\text{loc}} \mathbf{R}_A \quad p_A^{\text{loc}} = \sum_{i \in A} \sum_{j \in A} P_{i,j} \langle \chi_i | \chi_j \rangle$$

$\mu_A^{\text{dip}}$ : Atomic dipole moment, which reflects the electron dipole moment around an atom.  $\mathbf{r}_A$  is the coordinate variable with respect to nucleus A

$$\begin{aligned} \mu_A^{\text{dip}} &= -\sum_{i \in A} \sum_{j \in A} P_{i,j} \langle \chi_i | \mathbf{r}_A | \chi_j \rangle \quad \text{where } \mathbf{r}_A = \mathbf{r} - \mathbf{R}_A \\ &= -\sum_{i \in A} \sum_{j \in A} P_{i,j} \langle \chi_i | \mathbf{r} | \chi_j \rangle - \mu_A^{\text{pop}} \end{aligned}$$

$\mu_{AB}^{\text{pop}}$ : Dipole moment due to the overlap population between atom A and B

$$\mu_{AB}^{\text{pop}} = -p_{AB} \mathbf{R}_{AB} \quad p_{AB} = 2 \sum_{i \in A} \sum_{j \in B} P_{i,j} \langle \chi_i | \chi_j \rangle \quad \mathbf{R}_{AB} = (\mathbf{R}_A + \mathbf{R}_B) / 2$$

$\mu_{AB}^{\text{dip}}$ : Bond dipole moment, which somewhat reflects the electron dipole moment around geometry center of corresponding two atoms. Of course, if A and B are not close to each other, then this term will be very small, and thus inappropriate to be called as bond dipole moment.

$$\begin{aligned} \mu_{AB}^{\text{dip}} &= -2 \sum_{i \in A} \sum_{j \in B} P_{i,j} \langle \chi_i | \mathbf{r}_{AB} | \chi_j \rangle \quad \text{where } \mathbf{r}_{AB} = \mathbf{r} - \mathbf{R}_{AB} \\ &= -2 \sum_{i \in A} \sum_{j \in B} P_{i,j} \langle \chi_i | \mathbf{r} | \chi_j \rangle - \mu_{AB}^{\text{pop}} \end{aligned}$$

By means of Mulliken-type partition, the bond dipole moments can be incorporated into atomic dipole moments, so that the system dipole moment can be written as the sum of single

### 3 Functions

center terms

$$\mu = \sum_A (\mu_A^{\text{nuc}} + \mu_A'^{\text{pop}} + \mu_A'^{\text{dip}})$$

where  $\mu_A'^{\text{pop}}$  is the dipole moment due to the Mulliken population number of atom A

$$\mu_A'^{\text{pop}} = -p_A^{\text{Mul}} \mathbf{R}_A \quad p_A^{\text{Mul}} = \sum_B \sum_{i \in B} \sum_{j \in B} P_{i,j} \langle \chi_i | \chi_j \rangle$$

and  $\mu_A'^{\text{dip}}$  is the atomic overall dipole moment of atom A

$$\mu_A'^{\text{dip}} = -\sum_B \sum_{i \in B} \sum_{j \in B} P_{i,j} \langle \chi_i | \mathbf{r}_A | \chi_j \rangle = -\sum_B \sum_{i \in B} \sum_{j \in B} P_{i,j} \langle \chi_i | \mathbf{r} | \chi_j \rangle - \mu_A^{\text{Mul}}$$

Note that the  $B$  index in above formulae runs over all atoms.

#### Usage

The input file must contain basis function information (e.g. .fch, .molden and .gms).

After you enter present function, you can choose option 1 to output information of a specific atom, including: Atomic local population number,  $p_A^{\text{loc}}$ ; atomic dipole moment,  $\mu_A^{\text{dip}}$ ; contribution to system dipole moment due to nuclear charge,  $\mu_A^{\text{nuc}}$ ; contribution to system dipole moment due to electron,  $\mu_A^{\text{dip}} + \mu_A^{\text{pop}}$ ; contribution to system dipole moment,  $\mu_A^{\text{nuc}} + \mu_A^{\text{dip}} + \mu_A^{\text{pop}}$ .

You can also choose option 2 to output information between specific atom pair, including: bond population number,  $\mu_{AB}^{\text{pop}}$ ; bond dipole moment,  $\mu_{AB}^{\text{dip}}$ ; contribution to system dipole moment,  $\mu_{AB}^{\text{pop}} + \mu_{AB}^{\text{dip}}$ .

If choose 3, atomic overall dipole moment and related information of selected atoms will be outputted, including: Atomic Mulliken population number,  $p_A^{\text{Mul}}$ ; atomic overall dipole moment,  $\mu_A'^{\text{dip}}$ ; contribution to system dipole moment due to nuclear charge,  $\mu_A^{\text{nuc}}$ ; contribution to system dipole moment due to electron,  $\mu_A'^{\text{dip}} + \mu_A'^{\text{pop}}$ ; contribution to system dipole moment,  $\mu_A^{\text{nuc}} + \mu_A'^{\text{dip}} + \mu_A'^{\text{pop}}$ .

If you choose option 10, then X/Y/Z components of electron dipole moment matrix will be outputted to dipmatx.txt, dipmaty.txt and dipmatz.txt in current folder, respectively. For example, the  $(i, j)$  element of Z component of electron dipole moment matrix corresponds to

$$-\sum_i \sum_j P_{i,j} \langle \chi_i | z | \chi_j \rangle$$

**Information needed:** Atom coordinates, basis functions

### 3.200.3 Generate cube file for multiple orbital wavefunctions

By this function, grid data of multiple orbital wavefunctions can be calculated and then exported to a single cube file or separate cube files at the same time.

After you entered this function, you need to first define the orbitals you are interested in (e.g. 3,5,9-17), and then define grid setting, after that choose the scheme to export the grid data. If you select scheme 1, then grid data of all orbitals you selected will be outputted to orbital.cub in current folder. Lots of visualization programs, including VMD and Multiwfn, support the cube file containing multiple sets of grid data. If you select scheme 2, then the grid data will be exported as separate files, for example orb000003.cub, orb000005.cub, orb000009.cub, etc. The number in the filename corresponds to orbital index.

**Information needed:** Atom coordinates, GTFs

### 3.200.4 Generate iso-chemical shielding surfaces (ICSS) and related quantities

#### Theory

Nuclear independent chemical shielding (NICS) is commonly studied at some special points (e.g. ring center), and in some papers NICS is investigated by scanning its value in a line (1D) or in a plane (2D). The so-called iso-chemical shielding surface (ICSS) actually is the isosurface of NICS, which clearly exhibits the distribution of NICS in 3D space, and thus presents a very intuitive picture on aromaticity.

Present function is used to generate grid data and visualize isotropic ICSS, anisotropic ICSS,  $\text{ICSS}_{\text{XX}}$ ,  $\text{ICSS}_{\text{YY}}$  and  $\text{ICSS}_{\text{ZZ}}$ , they correspond to the isosurface of NICS,  $\text{NICS}_{\text{ani}}$ ,  $\text{NICS}_{\text{XX}}$ ,  $\text{NICS}_{\text{YY}}$  and  $\text{NICS}_{\text{ZZ}}$ , respectively. At a given point,  $\text{NICS}_{\text{ani}}$  is defined as  $\varepsilon_3 - (\varepsilon_1 + \varepsilon_2)/2$ , where  $\varepsilon$  denotes the eigenvalue of magnetic shielding tensor ranked from small to large (viz.  $\varepsilon_3$  is the largest one).

The original paper of ICSS is *J. Chem. Soc. Perkin Trans. 2*, **2001**, 1893. While  $\text{ICSS}_{\text{ani}}$ ,  $\text{ICSS}_{\text{XX}}$ ,  $\text{ICSS}_{\text{YY}}$  and  $\text{ICSS}_{\text{ZZ}}$  are proposed by me. I believe for planar systems, the component form of ICSS must be more meaningful and useful than ICSS, just like  $\text{NICS}_{\text{ZZ}}$  has conspicuous advantage over NICS.  $\text{ICSS}_{\text{ani}}$  is useful to reveal the anisotropic character of NICS in different regions.

#### Usage

Multiwfn itself is incapable of calculating magnetic shielding tensor and thus requires Gaussian to do that. The general steps is shown below

(1) Prepare an input file of Gaussian single point task for the system under study, %chk have to be explicitly specified. For example, see "examples\ICSS\anthracene.gjf". This file will be taken as template to automatically build Gaussian input file of NMR task

(2) After boot up Multiwfn, load the file containing the atomic coordinate of your system (e.g. .pdb/.xyz/.wfn/.fch ...), then enter subfunction 4 of main function 200. Beware that the atomic coordinates loaded must exactly accord with the ones in the file prepared in step 1.

(3) Set up grid by following the prompt. Beware that even using medium quality grid may be fairly time-consuming. Hence low quality grid is in general recommended for medium-size system.

(4) Input  $n$ , namely do not skip step 5 and 6.

(5) Input the path of the Gaussian input file you prepared in step 1.

(6) Many input files of Gaussian NMR task are generated in current folder, they are named as NICS0001.gif, NICS0002.gif ...

In these files, each Bq atom corresponds to a grid point. In the NMR task Gaussian will output magnetic shielding tensor at each Bq along with that at each nuclei. By default 8000 atoms (the real ones + Bq) are presented in each input file, but this can be altered via "NICSnptlim" parameter in settings.ini. The reason why separate files rather than a single file are generated is because Gaussian cannot run properly if the number of Bq atoms is too large due to over-consume of memory, also there is upper limit on the total number of atoms in each Gaussian run. You can try to set NICSnptlim to a larger value if you have large physical memory, this will reduce overall cost of ICSS analysis.

Note that for G09 D.01, due to a bug in memory allocation when using the default Harris initial guess, you should always add "guess=huckel" to route section, otherwise the NICSnptlim has to be set to a very small value (e.g. 1000) to make Gaussian work; in this case the overall cost of ICSS calculations is often quite high.

(7) Feed all of the input files generated in last step to Gaussian to yield output files. If possible, please keep Multiwfn running (If you have terminated it, reboot Multiwfn and repeat step 2, 3 with the same setting and input y at step 4).

Hint: You can make use of the script "examples\runall.sh" (for Linux) or "examples\runall.bat" (for Windows), which invokes Gaussian to run all .gif files in current folder to yield output files with the same name but with .out suffix.

(8) Input the path of the folder containing Gaussian output files yielded in the last step. Then Multiwfn will load the magnetic shielding tensors from the NICS0001.out, NICS0002.out ... in this folder.

(9) Select the property you are interested in.

(10) Visualize isosurface or export the grid data to cube file by corresponding option. For example, in step 9 you selected "ZZ component", then the isosurface and the grid data will correspond to ICSS<sub>ZZ</sub>. You can also select "-1 Load other property" to load other property.

Notice that if this is not the first time you analyze your system and you already have Gaussian output files of NMR task of present system in hand, you can start from step 2 and select y in step 4 to bypass the step 5, 6 and 7. Of course, the grid setting in step 3 must be exactly accord with the one used in generating the Gaussian output files of NMR task.

An example is given in Section 4.200.4.

**Information needed:** Atom coordinates, input file of Gaussian single point task, output file of Gaussian NMR task.

### 3.200.5 Plot radial distribution function for a real space function

This function is used to plot radial distribution function (RDF) for a real space function

$$RDF(r) = \int f(r, \Omega) r^2 d\Omega$$

where  $r$  is radial distance from sphere center, and  $\Omega$  denotes angular coordinate in a sphere layer.

The integration curve of RDF can also be plotted

$$I(r') = \int_{r_{\text{low}}}^{r'} \text{RDF}(r) dr = \int_{r_{\text{low}}}^{r'} \int f(r, \Omega) r^2 d\Omega dr$$

Clearly, if  $r_{\text{low}}$  is set to 0 (viz. sphere center), then  $I(\infty)$  will be the integral of  $f$  over the whole space.

In present function, one can choose the real space function to be studied, set the position of sphere center, set the lower and upper limit to be calculated and plotted, set the number of points in radial and angular parts. The larger the number of points, the more accurate the integration curve.

After the parameters are set, select option 0 to start the calculation, and then you will see a new menu, in which you can plot RDF and its integration curve, save the graph or export the corresponding original data.

An example is given in Section 4.200.5.

**Information needed:** Atom coordinates, GTFs

### 3.200.6 Analyze correspondence between orbitals in two wavefunctions

#### Theory

This function is used to analyze correspondence between the orbitals in two wavefunctions. The two sets of orbitals can be produced under different basis-sets, by different theoretical methods, at different external environments, in different electronic states, or at slightly different geometries. The two sets of orbitals can also be different types, for example the first set of orbitals are canonical MOs produced by Hartree-Fock calculation, while the second set of orbitals are natural orbitals produced by post-HF calculation.

The orbitals  $\{i\}$  in present wavefunction (the wavefunction loaded when Multiwfn boots up) can be represented as linear combination of the orbitals  $\{j\}$  in another wavefunction (the wavefunction you specified after entering present module), i.e.

$$|i\rangle = \sum_j C_{i,j} |j\rangle \quad \text{where } C_{i,j} = \langle i | j \rangle$$

Once we have the overlap integral, we immediately know how  $j$  is associated to  $i$ . The contribution from orbital  $j$  to orbital  $i$  is simply the square of overlap integral, namely  $\langle ij \rangle^2 \times 100\%$ .

#### Usage

After you enter this function, first you need to input the orbital range to be considered for present wavefunction (*istart1~iend1*), and then input the path of the second wavefunction and the orbital range to be considered (*istart2~iend2*). After that the overlap matrix between *istart1~iend1* and *istart2~iend2* will be calculated by Becke's multi-center numerical integration scheme. Then you will see the five largest contributions from *istart2~iend2* to each orbital in *istart1~iend1*. If you want to obtain all coefficients (as well as the corresponding contributions) of *istart2~iend2* in

### 3 Functions

a given orbital among istart1~iend1, you can then directly input the index of the orbital. If you need all overlap integrals between istart1~iend1 and istart2~iend2, input -1, then they will be outputted to convmat.txt in current folder.

If an orbital (*i*) in present wavefunction can be exactly expanded as linear combination of istart2~iend2, then the normalization condition must be satisfied:

$$\sum_{j=\text{istart2}}^{\text{iend2}} \langle i | j \rangle^2 \times 100\% = 100\%$$

From the Multiwfn output you can find the maximum deviation to normalization condition. If the value is zero, that means all orbitals in istart1~iend1 can be exactly represented by the orbitals in istart2~iend2.

Note that the atomic coordinate of present wavefunction and that of the second wavefunction are not necessarily identical, the two wavefunctions can even correspond to different molecules. However if the difference of the distribution scope of the atomic coordinates in the two wavefunctions is large, the integration accuracy must be low and the result is not reliable.

Commonly the default integration grid is fine enough, i.e. 50 radial points and 230 angular points. If you wish to improve the accuracy, you should set "iautointgrid" in settings.ini file to 0, then the number of radial and angular integration grids will be directly determined by "radpot" and "sphpot" in settings.ini; set them to a large value will result in good integration accuracy.

The computational cost of this function directly depends on the number of orbitals in consideration; so if your system contains very large number of orbitals, do not choose all orbitals at once.

#### Example

As an example, we use present function to study the conversion relationship between HF/6-31+G\* MOs and MP2/6-31+G\* natural orbitals (NO) for CH<sub>3</sub>NH<sub>2</sub>.

After boot up Multiwfn we input

C:\CH3NH2\_MP2.wfn // MP2/6-31+G\* wavefunction file, there are 48 NOs

200

6

[Press ENTER button directly to choose all orbitals]

C:\CH3NH2\_HF.wfn // HF/6-31+G\* wavefunction file, there are 9 MOs

[Press ENTER button directly to choose all orbitals]

Then you will see

1:	2( 94.63%)	1( 5.36%)	4( 0.01%)	3( 0.00%)	6( 0.00%)
2:	1( 94.64%)	2( 5.36%)	3( 0.00%)	9( 0.00%)	6( 0.00%)
3:	3( 85.21%)	4( 9.87%)	7( 3.24%)	9( 0.88%)	6( 0.79%)
4:	4( 86.88%)	3( 10.66%)	6( 1.94%)	9( 0.48%)	7( 0.02%)
5:	6( 54.88%)	7( 41.11%)	9( 3.20%)	4( 0.45%)	3( 0.34%)
6:	8( 57.50%)	5( 42.47%)	7( 0.00%)	6( 0.00%)	4( 0.00%)
7:	5( 57.50%)	8( 42.48%)	7( 0.00%)	4( 0.00%)	6( 0.00%)
8:	9( 86.62%)	6( 10.30%)	7( 1.63%)	4( 0.89%)	3( 0.50%)
9:	7( 53.98%)	6( 32.07%)	9( 8.76%)	3( 3.28%)	4( 1.89%)
10:	9( 0.00%)	7( 0.00%)	6( 0.00%)	4( 0.00%)	2( 0.00%)

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```

11:      5( 0.00%)   8( 0.00%)   3( 0.00%)   7( 0.00%)   4( 0.00%)
... (ignored)
47:      6( 0.01%)   7( 0.00%)   9( 0.00%)   3( 0.00%)   4( 0.00%)
48:      9( 0.04%)   7( 0.00%)   6( 0.00%)   4( 0.00%)   3( 0.00%)

```

The first column denotes the index of the MP2 NOs, the largest five contributions from the Hartree-Fock MOs to them are shown at right side. As can be seen, the first (second) NO is nearly equivalent to the second (first) MO. While the 9th NO cannot be solely represented by any MO, it mainly arises from the severe mix of the 7th (53.98%) and 6th MOs (32.07%), the 9th MO also has non-neglectable contribution (8.76%).

If you want to get all coefficients and compositions of an orbital of present wavefunction (e.g. the 5th NO), then simply input 5, you will see

1	Contribution:	0.000 %	Coefficient:	0.001509
2	Contribution:	0.000 %	Coefficient:	-0.000042
3	Contribution:	0.339 %	Coefficient:	-0.058201
4	Contribution:	0.447 %	Coefficient:	0.066869
5	Contribution:	0.000 %	Coefficient:	0.000000
6	Contribution:	54.882 %	Coefficient:	0.740826
7	Contribution:	41.113 %	Coefficient:	-0.641194
8	Contribution:	0.000 %	Coefficient:	0.000000
9	Contribution:	3.199 %	Coefficient:	-0.178856
Total : 99.980 %				

this output suggests  $|NO\ 5\rangle = 0.7408|MO\ 6\rangle - 0.6412|MO\ 7\rangle - 0.1788|MO\ 9\rangle \dots$  The 99.98% at the last line indicates that the 5th NO can be perfectly represented by linear combination of these nine MOs.

**Information needed:** Atom coordinates, GTFs

### 3.200.7 Parse output of (hyper)polarizability task of Gaussian

The output of (hyper)polarizability task of Gaussian (*polar* keyword) is difficult to understand, at least for beginners. This function is used to parse these outputs and then print them in a more readable format, and at the same time some quantities relating to (hyper)polarizability analysis will be outputted. Currently this function is only formally compatible with Gaussian 09, since the output of *polar* task in different versions of Gaussian may be quite different.

#### Basic concepts

Energy of a system can be written as Taylor expansion with respect to uniform external electric field  $\mathbf{F}$

$$\begin{aligned}
E(\mathbf{F}) &= E(\mathbf{0}) + \left. \frac{\partial E}{\partial \mathbf{F}} \right|_{\mathbf{F}=0} \mathbf{F} + \frac{1}{2} \left. \frac{\partial^2 E}{\partial \mathbf{F}^2} \right|_{\mathbf{F}=0} \mathbf{F}^2 + \frac{1}{6} \left. \frac{\partial^3 E}{\partial \mathbf{F}^3} \right|_{\mathbf{F}=0} \mathbf{F}^3 + \frac{1}{24} \left. \frac{\partial^4 E}{\partial \mathbf{F}^4} \right|_{\mathbf{F}=0} \mathbf{F}^4 + \dots \\
&\equiv E(\mathbf{0}) - \boldsymbol{\mu}_0 \mathbf{F} - \frac{1}{2} \boldsymbol{\alpha} \mathbf{F}^2 - \frac{1}{6} \boldsymbol{\beta} \mathbf{F}^3 - \frac{1}{24} \boldsymbol{\gamma} \mathbf{F}^4 - \frac{1}{120} \boldsymbol{\delta} \mathbf{F}^5 - \frac{1}{720} \boldsymbol{\varepsilon} \mathbf{F}^6 \dots
\end{aligned}$$

$$\boldsymbol{\mu}_0 = -\left. \frac{\partial E}{\partial \mathbf{F}} \right|_{\mathbf{F}=0} \quad \boldsymbol{\alpha} = -\left. \frac{\partial^2 E}{\partial \mathbf{F}^2} \right|_{\mathbf{F}=0} \quad \boldsymbol{\beta} = -\left. \frac{\partial^3 E}{\partial \mathbf{F}^3} \right|_{\mathbf{F}=0} \quad \boldsymbol{\gamma} = -\left. \frac{\partial^4 E}{\partial \mathbf{F}^4} \right|_{\mathbf{F}=0}$$

where  $\boldsymbol{\mu}_0$  is permanent dipole moment, which is a vector;  $\boldsymbol{\alpha}$  is polarizability, which is a matrix (second rank tensor);  $\boldsymbol{\beta}$  is first hyperpolarizability, which is a third rank tensor and known as second-order nonlinear optical response (NLO) coefficient;  $\boldsymbol{\gamma}$  is second hyperpolarizability, which is a fourth rank tensor and known as third-order NLO coefficient. The higher terms such as  $\boldsymbol{\delta}$  and  $\boldsymbol{\epsilon}$  are very unimportant and thus rarely discussed. The (hyper)polarizability tensors are directly correlated to the frequency of external field  $\mathbf{F}$ . If  $\mathbf{F}$  has zero-frequency (static electric field), then the (hyper)polarizabilities are known as static or frequency-independent ones. The dynamic or frequency-dependent (hyper)polarizabilities correspond to those at external electromagnetic fields with non-zero frequency.

Dipole moment of a system in uniform electric field can be written as

$$\boldsymbol{\mu} = -\frac{\partial E}{\partial \mathbf{F}} = \boldsymbol{\mu}_0 + \underbrace{\boldsymbol{\alpha} \mathbf{F}}_{\boldsymbol{\mu}_1} + \underbrace{(1/2)\boldsymbol{\beta} \mathbf{F}^2}_{\boldsymbol{\mu}_2} + \underbrace{(1/6)\boldsymbol{\gamma} \mathbf{F}^3}_{\boldsymbol{\mu}_3} + \dots$$

The linear response of dipole moment with respect to  $\mathbf{F}$ , namely the  $\boldsymbol{\mu}_1$  term, can be explicitly written as below

$$\boldsymbol{\mu}_1 = \boldsymbol{\alpha} \cdot \mathbf{F} \Rightarrow \begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} F_x \\ F_y \\ F_z \end{bmatrix}$$

The polarizability  $\boldsymbol{\alpha}$  is a symmetric matrix rather than a scalar, implying the difference of polarizability in different directions. In order to facilitate comparison of overall polarizability between various systems, it is convenient to define the isotropic average polarizability

$$\langle \boldsymbol{\alpha} \rangle = \text{Tr}(\boldsymbol{\alpha}) / 3 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$$

Anisotropy of polarizability can be defined in various ways:

**Definition 1** see *Chem. Phys.*, **410**, 90 for example

$$\Delta\alpha = \sqrt{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)] / 2}$$

**Definition 2** This definition is the most commonly use one, see *J. Chem. Phys.*, **98**, 3022 (1993) for example

$$\Delta\alpha = \sqrt{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2] / 2}$$

**Definition 3**  $\{\varepsilon\}$  stand for eigenvalues of  $\boldsymbol{\alpha}$  ranking from small to large

$$\Delta\alpha = \varepsilon_3 - (\varepsilon_1 + \varepsilon_2) / 2$$

Hyperpolarizability  $\boldsymbol{\beta}$  is a third rank tensor that can be described by a 3\*3\*3 matrix. For dynamic  $\boldsymbol{\beta}$ , Gaussian is capable of calculating its dc-Pockels form  $\beta_{i,j,k}(-\omega;\omega,0)$  and SHG form  $\beta_{i,j,k}(-2\omega;\omega,\omega)$ . For the former, the  $i$  and  $j$  index can be freely exchanged, while for the later the  $j$  and  $k$  index can be freely exchanged, therefore the 3\*3\*3=27 components can be reduced to 18

### 3 Functions

unique ones. For static case, viz.  $\beta_{i,j,k}(0;0,0)$ , since all of the three indices are exchangeable (known as Kleinman's symmetry, e.g.  $\beta_{xxy}=\beta_{yxy}=\beta_{yyx}$ ,  $\beta_{zyy}=\beta_{yzy}=\beta_{yyz}$  ...), only 10 components are unique. The Kleinman's symmetry is only approximately applied to dynamic  $\beta$  at low-frequency external field.

The  $\beta$  value in one of the three Cartesian axes can be calculated by the general equation

$$\beta_i = (1/3) \sum_j (\beta_{iji} + \beta_{jji} + \beta_{jjj}) \quad i, j = \{x, y, z\}$$

The magnitude of  $\beta$  is defined as

$$\beta_{\text{tot}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

$\beta_{\text{proj}}$  (also known as  $\beta_{\text{vec}}$ ), which is the projection of  $\beta$  on dipole moment vector  $\mu$ , can be sampled experimentally (electric field induced second harmonic generation (EFISH) experiment).  $\beta_{\parallel}$  is the  $\beta$  component in the direction of  $\mu$

$$\beta_{\text{proj}} = \sum_i \frac{\mu_i \beta_i}{|\mu|} \quad \beta_{\parallel} = (3/5)\beta_{\text{proj}}$$

Some people prefer to discuss the perpendicular and parallel components of  $\beta$  with respect to Z axis, they are defined respectively as

$$\beta_{\perp(Z)} = (1/5) \sum_j (2\beta_{zij} - 3\beta_{zjz} + 2\beta_{jzz}) \quad \beta_{\parallel(Z)} = (3/5)\beta_z$$

For static case, we can explicitly write out  $\beta$  in x, y and z directions as

$$\begin{aligned} \beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yxx} + \beta_{yyy} + \beta_{yzz} \\ \beta_z &= \beta_{zxz} + \beta_{zyy} + \beta_{zzz} \end{aligned}$$

and  $\beta_{\perp(Z)} = (1/5)\beta_z$ .

#### Usage

The *polar* keyword in Gaussian is specific for calculating  $\alpha$  and  $\beta$  based on analytic derivatives (by means of coupled-perturbed SCF equation) or numerical derivatives (by means of finite field treatment).

After you enter this function of Multiwfn, you should select which calculation combination is used, so that Multiwfn can properly parse the output. In Gaussian 09 there are several circumstances:

- (1) *polar* keyword + the methods supporting analytic 3-order derivatives (HF/DFT/Semi-empirical methods)
- (2) *polar* keyword + the methods supporting analytic 2-order derivatives (e.g. MP2)
- (3) *polar=Cubic* keyword + the methods supporting analytic 2-order derivatives
- (4) *polar* keyword + the methods supporting analytic 1-order derivatives (CISD, QCISD, CCSD, MP3, MP4(SDQ), etc.)
- (5) *polar=DoubleNumer* (equivalent to *Polar=EnOnly*) keyword + the methods supporting analytic 1-order derivatives
- (6) *polar* keyword + the methods only supporting energy calculation (CCSD(T), QCISD(T),

### 3 Functions

MP4(SDTQ), MP5, etc.)

Only (1), (3) and (5) produce hyperpolarizability, other combinations only produce polarizability. Notice that in the Gaussian input file you must specify **#P!**

Only for (1), if *CPHF=RdFreq* is also specified along with *polar*, or you used *polar=DCSHG*, and meantime the external field frequencies (e.g. 0.05 0.07 0.1) are written after molecular geometry with a blank line in front of it, Gaussian will calculate and output frequency-dependent (hyper)polarizabilities along with static (hyper)polarizability. *CPHF=RdFreq polar* cases only evaluate  $\beta(-\omega; \omega, 0)$  values, while *polar=DCSHG* cases evaluate both  $\beta(-\omega; \omega, 0)$  and  $\beta(-2\omega; \omega, \omega)$  values. By default Multiwfn only parses the static (hyper)polarizability. If you wish to parse the frequency-dependent ones instead of the static one, before selecting option 1 you should select -1 first. The user then can choose the result at which frequency will be parsed. Also, one can choose parsing the  $\beta(-\omega; \omega, 0)$  one or the  $\beta(-2\omega; \omega, \omega)$  one, the latter can be chosen only for the case of *polar=DCSHG*.

Worthnotingly, it is well known that the sign of all hyperpolarizability components outputted by Gaussian are wrong and should be multiplied by -1, Multiwfn automatically accounts for this problem. This problem exists at least in G09 D.01.

In this function, Multiwfn outputs all unique components of dipole moment, polarizability and hyperpolarizability (if available) with explicit labels, as well as isotropic polarizability, polarizability anisotropy (in definitions 1 and 2), hyperpolarizability in three axes ( $\beta_x$ ,  $\beta_y$ ,  $\beta_z$ ), magnitude of hyperpolarizability ( $\beta_{tot}$ ) and so on. All of them have been introduced above.

By using option -3, you can choose the unit in the output. Atomic unit, SI unit and esu unit can be chosen. The conversion factors are

		SI	esu
$\mu$	1 a.u.	$8.47835 \times 10^{-30}$ C m	$2.54175 \times 10^{-18}$ esu
$\alpha$	1 a.u.	$1.6488 \times 10^{-41}$ C <sup>2</sup> m <sup>2</sup> J <sup>-1</sup>	$1.4819 \times 10^{-25}$ esu
$\beta$	1 a.u.	$3.20636 \times 10^{-53}$ C <sup>3</sup> m <sup>3</sup> J <sup>-2</sup>	$8.63922 \times 10^{-33}$ esu
$\gamma$	1 a.u.	$6.23538 \times 10^{-65}$ C <sup>4</sup> m <sup>4</sup> J <sup>-3</sup>	$5.03670 \times 10^{-40}$ esu

In "example" folder, *DFT\_polar\_static.out* and *DFT\_polar\_freq.out* are example files of static and frequency-dependent calculations of case (1), respectively.

**Information needed:** Output file of "polar" task of Gaussian09

#### 3.200.8 Calculate (hyper)polarizability by sum-over-states (SOS) method

This function is used to calculate polarizability, first, second, and third hyperpolarizabilities based on sum-over-states method.

##### A brief survey of the theories for evaluating (hyper)polarizability

Some basic concepts of (hyper)polarizability are introduced in Section 3.200.7. There are a few different ways to calculate (hyper)polarizability, including derivative method, sum-over-states (SOS) and response method

(1) Derivative method: This is the most straightforward and commonly used one. The derivatives needed by static (hyper)polarizability can be evaluated analytically by means of coupled-perturbed SCF (CPSCF) equation; specifically, CPHF for HF and CPKS for KS-DFT. These derivatives can also be evaluated numerically by means of finite difference technique, which is also known as finite field (FF) method. Evidently FF is much slower and not as accurate as CPSCF, however it is still useful, because high-order of analytic derivatives, especially the ones at sophisticated post-HF levels, are not widely supported by many quantum chemistry programs due to the difficulties in coding. When all requested derivatives are available analytically, derivative method will be very efficient. The frequency-dependent variant of CPSCF equation enables the derivative method to evaluate dynamic (hyper)polarizability, but there is no way to evaluate dynamic (hyper)polarizability in terms of FF treatment. The *polar* keyword in Gaussian, as discussed carefully in Section 3.200.7, corresponds to this derivative method.

(2) SOS method: This method for evaluating static and dynamic (hyper)polarizability is relatively inefficient, because in principle it involves a sum over all excited states (in practical applications, taking 60~120 lowest states into account is often enough), while determination of a large number of excited states is usually quite time consuming in *ab initio* cases (e.g. CIS and TDDFT), especially for large system (e.g. >40 atoms). Due to the high computational cost, SOS is generally not recommended for evaluation of (hyper)polarizability when derivative method can be carried out analytically. The only advantages of SOS may be that the contribution from different states can be separated and discussed respectively, and when transition dipole moments between different excited states are available in hand, the (hyper)polarizability at different frequencies can be evaluated rather rapidly. Worthnotingly, the SOS based on the cheap semi-empirical ZINDO calculation (SOS/ZINDO) is very popular for evaluating (hyper)polarizability of large system.

(3) Response method: This method is specific for dynamic (hyper)polarizability and also known as propagator method. TDHF and TDDFT are its two practical realizations. This method is not prevalently supported by mainstream quantum chemistry codes.

(4) Correction vector method: Proposed by Zhigang Shuai, not popular currently.

### Working equations of SOS method

The explicit SOS equations for evaluating polarizability and 1st/2nd/3rd hyperpolarizability can be found in *J. Chem. Phys.*, **99**, 3738 (1993), the idea was originally proposed by Orr and Ward in *Mol. Phys.*, **20**, 512 (1971).

The equations for polarizability  $\alpha$  and first hyperpolarizability  $\beta$  are (all units are in a.u.)

$$\alpha_{AB}(-\omega; \omega) = \sum_{i \neq 0} \left[ \frac{\mu_{0i}^A \mu_{i0}^B}{\Delta_i - \omega} + \frac{\mu_{0i}^B \mu_{i0}^A}{\Delta_i + \omega} \right] = \hat{P}[A(-\omega), B(\omega)] \sum_{i \neq 0} \frac{\mu_{0i}^A \mu_{i0}^B}{\Delta_i - \omega}$$

$$\beta_{ABC}(-\omega_\sigma; \omega_1, \omega_2) = \hat{P}[A(-\omega_\sigma), B(\omega_1), C(\omega_2)] \sum_{i \neq 0} \sum_{j \neq 0} \frac{\mu_{0i}^A \overline{\mu_{ij}^B} \mu_{j0}^C}{(\Delta_i - \omega_\sigma)(\Delta_j - \omega_2)}$$

where

$$\mu_{ij}^A = \langle i | \hat{\mu}^A | j \rangle \quad \overline{\mu_{ij}^A} = \mu_{ij}^A - \mu_{00}^A \delta_{ij} \quad \omega_\sigma = \sum_i \omega_i$$

$A, B, C \dots$  denote one of directions {x,y,z};  $\omega$  is energy of external fields,  $\omega=0$  corresponds to static electric field;  $\Delta_i$  stands for excitation energy of state  $i$  with respect to ground state 0.  $\hat{P}$  is

### 3 Functions

permutation operator, for  $\alpha$  and  $\beta$  evidently there are  $2!=2$  and  $3!=6$  permutations, respectively.

$\mu_{ij}^A$  is A component of transition dipole moment between state  $i$  and  $j$ ; when  $i=j$  the term simply

corresponds to electric dipole moment of state  $i$ .  $\hat{\mu}$  is dipole moment operator, e.g.  $\hat{\mu}^x \equiv -x$ .

The SOS equation for second hyperpolarizability  $\gamma$  is

$$\begin{aligned}\gamma_{ABCD}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) &= \hat{P}[A(-\omega_\sigma), B(\omega_1), C(\omega_2), D(\omega_3)](\gamma^I - \gamma^{II}) \\ \gamma^I &= \sum_{i \neq 0} \sum_{j \neq 0} \sum_{k \neq 0} \frac{\mu_{0i}^A \overline{\mu_{ij}^B} \mu_{jk}^C \mu_{k0}^D}{(\Delta_i - \omega_\sigma)(\Delta_j - \omega_2 - \omega_3)(\Delta_k - \omega_3)} \\ \gamma^{II} &= \sum_{i \neq 0} \sum_{j \neq 0} \frac{\mu_{0i}^A \mu_{i0}^B \mu_{0j}^C \mu_{j0}^D}{(\Delta_i - \omega_\sigma)(\Delta_i - \omega_1)(\Delta_j - \omega_3)}\end{aligned}$$

The Z components of  $\gamma$  is defined as

$$\gamma_z = (1/15) \sum_A (\gamma_{zAAz} + \gamma_{zAzA} + \gamma_{zzAA})$$

Similarly for X and Y components. The total magnitude of  $\gamma$  may be measured as

$\gamma_{\text{tot}} = \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2}$ . There are two common definitions of average value of  $\gamma$ :

def 1:  $\langle \gamma \rangle = \gamma_x + \gamma_y + \gamma_z$

def 2:  $\langle \gamma \rangle = (1/5)[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz} + \gamma_{yyxx} + \gamma_{zzxx} + \gamma_{zzyy}]$

The SOS equation for third hyperpolarizability  $\delta$  is

$$\begin{aligned}\delta_{ABCDE}(-\omega_\sigma; \omega_1, \omega_2, \omega_3, \omega_4) &= \hat{P}[A(-\omega_\sigma), B(\omega_1), C(\omega_2), D(\omega_3), E(\omega_4)](\delta^I - \delta^{II} - \delta^{III}) \\ \delta^I &= \sum_{\substack{i,j,k,l \\ (\neq 0)}} \frac{\mu_{0i}^A \overline{\mu_{ij}^B} \mu_{jk}^C \overline{\mu_{kl}^D} \mu_{l0}^E}{(\Delta_i - \omega_\sigma)(\Delta_j - \omega_\sigma + \omega_1)(\Delta_k - \omega_3 - \omega_4)(\Delta_l - \omega_4)} \\ \delta^{II} &= (1/2) \sum_{\substack{i,j,k \\ (\neq 0)}} \frac{\mu_{0i}^A \mu_{i0}^B \mu_{0j}^C \overline{\mu_{jk}^D} \mu_{k0}^E}{(\Delta_j + \omega_2)(\Delta_k - \omega_4)} \left( \frac{1}{\Delta_i - \omega_\sigma} + \frac{1}{\Delta_i - \omega_1} \right) \left( \frac{1}{\Delta_j - \omega_3 - \omega_4} + \frac{1}{\Delta_k + \omega_2 + \omega_3} \right) \\ \delta^{III} &= (1/2) \sum_{\substack{i,j,k \\ (\neq 0)}} \frac{\mu_{0i}^A \mu_{i0}^B \mu_{0j}^C \overline{\mu_{jk}^D} \mu_{k0}^E}{(\Delta_i - \omega_\sigma)(\Delta_i - \omega_1)} \left[ \frac{1}{(\Delta_j - \omega_3 - \omega_4)(\Delta_k - \omega_4)} + \frac{1}{(\Delta_j + \omega_2)(\Delta_k + \omega_2 + \omega_3)} \right]\end{aligned}$$

#### Input file

Two kinds of input files can be used:

(1) Gaussian output file of common CIS, TDHF, TDDFT or ZINDO task. Since Gaussian does not output all transition dipole moments needed by SOS hyperpolarizability calculation, only polarizability will be calculated by Multiwfn in this case. In order to obtain accurate polarizability, the number of calculated states should be large enough. If *nstates* keyword is specified to a very large value, e.g. 1000000, then all states will be calculated. #P is suggested to be used, since the

excitation energy will then be printed in a higher precision format.

(2) Plain text file containing excitation energies and transition dipole moments for all involved states. Below format should be followed (assume a very simple case, only 2 excited states). Polarizability, first, second and third hyperpolarizabilities can be calculated in this case.

```

2 // The number of excited states
1 1.1 // Excited state 1, its index and excitation energy (eV)
2 3.2
0 0 0.845 0.2 0.4 // Electric dipole moment of ground in X, Y, Z (a.u.)
0 1 0.231 0.3 0.7 // Transition dipole moment between ground state and excited state 1
0 2 0.112 0.564 0.21
1 1 0.021 0.465 0.0 // Electric dipole moment of excited state 1
1 2 0.001 0.3 0.11 // Transition dipole moment between excited states 1 and 2
2 2 0.432 0.14 0.42

```

Hint: You can directly utilize the function introduced in Section 3.21.5 to generate such a plain text file based on the Gaussian output file of electron excitation task.

If merely polarizability is interesting, only the content before the line "1 1" is needed to be provided, all other contents can be omitted; in this case, the number of excited states should be written as a negative number (-2 in above case) to tell Multiwfn do not to load them.

### Usage

After you entered this function you will see a menu, there are three kinds of functions:

(1) Option 1~4: Used to calculate  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  at a given frequency, respectively. User needs to input frequency of each external field. Since calculation of  $\gamma$  and  $\delta$  are often time-consuming, in these cases users will be prompted to input the number of states in consideration, small number is evidently cheaper, but may give rise to lower accurate result.

(2) Option 5~7: Used to study the variation of  $\alpha$ ,  $\beta$  and  $\gamma$  with respect to the number of states in consideration. User needs to input frequency of each external field. For  $\alpha$  and  $\beta$ , the number of states taken into account ranges from 1 to all states loaded, the stepsize is 1. While for  $\gamma$ , since the computational cost may be quite high, users are allowed to customly defined the ending value and stepsize. The result will be outputted to plain text file "alpha\_n.txt" or "beta\_n.txt" or "gamma\_n.txt" in current folder, the meaning of each column can be seen in command-line window. One can directly drag these plain text files into window of Origin program to plot the variations as curve maps.

(3) Option 15~17: Used to study the variation of the  $\alpha$ ,  $\beta$  and  $\gamma$  with respect to frequency of external fields. For  $\alpha$ , users need to input initial value, ending value and stepsize of external field frequencies. For  $\beta$  and  $\gamma$ , users should write a plain text file, each row corresponds to a pair of frequency (in a.u.) to be calculated. Multiwfn will prompt users to input the path of the file. Below is an example file used to study how  $\gamma(-0;0,\omega,-\omega)$  varies as  $\omega$  goes from 0 to 0.2 a.u. with stepsize of 0.02

```

0.0 0.0 0.0
0.0 0.02 -0.02
0.0 0.04 -0.04
... [ignored]
0.0 0.2 -0.2

```

Since the computational cost for evaluating  $\gamma$  may be quite high, in this case users are

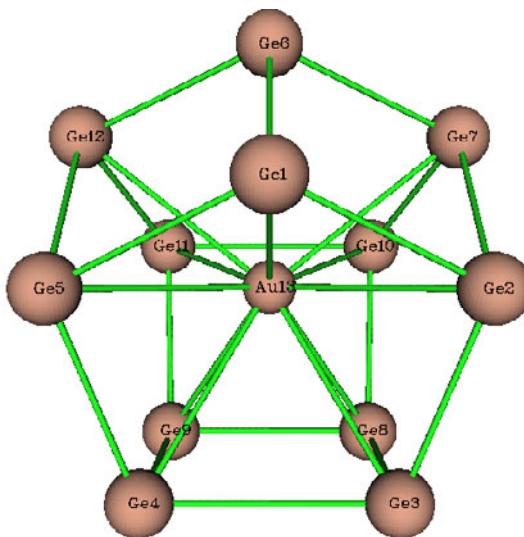
allowed to set the number of states in consideration. The result will be outputted to plain text file "alpha\_w.txt" or "beta\_w.txt" or "gamma\_w.txt" in current folder, the meaning of each column can be seen in command-line window. One can directly drag these plain text files into window of Origin program to plot the variations as curve maps.

Multiwfn not only outputs the tensor of (hyper)polarizability, but also outputs many related quantities, such as anisotropy, magnitude and the component along Z axis. The quantities involving  $\alpha$  and  $\beta$  are discussed in Section 3.200.7, the ones involving  $\gamma$  have been introduced above.

An example is given in Section 4.200.8.

### 3.200.9 Calculate average bond length and average coordinate number

This function is used to calculate average bond length between two elements and average coordinate number. This function is particularly useful for analyzing structure character of atom clusters, for example the Ge<sub>12</sub>Au cluster shown below (the structure file is provided as *examples\Ge12Au.pdb*). By using this function, we can immediately obtain the average Ge-Ge bond length and average Au-Ge bond length, as well as average coordinate number of Ge due to Ge-Au or Ge-Ge bonds, or of Au due to Ge-Au bonds. A nice application of this kind of analysis on Al clusters can be found in *J. Chem. Phys.*, **111**, 1890 (1999).



The average bond length is defined as follows

$$\langle R \rangle = \frac{1}{n_b} \sum_{i>j} R_{ij}$$

where  $R_{ij}$  is the distance between atom  $i$  and  $j$ , only the terms smaller than or equal to a given distance cutoff (e.g. 2.2Å) will be regarded as bonds and thus be taken into the summation.  $n_b$  is the total number of bonds.

The average coordinate number is calculated as follows

$$CN = \frac{1}{n} \sum_i N_i$$

where  $N_i$  is the number of bonds surrounding the atom  $i$ ,  $n$  is the total number of atoms.

After you entered this function, you need to input two elements, for example *Ge,Au*, and input a distance cutoff, for example 3.2, then the Ge-Au contacts  $\leq 3.2\text{\AA}$  will be regarded as Ge-Au bonds and the average bond length will be calculated, the minimum and maximum bond lengths will also be outputted. After that, if you select y, the average coordinate number of Ge due to Ge-Au bonds will be shown.

**Information needed:** Atom coordinates

### 3.200.10 Output various kinds of integral between orbitals

This function is used to calculate electric/magnetic dipole moment integral, velocity integral, kinetic energy integral and overlap integral between orbitals, advanced users may recognize the significance of these data. In the case of a range of orbitals, the results are exported to orbint.txt in current folder, the first and second columns correspond to the index of the two orbitals; In the case of a pair of orbitals, the result is directly printed on screen.

The electric dipole moment integral vector between two orbitals is defined as

$$\mathbf{p}_{ij} = \mathbf{p}_{ji} = \langle \varphi_i | -\mathbf{r} | \varphi_j \rangle$$

The magnetic dipole moment integral vector between two orbitals is calculated as (more detail can be found in Section 3.21.1.1. The negative sign is ignored)

$$\mathbf{M}_{ij} = i \langle \varphi_i | \mathbf{r} \times \nabla | \varphi_j \rangle$$

The velocity integral vector between two orbitals is evaluated as (the negative sign is ignored)

$$\mathbf{v}_{ij} = i \langle \varphi_i | \nabla | \varphi_j \rangle$$

Worthnoting, due to the Hermitian of the operators, we have

$$\begin{aligned} \mathbf{M}_{ii} &= 0 & \mathbf{M}_{ij} = \mathbf{M}_{ji}^* &= -\mathbf{M}_{ji} \\ \mathbf{v}_{ii} &= 0 & \mathbf{v}_{ij} = \mathbf{v}_{ji}^* &= -\mathbf{v}_{ji} \end{aligned}$$

Note that the imaginary sign is not explicitly shown in the output.

The kinetic energy and overlap integrals between two orbitals are respectively evaluated as

$$K_{ij} = -(1/2) \langle \varphi_i | \nabla^2 | \varphi_j \rangle \quad S_{ij} = \langle \varphi_i | \varphi_j \rangle$$

**Information needed:** Atom coordinates, GTFs

### 3.200.11 Calculate center, the first and second moments of a real space function

This function is used to calculate center, integral value, the first and second moments of a specific real space function for present system.

#### Theory

The center of a real space function  $f$  is defined as

$$\mathbf{r}_c = \frac{\int \mathbf{r} \times f(\mathbf{r}) d\mathbf{r}}{\int f(\mathbf{r}) d\mathbf{r}}$$

where the denominator is the integral of the function over the whole space.

The first moment is a vector and is evaluated as

$$\mathbf{\mu} = \begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \int \begin{bmatrix} x \\ y \\ z \end{bmatrix} f(\mathbf{r}) d\mathbf{r}$$

The second moment is a matrix and defined as

$$\mathbf{\Theta} = \begin{bmatrix} \Theta_{xx} & \Theta_{xy} & \Theta_{xz} \\ \Theta_{yx} & \Theta_{yy} & \Theta_{yz} \\ \Theta_{zx} & \Theta_{zy} & \Theta_{zz} \end{bmatrix} = \int \begin{bmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zy & z^2 \end{bmatrix} f(\mathbf{r}) d\mathbf{r}$$

where  $x, y, z$  are the coordinate components relative to  $\mathbf{r}_c$ .

If its eigenvalues  $\{\varepsilon\}$  are sorted from low to high, then the anisotropy of  $\mathbf{\Theta}$  can be calculated

as  $\varepsilon_3 - (\varepsilon_1 + \varepsilon_2) / 2$ . The radius of gyration can be calculated as  $\sqrt{\frac{\varepsilon_1 + \varepsilon_2 + \varepsilon_3}{\int f(\mathbf{r}) d\mathbf{r}}}.$

#### Usage

This function employs Becke's multicenter integration method for evaluating above mentioned quantities. The accuracy is determined by radial points and angular points, which can be set by "radpot" and "sphpot" in settings.ini, respectively.

The option 1 calculates and outputs the integral, the first and second moments (relative to  $\mathbf{r}_c$ ), and the corresponding anisotropy and radius of gyration of the real space function selected by option 3. The center ( $\mathbf{r}_c$ ) should be properly first set by option 4. Of course, commonly  $\mathbf{r}_c$  is initially unknown, the default value is (0,0,0), you may use option 2 to evaluate the actual center of a real space function and take it as the center for the succeeding calculations triggered by option 1.

For example, to evaluate the first and second moments of spin density (relative to the center of spin density), after you entered this function you should input

```
3 // Select real space function
5 // Spin density
2 // Calculate center of spin density
y // Take the resultant center as the one for evaluating the first and second moments
```

### 3 Functions

*I* // Evaluate the first and second moments

When using option 1, if the function to be studied is chosen as electron density, then the nuclear quadrupole and molecular quadrupole moment tensors will also be outputted, the latter can be straightforwardly obtained by subtracting the former by the second moment of electron density.

**Information needed:** Atom coordinates, GTFs

#### 3.200.12 Calculate energy index (EI) or bond polarity index (BPI)

This function is used to calculate energy index (EI) or bond polarity index (BPI), which were defined in *J. Phys. Chem.*, **94**, 5602 (1990).

The EI for atom *A* in a molecule is defined as follows

$$EI_A = \frac{\sum_i^{val} \varepsilon_i \eta_i \Theta_{i,A}}{\sum_i^{val} \eta_i \Theta_{i,A}}$$

where  $\Theta_{i,A}$  denotes composition of atom *A* in MO *i*.  $\eta_i$  and  $\varepsilon_i$  are occupation and energy of MO *i*, respectively. The summation runs over valence MOs. In fact, the denominator is simply the number of valence electrons of atom *A*, and the numerator corresponds to total energy of its valence electrons. Therefore,  $EI_A$  can be regarded as average energy per valence electron of atom *A*. In the original paper of EI, Mulliken method was used to compute the atomic contribution to MOs, thus this method is also employed in present implementation of EI, though other methods such as Hirshfeld partition should work equally well or even better. (Note that since Mulliken method is used, which is incompatible with diffuse functions, the use of diffuse basis functions must be avoided!)

The BPI between atoms *A* and *B* in a molecule is defined as

$$BPI_{AB} = (EI_A - EI_A^{\text{ref}}) - (EI_B - EI_B^{\text{ref}})$$

where  $EI^{\text{ref}}$  is reference EI value derived from calculation of homonuclear species. For example, you study  $BPI_{CN}$  for  $H_3C-NH_2$ , then  $EI_C^{\text{ref}}$  is computed as  $EI_C$  in ethane, and  $EI_N^{\text{ref}}$  is computed as  $EI_N$  in  $H_2N-NH_2$ . The larger value of  $BPI_{AB}$  implies higher bond polarity of the A-B bond.

Group electronegativity is evaluated as negative of  $EI_X$  for corresponding radical, X is the attaching atom. For example, to obtain group electronegativity for  $-CH_3$  group, you should calculate  $-EI_C$  for  $\bullet CH_3$  radical.

This function of Multiwfn is used to calculate EI for specific atom in present system, all the R, RO and U types of HF/DFT wavefunction are supported. Multiwfn automatically detects the number of inner-core electrons and determines which MOs are the valence ones and thus should be taken into account.

An example is given in Section 4.200.12.

**Information needed:** Atom coordinates, basis functions

### 3.200.13 Pipek-Mezey orbital localization

Canonical molecular orbital often shows strong delocalization character and thus does have direct correlation with bonding. There are many ways to localize MOs, the most popular ones are Boys localization, Edmiston–Ruedenberg localization and Pipek–Mezey (PM) localization. PM localization is preferred over the other two because it is relatively cheap and easy to be implemented. The essence of PM localization is to maximize below quantity:

$$P = \sum_i \sum_A (Q_A^i)^2$$

where  $Q_A^i$  denotes Mulliken population of atom A in MO  $i$ . For details, see its origin paper *J. Chem. Phys.*, **90**, 4916 (1989), the working equation can be found in *J. Comput. Chem.*, **14**, 736 (1993).

Present function was developed for realizing PM localization. The input file must contain basis function information, thus you can use e.g. .fch, .molden and .gms as input file. This function only works for restricted and unrestricted SCF wavefunction.

PM localization is an iterative process, thus you should set criterion of convergence and maximum number of cycles. The default values are commonly appropriate and need not to be changed. You can choose to localize occupied MOs only, or localize both occupied and unoccupied MOs (the two set of orbitals are localized separately, i.e. no mixture between occupied and unoccupied orbitals will occur). For unrestricted wavefunction, the alpha and beta parts are dealt with separately.

By default, once the localization is converged, the localized wavefunction will be exported to new.fch in current folder, and then Multiwfn automatically load it, after that you can analyze the localized orbitals in various ways, for example, plotting them as isosurfaces by main function 0. If you don't want to let Multiwfn automatically load the newly generated new.fch, you can choose option -3 once.

If you want to obtain energy of the localized orbitals, you need to choose option -4, and input path of a file containing Fock (or Kohn-Sham) matrix in original basis functions. The matrix elements should be provided in lower-triangular form, namely in this sequence:  $F(1,1)$   $F(2,1)$   $F(2,2)$   $F(3,1)$   $F(3,2)$   $F(3,3)$  ...  $F(nbasis,nbasis)$ , where  $nbasis$  is the total number of basis functions. The format is free. The Fock matrix can be obtained from output of some quantum chemistry codes. The energy of localized orbital is corresponding diagonal term of Fock matrix in localized orbital representation. Specifically, Multiwfn performs below representation transform:

$$\mathbf{F}_{\text{LMO}} = \mathbf{C}^T \mathbf{F}_{\text{AO}} \mathbf{C}$$

where  $\mathbf{F}_{\text{AO}}$  is the Fock matrix in original basis function that loaded from external file,  $C(r,i)$  corresponds to coefficient of basis function  $s$  in localized orbital  $i$ . Energy of localized orbital  $j$  is simply  $E_{\text{LMO}}(j,j)$ .

Although PM localization is fast for small systems, for large systems it becomes computationally expensive. If you really want to apply it to large systems, the basis set used should not be too large. In addition, PM localization should not be used when diffuse functions are used, because this method is essentially based on Mulliken population, which is not compatible with diffuse functions.

Hint: If you do not have special reasons, **you only need to localize occupied orbitals**. Localization of unoccupied orbitals is much more time-consuming than that of occupied orbitals, since the number of unoccupied orbitals is often very higher when extended basis set is used. Moreover, only occupied orbitals are commonly chemically interesting.

An example is provided in Section 4.200.13.

**Information needed:** Atom coordinates, basis functions

### 3.200.14 Perform integration within isosurfaces of a real space function

This function is used to integrate specific real space function in domains, which denote individual spatial regions enclosed by isosurfaces of a given real space function. For example, you can integrate electron density within various domains defined by isosurfaces of reduced density gradient (RDG) to study strength of weak interaction.

Below is basic procedure of using this module:

- (1) Use option 2 and 3 to set the way to define the domains. For example, you selected RDG by option 2 and input <0.5 in option 3, then the region where RDG is less than 0.5 will be integrated.
- (2) Choose option 1 and properly define grid, then Multiwfn starts to calculate the grid data for the real space function you selected and identifies domains that satisfied the criterion you set. (If you already have grid data in memory, you may also choose option -1 to directly use it rather than calculate new grid data)
- (3) Once calculation in last step is finished, Multiwfn prints the number of grids in each domain. In very simple case, from these information you may directly infer which domain is the one you want to study, while for common case, you need to use option "3 Visualize domains" to visualize domains in a GUI, in which you can select domain at the right-bottom list and check its profile, each green point on the graph corresponds to a grid in the domain. Once you found the domain you are interested in, close GUI and choose "1 Perform integration for a domain", the real space function (can be selected by option 4, the default one is electron density) will be integrated in the domain, the integral value, domain volume and average/maximum/minimum value of the integrand in the domain are outputted. You can also select "2 Perform integration for all domains" to obtain integral values for all domains. In addition, some regions you are interested in may be identified as separate domains by Multiwfn, to study the property of the regions more conveniently, you can choose "-1 Merge specific domains" to merge selected domains are a single domain, so that you do not need to manually sum up their integral values.

By the way, in the menu there is an option "5 Calculate  $q_{\text{bind}}$  index for a domain", this is used to calculate the  $q_{\text{bind}}$  index defined in *J. Phys. Chem. A*, **115**, 12983 (2011), in which it was demonstrated that for hydrogen-bond dimer, the scan curve of  $q_{\text{bind}}$  index well mimics to actual potential energy curve. This index for a domain is defined as:

### 3 Functions

$$\begin{aligned} q_{\text{att}} &= \int_{\lambda_2(\mathbf{r})<0} \rho^n(\mathbf{r}) d\mathbf{r} && \text{attractive effect} \\ q_{\text{rep}} &= \int_{\lambda_2(\mathbf{r})>0} \rho^n(\mathbf{r}) d\mathbf{r} && \text{repulsive effect} \\ q_{\text{bind}} &= -(q_{\text{att}} - q_{\text{rep}}) \end{aligned}$$

where  $\lambda_2(\mathbf{r})$  is the second largest eigenvalue of electron density Hessian matrix at  $\mathbf{r}$ , its sign can be utilized to discriminate interaction type. Since the paper showed that  $n=4/3$  gives best correlation between  $q_{\text{bind}}$  and actual potential curve, in Multiwfn the  $n$  parameter is chosen as  $4/3$ . Note that the paper used isosurface of RDG=0.6 when calculating this index. More negative of  $q_{\text{bind}}$  may imply more stabilized interaction.

The method used to integrate domains is even-grid integration method. In other words, the integration value of a real space function for a domain is simply the sum of the real space function value of the grids constituting the domain multiplied by grid volume. Therefore, the accuracy of integration result is directly affected by the quality of grid you set.

An illustrative example of present module is given in Section 4.200.14.

**Information needed:** Atom coordinates, GTF information

# 4 Tutorials and Examples

## Prologue and generation of input files

Welcome to use Multiwfn! If you have not read "ALL USERS MUST READ" at page 2 of this manual, please read it first.

Different functions in Multiwfn require different type of input file, see Section 2.5 for explanation. .wfn/.wfx/.fch/.molden/.gms files can be used as input file for most functions of Multiwfn, before getting start I would like to first show you how to generate them. A few functions (e.g. AdNDP analysis) in Multiwfn rely on some special files, the requirements on the input files in these cases are clearly indicated in corresponding section in Chapter 3.

### Generating .wfn and .wfx files

In Gaussian, write *out=wfn* in route section, leave a blank line after molecular coordinate section and write the destination path of .wfn file, e.g. *C:\otoboku\H2O.wfn* (you can consult H2O.gif in "examples" folder), then run this file. If the task terminates normally, H2O.wfn will appear in *C:\otoboku* folder. If you are using Gaussian older than G09 C.01, please carefully read below information:

If the theoretical method is post-HF type, you have to also add "density" keyword in route section to use current density, otherwise what outputted to .wfn file will still be HF orbitals. If you are using TD-DFT or CIS and you want to export natural orbitals corresponding to excited state wavefunction, you also need to specify "density" keyword.

For CCD/CCSD, QCISD or MP2/3, MP4SDQ tasks based on unrestricted HF reference state, only when "pop=NOAB" keyword is also specified then spin natural orbitals rather than space natural orbitals will be saved to the .wfn file. TD, CI and MCSCF tasks of Gaussian can not produce spin natural orbitals.

If the Gaussian you are using is older than G09 B.01, be aware that there is a serious bug, if your task is restricted open-shell (ROHF and RODFT), the occupation numbers of singly occupied orbitals in .wfn file will erroneously be 2.0, you have to open the file by text editor, locate the last entry "OCC NO =", and then manually change the value behind it to 1. 0000000.

In GAMESS-US, add *AIMPAC=.TRUE.* in \$CONTRL section. After the task is finished, the generated .dat file in the folder defined by \$SCR environment variable (see *rungms* script) will contain wavefunction information with the same format as .wfn file, extract the content between "---- TOP OF INPUT FILE FOR BADER'S AIMPAC PROGRAM ----" and "---- END OF INPUT FILE FOR BADER'S AIMPAC PROGRAM ----" and save them to a new file with ".wfn" prefix.

In ORCA, .wfn file can be generated simply using *aim* keyword in the input file, or using the command *orca\_2aim XXX* to convert XXX.gbw to XXX.wfn. However, the .wfn file generated by ORCA are usually non-standard and cannot be properly recognized by Multiwfn. Therefore, using .molden file as input file of Multiwfn instead is highly recommended, see below.

As regards the method of outputting .wfn files in other quantum chemistry packages, please consult corresponding manuals.

If you would like to generate .wfx file in Gaussian09 (since revision B.01), simply write *out=wfx* instead of *out=wfn* in route section.

### Generating .fch file

Some functions of Multiwfn require basis function information, you have to use formatted checkpoint file of Gaussian (.fch) or Molden input file (.molden) as input. Since .fch/molden file contain richer information than .wfn/wfx file, for all of the functions that require .wfn/wfx file as input, you can also use .fch/molden instead. See Section 2.5 for more details.

In Gaussian, you can run command such as *formchk h2o2.chk* to convert binary checkpoint file h2o2.chk to h2o2.fch.

When post-HF task is performed, the orbitals and occupation status recorded in .fch file by default are the HF ones, hence the analysis results are still identical to HF (Similarly, analysis result of TDDFT wavefunction by default will be identical to that of ground state DFT wavefunction). In order to write natural orbitals into .fch file, so that we can analyze post-HF/TDDFT wavefunction, one should first perform post-HF/TDDFT task with “density” keyword, and then rerun the task only with "guess=(save,only,naturalorbitals) chkbasis" in route section. Note that Gaussian fills orbital occupation numbers into orbital energy field in .fch file, hence you have to write “*saveNO*” in the first line of .fch file to let Multiwfn know this behavior. Beware that if what you performed is open-shell post-HF calculation, even above process is unable to correctly store natural spin orbitals into .fch file. Generally, I strongly recommend using .wfn file to view natural orbitals and analyze real space functions for post-HF wavefunctions.

Note: There is no any difference between .fch and .fchk formats. The former and the latter are the default extensions of formatted checkpoint file of Windows and Linux version of Gaussian, respectively. You can use either of them as input file of Multiwfn.

### Generating .molden file

In ORCA, use the command *orca\_2mkl XX -molden* to convert XX.gbw to Molden input file.

In Molpro, write such as *put,molden,ltd.molden* at the last line of your input file, the Molden input file ltd.molden will be produced.

Regarding the method of outputting Molden input files in other quantum chemistry packages, please consult corresponding manuals.

When pseudo-potential is used and you need to do some analyses relating to nuclear charges, do not forget to manually change atomic indices in the .molden file as nuclear charges, see Section 2.5 for details.

Note: Currently, only the Molden input file generated by Molpro, ORCA, deMon2k and BDF program are formally supported. If the file is generated by other programs, the result may or may not be correct, because the files produced by numerous programs are non-standard or problematic. Fortunately, molden2aim utility is able to deal with the Molden input files produced by wider scope of programs and can output standardized Molden input files, which is then able to be used as Multiwfn input file. See Section 5.1 for detail.

### Generating .gms file

GAMESS-US output file can also be used as Multiwfn input file, you need to change its suffix as .gms so that Multiwfn can recognize it. Currently, I can only guarantee that output file of HF/DFT calculation with default NPRINT option can be normally loaded by Multiwfn. A sample of input and output files of GAMESS-US are provided as GAMESS\_US.inp and UKS\_cc-pVDZ.gms in examples folder, respectively.

Now let's start! Note that the examples in 4.x section are relevant to main function *x*, therefore you can quickly find the examples you needed. Section 4.A includes special topics and advanced tutorials, in which more than one functions and some advanced skills may be involved,

such as studying aromaticity and weak interactions. You can find almost all of the files involved in these examples in “examples” folder. All the texts behind // are comments and should not be inputted as command. Tutorials in this chapter only cover basic applications of Multiwfn, if you want to learn the usage of more functions and more options, please read corresponding sections in Chapter 3 and play with the options that not mentioned in the examples.

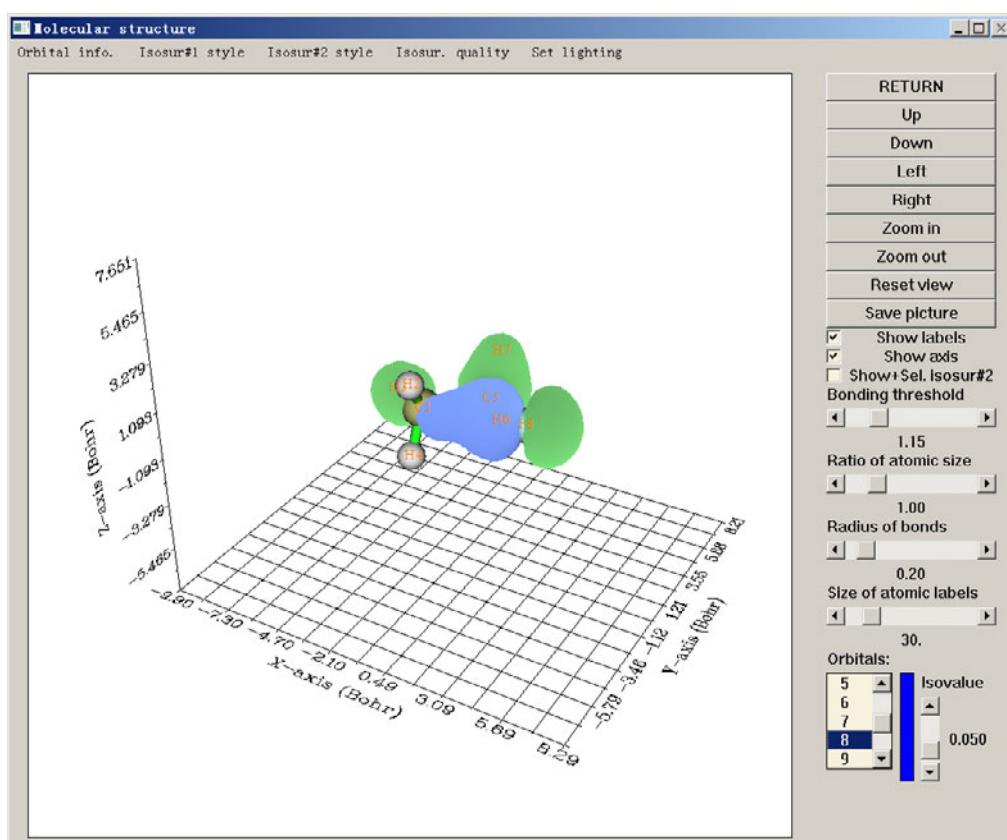
PS: If you can read Chinese, reading these two articles is highly helpful: "Tips for getting start with Multiwfn" (<http://sobereva.com/167>), "The significance, functions and uses of multifunctional wavefunction analysis program Multiwfn" (<http://sobereva.com/184>).

## 4.0 View orbitals and structure

In Multiwfn, you can use main function 5 to generate cube file of an orbital wavefunction, or you can use subfunction 3 in main function 200 to generate single or multiple cube files for a batch of orbitals, then you can load them to your favourite visualization programs (e.g. VMD) to visualize corresponding orbitals. However, the simplest way to view orbitals is using main function 0 of Multiwfn, as described below.

### 4.0.1 Viewing molecular orbitals of monofluoroethane

First, run a single point task for monofluoroethane to get its wavefunction file, which has already been provided as *examples\C2H5F.wfn*. Boot up Multiwfn, input this path, then select main function 0, a GUI window will pop up, meanwhile all atom coordinates are printed on Multiwfn console window.



You can rotate molecule, zoom in/out, adjust bonding threshold, save graph and so on via corresponding widgets. The numbers in right-bottom list are orbital indices, you can view orbital isosurface by selecting corresponding number, green and blue isosurfaces correspond to positive and negative regions, respectively. The isovalue can be adjusted by dragging slide bar. Isosurface style and colors and be altered by corresponding suboptions in "Isosur#1 style". The quality of the isosurface can be set by the option in "Isosur. quality", the isosurface will be finer/coarser if you input a larger/smaller value than default. See Section 3.2 for detail. In Section 4.0.2, you will learn how to plot two orbitals simultaneously in this window. By selecting "Orbital info." - "Show all", energy, occupation number and type of all orbitals will be shown in Multiwfn console window. If you do not want too many high-lying virtual MOs are shown, you can choose "Show up to LUMO+10". If irreducible representations are recorded in the loaded .molden/.gms file, then they will be shown as the last column.

The color of bonds, atomic labels and atom spheres can be set by parameters "bondRGB", "atmlabRGB" and "atmcolorfile" in settings.ini, respectively. See corresponding comments for detail. After adjusting these parameters, you need to reboot Multiwfn to make them take effect.

To close the window, click "RETURN" button.

Note: Visualizing isosurface of Rydberg orbitals by main function 0 of Multiwfn is also possible, however, since they show very diffuse character, in order to avoid truncating of isosurfaces, you should enlarge "aug3D" in settings.ini. An example of visualizing Rydberg orbitals is given in Part 2 of Section 4.200.5.

## 4.0.2 Viewing natural bond orbitals (NBO) of ethanol

There are two ways to view NBOs, if you are a Gaussian user, way 2 may be more convenient, however if you also need to view natural hybrid orbital (NHO) or natural atomic orbital (NAO) or some other types of orbitals generated by NBO program, you have to use way 1.

### Way 1: Use NBO plot files

The common way is to generate NBO plot files (.31~.40) and load them into Multiwfn. To generate these files by Gaussian, you should add "pop=nboread" in route section, that means the keywords of NBO at the end of input file will be passed to NBO module (Link 607 in Gaussian), then add e.g. "\$NBO plot file=c:\NH2COH \$END" at the end of the input file (leave a blank line before), you can refer to NH2COH\_NBO.gjf in "example" directory. Run the input file by Gaussian, you will find NH2COH.31, NH2COH.32 ... NH2COH.41 are generated in c:\. Now boot up Multiwfn and input following commands

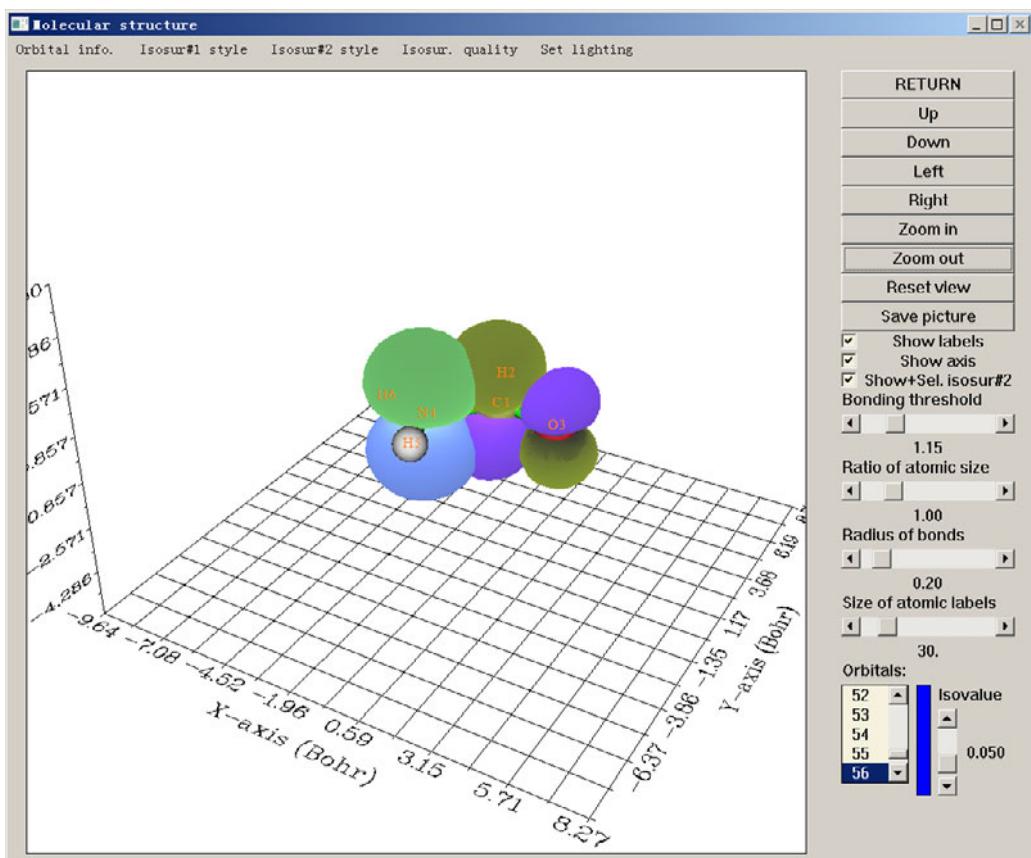
c:\NH2COH.31 // .31 file contains necessary basis function information for plotting

c:\NH2COH.37 // .37 file contains NBO information. .32~.40 files correspond to PNAO/NAO/PNHO/NHO/PNBO/NBO/PNLMO/NLMO/MO respectively. **Hint:** You can only input .37, because in present example the .37 and the .31 file share the same name

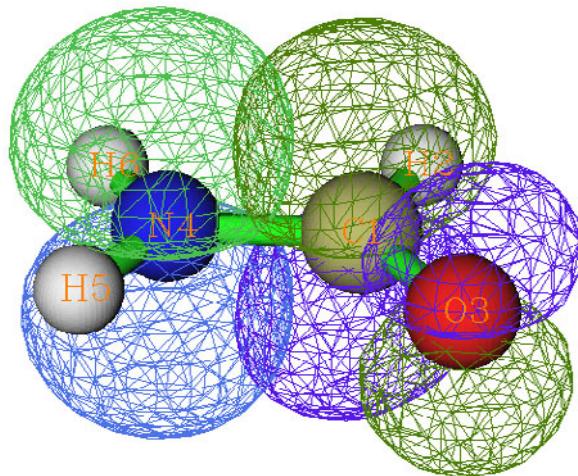
0 // Enter the GUI

You can choose corresponding NBO orbital from right-bottom list to view the isosurface. Multiwfn is also capable to plot two orbitals simultaneously, for instance, here we will plot NBO 12 and NBO 56, which correspond to occupied lone pair of nitrogen atom and unoccupied anti- $\pi$  bond between carbon and oxygen atoms respectively. Firstly, we choose 12 from the orbital list to plot NBO 12, and then click "Show+Sel. isosur#2", after that we click 56 in the list, you will see both of NBO 12 and NBO 56 are shown. The yellow-green and purple parts of NBO 56

(isosurface#2) correspond to positive and negative parts, respectively.



It is somewhat difficult to study overlapping extent between the two orbitals from the solid face graph, so we choose "Use mesh" in "Isosur#1 style" and the counterpart in "Isosur#2 style" to make the two isosurfaces represented as mesh, see below. (Please also try "transparent face" style) Now the overlapping extent become distinct, it is quite clear that NBO 12 substantially overlapped with NBO 56, the resulting strong delocalization is one of the main reasons why the second-order perturbation energy between them is very large (~60kcal/mol). In Section 4.4.5, you will learn how to obtain contour map for the two orbitals.



Notice that for unrestricted calculations, .32 and .33 files outputted by NBO 3.1 module in Gaussian are incorrect -- the title parts are missing, which will lead to strange result, you should fix them by imitating other plot files such as .34, it is very easy.

As regards the ways to pass the keywords for generating plot files to NBO module in other quantum chemistry packages, please consult corresponding manual. You can also use stand-alone version of NBO program (GENNBO) to generate plot files, an input file (.47) is needed to be prepared first. In Gaussian, run a single point task with “\$NBO archive file=C:\NH2COH \$end” at the end of input file, then add “plot file=C:\NH2COH” between “\$NBO” and “\$END” in the resultant ethanol.47, after that feed this file into GENNBO you will get the NBO plot files.

### Way 2: Use .fch as NBO/NLMO information carrier

Gaussian provides keywords “pop=saveNBO” and “pop=saveNLMO”, if you specified one of them in your input file, NBOs or NLMOs will be saved to checkpoint file instead of MOs when the task is finished. You can use corresponding .fch file as Multiwfn input file to view NBOs or NLMOs. If theoretical level of the task is HF or DFT, you should add “saveNBOene” in the first line of .fch file; if post-HF is used and “density” keyword is also specified, you should add “saveNBOocc” in the first line of .fch file, Multiwfn will do some special treatments internally, however, if your aim is just viewing NBOs and NLMOs in function 0, you can ignore this step.

Beware that when Gaussian storing the NBOs/NLMOs to checkpoint file, they may be automatically reordered. For example, you may see the information like below in the Gaussian output file:

```
Reordering of NBOs for storage:    7   8   3   1   2   4   6   5   9   38 ...
```

That means the 1st, 2nd, 3rd, 4th ... orbitals in the .chk/.fch file correspond to the 7th, 8th, 3rd, 1st ... NBOs generated by the NBO module, respectively.

## 4.1 Calculate properties at a point

### 4.1.1 Show all properties of triplet water at a given point

In this example we calculate a wide variety of real space functions at a given point for triplet water. Boot up Multiwfn and input below commands

```
examples\h2o-m3ub3lyp.wfn
1 // Function 1, show properties at a point
0.2,2.1,2 // X, Y, Z coordinate of the point
1 // The unit of inputted coordinate is Bohr
```

Now all real space functions supported by Multiwfn at this point are printed along with components of electron density gradient/Laplacian, Hessian matrix and its eigenvalues/eigenvectors:

```
Density of all electrons: 0.4598301528E-02
Density of Alpha electrons: 0.2861566387E-02
Density of Beta electrons: 0.1736735141E-02
Spin density of electrons: 0.1124831246E-02
Lagrangian kinetic energy G(r): 0.3365319167E-02
```

## 4 Tutorials and Examples

Hamil tonian kinetic energy K(r): 0.1088761528E-03  
Potential energy density V(r): -0.3474195320E-02  
Energy density: -0.1088761528E-03  
Laplacian of electron density: 0.1302577206E-01  
Electron localization function (ELF): 0.1998328717E+00  
Localized orbital locator (LOL): 0.1008002781E+00  
Local information entropy: 0.3533635333E-02  
Reduced density gradient (RDG): 0.2033111359E+01  
Reduced density gradient with promolecular approximation: 0.2294831921E+01  
Sign(lambda2)\*rho: -0.4598301528E-02  
Sign(lambda2)\*rho with promolecular approximation: -0.3918852312E-02  
Corr. hole for alpha, ref.: 0.00000 0.00000 0.00000 : -0.1251859403E-03  
Source function, ref.: 0.00000 0.00000 0.00000 : -0.3565867942E-03  
Wavefunction value for orbital 1: 0.1536978161E-03  
Average local ionization energy: 0.4664637535E+00  
User defined real space function: 0.1000000000E+01  
ESP from nuclear charges: 0.3453377860E+01  
ESP from electrons: -0.3439063818E+01  
Total ESP: 0.1431404144E-01 a.u. ( 0.3895049E+00 J/C, 0.8981488E+01 kcal/mol )

Note: Below information are for electron density

Components of gradient in x/y/z are:

-0.7919856828E-03 -0.6903543769E-02 -0.6651181972E-02

Norm of gradient is: 0.9618959378E-02

Components of Laplacian in x/y/z are:

-0.3809549089E-02 0.1052804857E-01 0.6307272576E-02

Total: 0.1302577206E-01

Hessian matrix:

-0.3809549089E-02 0.1394394193E-02 0.1197923973E-02

0.1394394193E-02 0.1052804857E-01 0.1008387143E-01

0.1197923973E-02 0.1008387143E-01 0.6307272576E-02

Eigenvalues of Hessian: -0.3959672207E-02 0.1886890004E-01 -0.1883455778E-02

Eigenvectors(columns) of Hessian:

0.9964397434E+00 0.8076452238E-01 0.2418531975E-01

-0.4735415689E-01 0.7734993430E+00 -0.6320255930E+00

-0.6975257409E-01 0.6286301443E+00 0.7745700228E+00

Determinant of Hessian: 0.1407217564D-06

Ellipticity of electron density: 1.102344

All data are expressed in scientific notation, the value behind E is exponent, e.g. 0.6307272576E-02 corresponds to 0.006307272576.

In the line of Corr. hole (correlation hole) and source function, the so-called "ref" is the position of reference point, which is determined by "refxyz" in settings.ini.

By default the wavefunction value outputted is for orbital 1, you can input such as "o6" to choose orbital 6.

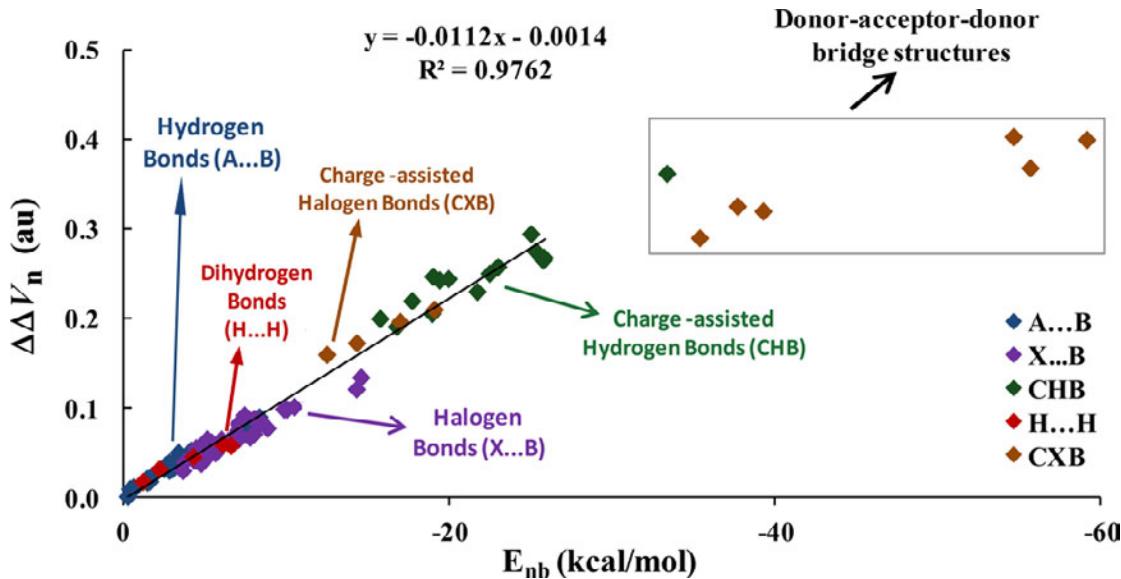
By default, the components of gradient and Laplacian as well as Hessian and its eigenvalue/eigenvectors are for electron density. You can input such as *f10* to choose the real space function with index of 10 (namely ELF), after that all these quantities will be for ELF. If you want to inquire indices of all real space functions, input *allf*.

You can continue to input other coordinates, when you want to return to upper level menu, input "q"; If you want to exit the program, press "CTRL+C" or close command-line window.

#### 4.1.2 Calculate ESP at nuclear positions to evaluate interaction strength of $\text{H}_2\text{O}\cdots\text{HF}$

This is an advanced example, if you are not interested in weak interactions you may skip this section.

In *J. Phys. Chem. A*, **118**, 1697 (2014), Mohan and Suresh studied a batch of electrostatic dominated interacting systems, including hydrogen, halogen and dihydrogen bonds, all of them belong to electron donor-acceptor interactions, where donor stands for electron-rich moiety (Lewis base), while acceptor is electron-deficient moiety (Lewis acid). They fitted a surprisingly good linear equation to correlate  $\Delta\Delta V_n$  index with interaction energy ( $E_{nb}$ ) for all kinds of interactions, the  $R^2$  is as high as 0.9762. Their results can be summarized as following graph



For an electrostatic dominated complex, assume that we can obtain  $\Delta\Delta V_n$ , then according to the equation shown in above graph, we can easily predict the interaction energies as

$$E_{nb} = -89.2857 \times \Delta\Delta V_n - 0.125$$

The  $\Delta\Delta V_n$  is defined based on ESP at nuclear positions

## 4 Tutorials and Examples

$$\Delta\Delta V_n = \Delta V_{n-D} - \Delta V_{n-A} = (V_{n-D'} - V_{n-D}) - (V_{n-A'} - V_{n-A})$$

where  $V_{n-D'}$  is the ESP at nuclear position of donor atom in complex environment, but the contribution due to nucleus of this donor atom is ignored. The only difference between  $V_{n-D}$  and  $V_{n-D'}$  is that the former is calculated in monomer state, therefore  $\Delta V_{n-D} = V_{n-D'} - V_{n-D}$  can be regarded as the change in ESP at nuclear position of donor atom due to presence of another molecule, which directly reflects strength of intermolecular interaction. The definition of  $V_{n-A'}$  and  $V_{n-A}$  are identical to  $V_{n-D'}$  and  $V_{n-D}$ , respectively, but they are calculated for acceptor atom.

In this example, we calculate  $\Delta\Delta V_n$  for  $H_2O\cdots HF$  and check if the interaction energy predicted based on  $\Delta\Delta V_n$  is really closed to the accurately calculated interaction energy. In this complex the oxygen of  $H_2O$  is electron donor atom and hydrogen of HF is electron acceptor atom. Because the equation presented by Mohan and Suresh was fitted for specific calculation level, in order to properly use their equation, the calculation level we employed here is identical to them. The .wfn files used below were produced at MP4(SDQ)/aug-cc-pVTZ level at MP2/6-311++G\*\* optimized geometries, these .wfn files and the corresponding Gaussian input files can be found in "examples\Vn" folder.

Note that because we employed post-HF method, "density" keyword is indispensable, otherwise the density in the resultant .wfn file may be Hartree-Fock density. Besides, in Gaussian09, the density cannot be produced at MP4 level, so we use MP4(SDQ) keyword instead (MP4 keyword is default to MP4(SDTQ), which is more accurate and but much expensive than MP4(SDQ)).

First we calculate  $V_{n-A'}$  and  $V_{n-D'}$ . Set "iuserfunc" parameter in settings.ini to 39 to enable the 39th user-defined function, which is used to calculate ESP without contribution of a specific nucleus (see Section 2.7 for more details), then boot up Multiwfn and input

*examples\Vn\H2O-HF.wfn*

1000 // A hidden interface

3 // Set which nucleus will be ignored in the calculation of ESP

1 // Oxygen is atom 1

1 // Calculate properties at a point

a1 // Nuclear position of atom 1

From the output you can see

User defined real space function: -0.2228775074E+02

That means  $V_{n-D'}$  is **-22.2877 a.u.** Then input

q // Return to main menu

1000

3

5 // Hydrogen of HF is atom 5

1

a5

You can find  $V_{n-A'}$  is **-0.9608 a.u.**

Next we calculate  $V_{n-D}$ . Reboot up Multiwfn and input below commands

*examples\Vn\H2O.wfn*

1000

3

1 // In H2O.wfn oxygen is atom 1

1

a1

We find  $V_{n-D}$  is -22.3339 a.u. Then we calculate  $V_{n-A}$ . Reboot Multiwfn and input  
`examples\Vn\HF.wfn`

```
1000
3
2 // In HF.wfn hydrogen is atom 2
1
a2
```

The  $V_{n-A}$  is -0.9136 a.u.

The  $\Delta\Delta V_n$  is thus  $-22.2877 - (-22.3339) - [-0.9608 - (-0.9136)] = 0.0462 + 0.0472 = 0.0933$  a.u.

Using the equation mentioned earlier, the interaction energy can be approximately predicted as  $-89.2857 * 0.0933 - 0.125 = -8.45$  kcal/mol, this value is quite close to the accurate interaction energies (-8.31 kcal/mol) obtained by Mohan and Suresh at MP4/aug-cc-pVTZ level with Counterpoise correction.

Generating wavefunction at MP4(SDQ)/aug-cc-pVTZ is quite time consuming even for small complex such as the system we studied here, thus it is important to find a calculation level that significantly saves computational time but without too much sacrifice in accuracy. For present system, based on the MP2/6-311++G\*\* geometry, I tried using several levels to evaluate the  $\Delta\Delta V_n$ :

- B3LYP/6-311+G\*\*: 0.1021 a.u.
- MP2/cc-pVTZ: 0.1052 a.u.
- MP2/aug-cc-pVTZ: 0.0955 a.u.
- B3LYP/aug-cc-pVTZ: 0.0985 a.u.
- MP2/aug-cc-pVDZ: 0.0939 a.u.
- B3LYP/aug-cc-pVDZ: 0.0980 a.u.

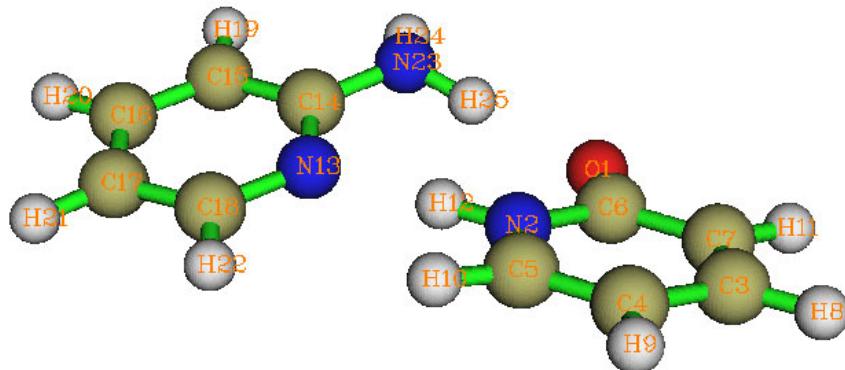
The  $\Delta\Delta V_n$  produced at MP2/aug-cc-pVDZ (0.0939) is very close to the value we obtained above at MP4(SDQ)/aug-cc-pVTZ (0.0933), while the computational cost is reduced by factors of two. So, in practical studies, using MP2/aug-cc-pVDZ level to evaluate  $\Delta\Delta V_n$  is a very ideal choice.

## 4.2 Topology analysis

Multiwfn is able to perform topology analysis for various kinds of real space functions, such as electron density, its Laplacian function, ELF, LOL, orbital wavefunctions, as well as user-defined functions. Four kinds of critical points (CPs) can be located and real space function values at these points can be easily obtained; topology paths linking CPs and interbasin surfaces can be generated. There are also many additional capacities, see Section 3.14 for details. Below I will present some practical applications to illustrate how to use this powerful module.

### 4.2.1 Atoms in molecules (AIM) and aromaticity analysis for 2-pyridoxine 2-aminopyridine

Topology analysis of electron density is a main ingredient of Bader's atoms in molecules (AIM) theory. In this example we will perform this kind of analysis for 2-pyridoxine 2-aminopyridine complex.



Boot up Multiwfn and input following commands

*examples\2-pyridoxine\_2-aminopyridine.wfn* // Assume that the input file is in a subdirectory of current directory, we can only input relative path rather than entire absolute path

## 2 // Topology analysis

Then we search all critical points (CPs) by inputting:

2 // Use nuclear positions as initial guesses, generally used to search (3,-3) CPs

3 // Use midpoint of each atom pair in turn as initial guesses, generally all (3,-1) CPs could be found, some (3,+1) or (3,+3) may be found at the same time

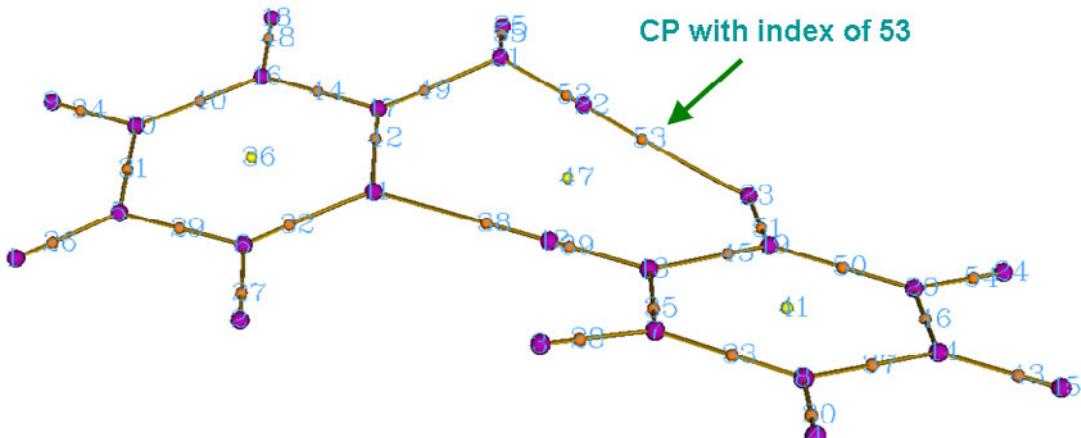
The search of CPs is very fast. After that input 0, the positions and types of all found CPs will be printed in the command-line window, at the end of the output the number of each type of CPs is shown:

$$(3, -3): \quad 25, \quad (3, -1): \quad 27, \quad (3, +1): \quad 3, \quad (3, +3): \quad 0$$

$$25 - 27 + 3 - 0 = 1$$

These two lines show that Poincaré-Hopf relationship is satisfied, that means all CPs may have been found. If this relationship is unsatisfied, then some CPs must be missing. From the GUI that popped up, we can see all expected CPs are presented, hence we can confirm that all CPs have been found.

Click "RETURN" button in the GUI window and input 8 to generate bond paths, select function 0 again to view CPs and paths, after slightly adjust of plot settings, the graph looks like below (Click "CP labels" at the right side of the GUI if index of the CPs are not shown):



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Magenta, orange and yellow spheres correspond to (3,-3), (3,-1) and (3,+1) critical points, brown lines denote bond paths. The indices of CPs are labelled by cyan numbers. It can be seen that index 53 and 38 corresponds to the bond critical point (BCP) of N-H---O and N-H---N hydrogen bond, respectively.

Now close the GUI window. As an exercise, let's measure the distance between CP30 and the nucleus of H25. Select option -9, and input *c30 a25*, the result is 1.268379 Bohr. Then we measure the angle between C14-N13-H12, namely input *a14 a13 a12*, the result is 120.297432 degree. Now, we input *q* to return.

In *Chem. Phys. Lett.*, **285**, 170, the authors stated that for the hydrogen bond [X-H---O (X=C,N,O)], the relationship between bond energy  $E_{\text{HB}}$  and potential energy density  $V(\mathbf{r})$  at corresponding BCP can be approximately described as

$$E_{\text{HB}} = V(\mathbf{r}_{\text{bcp}})/2$$

Let's evaluate the energy of N-H---O hydrogen bond in our system by this formula. Choose function 7 and then input the index of corresponding BCP, namely 53, you will see value of all real space functions at this point

CP Position: 0.44887255865472 3.56434324597741 -0.10652884364257

CP type: (3, -1)

Density of all electrons: 0.3129478049E-01

Density of Alpha electrons: 0.1564739024E-01

Density of Beta electrons: 0.1564739024E-01

Spin density of electrons: 0.0000000000E+00

Lagrangian kinetic energy G(r): 0.2530207716E-01

Hamiltonian kinetic energy K(r): 0.8463666362E-03

Potential energy density V(r): -0.2614844379E-01

Energy density: -0.8463666362E-03

Laplacian of electron density: 0.9782284209E-01

Electron localization function (ELF): 0.1105388527E+00

... (Ignored)

The output indicates that the  $V(\mathbf{r})$  at this BCP is -0.026148, therefore the hydrogen bond energy could be evaluated as  $E_{\text{HB}} = -0.026148/2 \times 2625.5 = -34.3 \text{ KJ/mol}$ .

Here we use information entropy method to examine if the aminopyridine (the monomer at the left side of above graph) in the dimer can be regarded as an aromatic molecule. This method was proposed in *Phys. Chem. Chem. Phys.*, **12**, 4742 and is based on electron density at BCPs of a ring, see Section 3.14.6 for detail. First, we select option 20, and then input indices of the BCPs in the ring, namely 44,42,32,29,31,40, the outputted Shannon aromaticity index (SA) is 0.000812. The smaller the SA index, the more aromatic is the ring. In origin paper,  $0.003 < \text{SA} < 0.005$  is chosen as the boundary of aromaticity/antiaromaticity. Since our result is much smaller than 0.003, we can conclude that aminopyridine is an aromatic molecule. The SA for 2-pyridoxine (the monomer at the right side of above graph) is 0.000865, hence shows slightly weaker aromaticity than aminopyridine.

Next, we calculate the curvature of electron density perpendicular to ring plane at RCP. In

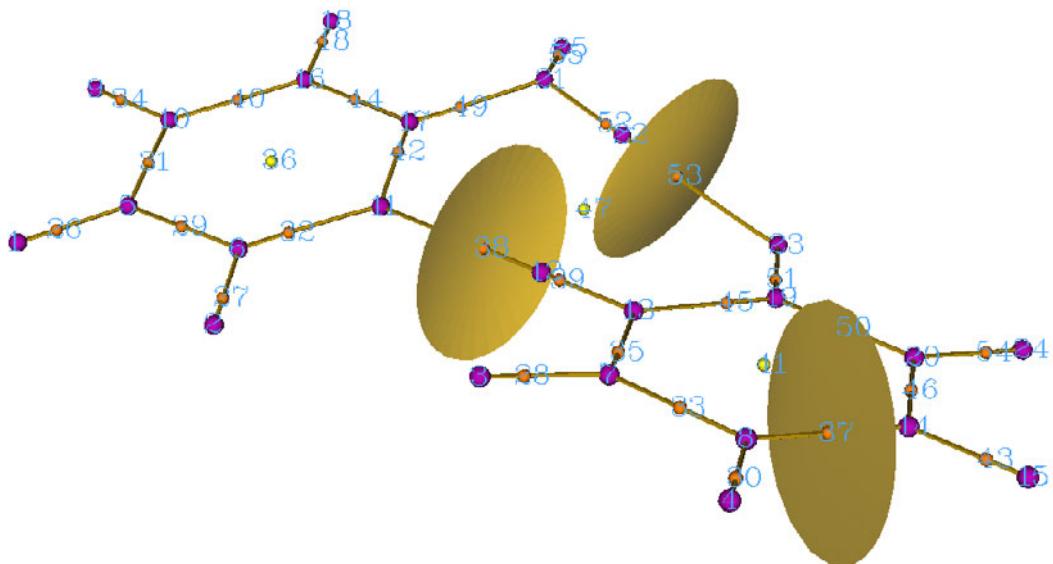
*Can. J. Chem.*, **75**, 1174, it was shown that more negative curvature implies stronger aromaticity. We first calculate the curvature for aminopyridine. Select option 21, input the index of the RCP (namely 36), and then input three atoms to define the ring plane, here we input 15,13,17 (also, you can input such as 14,16,18 and 13,15,18, because all of them correspond to the same plane). From the output we find the curvature is -0.0187. Then we calculate the curvature for 2-pyridoxine, namely input 41 and 2,7,4, the result is -0.0164. Comparison between the two curvatures again shows that aminopyridine has stronger aromaticity. In Multiwfn, aromaticity can also be measured in many other schemes, such as HOMA, FLU, PDI, ELF- $\pi$  and multicenter bond order, they are collectively discussed in Section 4.A.3.

Interbasin surfaces (IBS) dissect the whole molecular space into individual basins, each IBS actually is a bunch of gradient paths derived from a (3,-1) CP. Now we generate IBS corresponding to the (3,-1) with index of 53, 38 and 37. Choose function 10, and input

53 // Generate the IBS corresponding to the (3,-1) CP with index of 33, the same as below.  
You may need to wait a few seconds for each generation of IBS

```
38
37
q // Return
```

Visualize the results by choose function 0, the graph will be shown as below. The three surfaces are IBS.



There are two important points regarding AIM topology analysis I would like to mention here, though they are not related to present example.

#### Tip 1: What should I do if some CPs of electron density are missing?

For small systems, commonly we can check whether all CPs have been located by simply enter the GUI and visualize the distributions of the CPs. There is also an useful equation named Poincaré-Hopf relationship. For isolate system, the relationship is

$$n_{\text{NCP}} - n_{\text{BCP}} + n_{\text{RCP}} - n_{\text{CCP}} = 1$$

If all CPs have been found, this relationship must be satisfied, but the satisfaction of this relationship does not necessarily mean all CPs have been found. If the Poincaré-Hopf relationship is unsatisfied, then some CPs must be missing.

Sometimes, you may find some expected CPs are not successfully located after searches. There are two reasons may cause this problem: (1) The position of initial guesses are not close enough to the CPs (2) The default CP searching parameters are not well-suited for present case. There are some commonly used ways to solve this problem. More detailed descriptions may be found in Section 3.14.2.

a) If you have tried options 2~5 and some CPs are not located, try to use suboption -1 of option 6. This searching mode is powerful but expensive, which by default places 1000 guessing points within in a spherical region around every atom. If after repeating this mode several times the missing CPs are still unable to be located, it is highly possible that the reason is due to the inappropriate searching parameters rather than the positions of guessing points.

b) If some BCPs are unable to be located, you can enter option -1, set the scale factor of stepsize to 0.5, and then try again

c) NCPs of very heavy atoms are difficult to be located, because the peak of electron density at nucleus in these cases are very sharp, thus under default parameters the searching algorithm is difficult to capture the NCPs. In order to locate them, you can enter option -1, loose the criteria for gradient-norm and displacement convergences by several factors, and then try to use option to 2 search the NCPs again. If the NCPs are then successfully found, do not forget to recover the convergence criteria. In fact, since NCP of heavy atoms are almost exactly located at nuelcus position, you can directly enter option -4 and choose suboption 3 to add NCPs artificially at the corresponding nuclear positions.

d) If some missing CPs are far away from atoms, for example, the CCP at the center of a very large cage or tube system, try to enter option -1 and decrease the criterion for determining singularity of Hessian matrix via option 8 by several factor, and then search the CPs again.

### **Tip 2: Describing electron density of very heavy atoms**

Very heavy atoms (heavier than Kr) bring much more computational burden than light atoms, and relativistic effect is non-neglectable. There are several different ways to describe them.

(1) Using pseudo-potential (PS): If you decide to use PS, you **must** use small core PS! If large core PS is used, the electron structure in valence regions will be far from truth, and thus the positions and properties of related CPs will be highly artificial. Small core PS means at least sub-valence electrons are explicitly taken into consideration. Commonly used PS are listed below, note that for main group elements only cc-pVnZ-PP series are small core.

	Lanl1	Lanl2, Lan2TZ/08	SDD	cc-pVnZ-PP	SBKJC
Main groups	Large	Large	Large	Small	Large
Transition metals	Large	Small	L/S (optional)	Small	Small

Since when PS is used the inner-core electron density is missing, evidently it is impossible to find out (3,-3) CP at nuclear position, and accordingly, the bond paths emitted from BCP will be unable to connect to the nucleus. Instead, you may find (3,+3) at nucleus position due to the vacancy of inner-core density, and a lot of CPs in different types will occur around the nucleus, this is because the electron density no longer decreases exponentially from nucleus, so the topology structure of electron density becomes quite complicated. However, you can simply

ignore those irrelevant CPs but only focus on the BCPs that you are really interested in.

(2) Using pseudo-potential but with EDF (electron density functions) information supplied: As mentioned in Section 2.5, if PS is employed but the .wfx file produced by Gaussian is used as input file, the EDF field in the .wfx file will be loaded into Multiwfn, which represents the inner-core electron density. In this case, all CPs of electron density can be properly located and artificial CPs will never occur, the bond paths emitting from BCPs can connect to NCPs normally, all CP properties that solely based on electron density will be reasonable. Although large core PS can be employed without problems in this situation, I still recommend using small core PS, because the accuracy of resultant CP positions and properties must be better than using large core PS. Note that currently only the .wfx produced by Gaussian contains EDF field, which does not exist in the .wfx file produced by other programs such as Firefly.

For other type of input files, such as .wfn, .fch, .molden and .gms, by default Multiwfn automatically loads proper EDF information from built-in EDF library. Alternatively, you can let Multiwfn to load EDF information from atomic .wfx file produced by Gaussian. The behavior to load EDF information can be changed by "isupplyEDF" parameter in settings.ini, please check Appendix 4 for details

(3) Using all-electron basis-set with relativistic Hamiltonian: Clearly, this is the perfect solution for representing electron structure of heavy atoms, but the most expensive. In this case, the position and all properties of CPs are the most accurate. The lowest level of consideration of relativistic effect, namely scalar relativistic, is totally enough. DKH2 Hamiltonian is a very good choice (in Gaussian, simply using "int=DKH2" to employ it, beware that basis set optimized for DKH calculation must be used in combination, e.g. cc-pVDZ-DK).

For more discussions, please consult my post "Some explanation of performing wavefunction analysis under pseudo-potentials" (in Chineses, <http://sobereva.com/156>)

#### 4.2.2 LOL topology analysis for acetic acid

A brief of localized orbital locator (LOL) has been given in Section 2.6, and its graphical interpretation will be illustrated in later examples. In this example, we will locate CPs and generate topology paths of LOL for acetic acid.

Boot up Multiwfn and input following commands

```
examples\acetic_acid.wfn
2 // Enter topology analysis module
-11 // Select real space function
10 // Localized orbital locator (LOL)
```

Notice that the surfaces of LOL is much more complex than electron density, so it is very difficult to locate all CPs. Fortunately, in general only a small subset of CPs is what we are interested in, the search of CPs can be terminated once all expected CPs have been found.

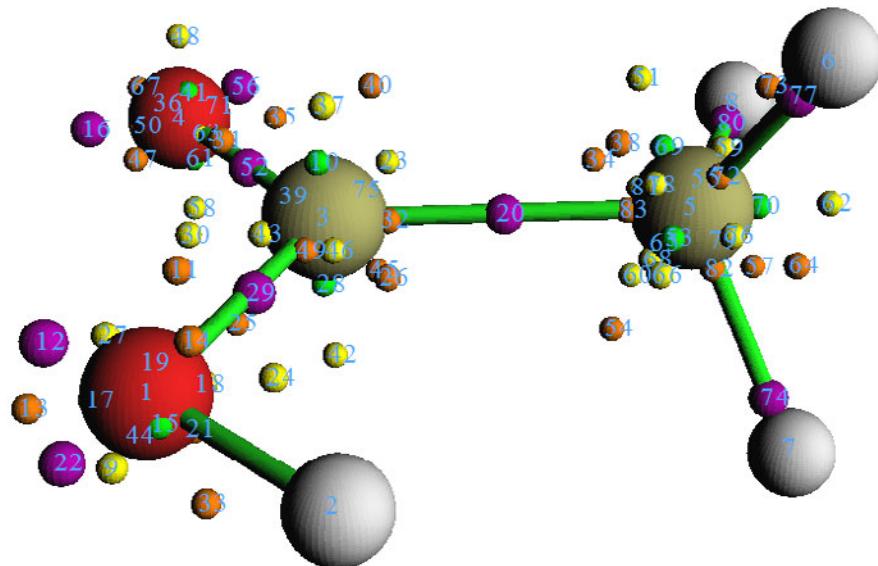
We first use option "2 Search CPs from nuclear positions" to locate the CPs that very close to nuclei. However the positions of CPs in other regions are somewhat unpredictable, hence a lot of initial guess points have to be randomly scattered around each atom to try to locate those CPs.

6 // In this searching mode, initial guessing points will randomly scattered in a sphere, the sphere center, radius, number of points and so on can be defined by users, this time we leave the default value unchanged

-1 // Use each nucleus as sphere center in turn to search CPs. Since there are 8 atoms, and guessing points in each sphere is 1000, Multiwfn will try to search CPs from 8\*1000 guessing points. Of course, the more the guessing points you set, the larger probability all CPs could be found in this search

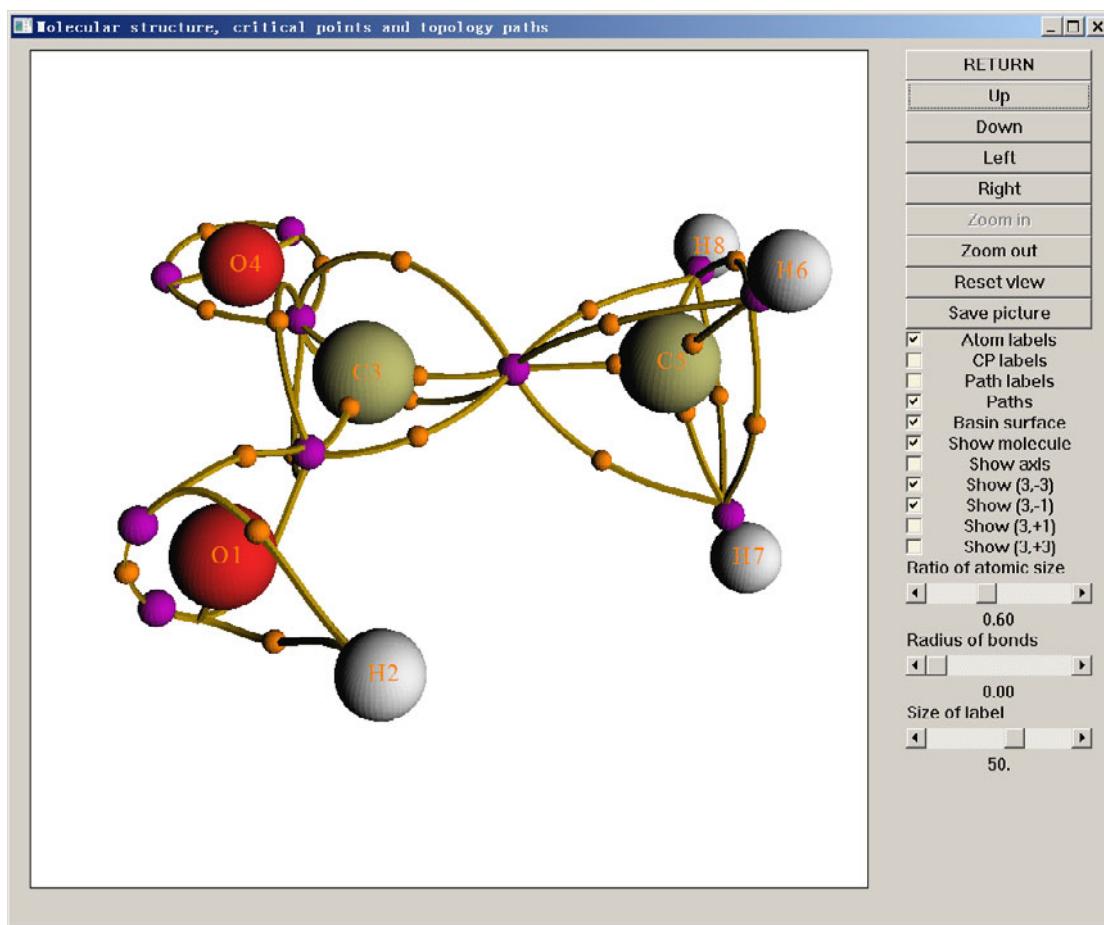
-9 // Return to upper menu

0 // Visualize the searching result



It is clear that the number of CPs in LOL function space is very large. Actually there are still some CPs were not been found in the search, if you repeat the search one time or several times, some missing CPs could be found. Since all interesting CPs have been found, repeat the search is unnecessary. From the graph, it can be seen that the three (3,-3) type CP, namely CP20, 29 and 52 correspond to the locally maximal electron localization in covalent bond regions. Note that the three CPs very close to hydrogens have no strong physical meaning, in my own viewpoint they are the consequence of failure of definition of LOL. CP12, 22, 16 and 56 correspond to lone pairs of oxygens.

Now choose option 8 to generate the topology paths linking (3,-1) and (3,-3) CPs, then choose option 0 to visualize the result again. The paths clarify the intrinsic relationship between CPs. You may find there are too many objects in the graph and they confused you visually. To relieve your visual burden, some uninteresting object can be screened by properly adjusting GUI widgets, as shown below.



With completely identical procedure shown in this example, you can also analyze topology structure for electron localization function (ELF) as well as Laplacian of electron density.

#### 4.2.3 Plot electron density ellipticity along bond path

In this example we plot ellipticity of electron density along bond path of boundary C-C bond of butadiene.

First open settings.ini file and change "iuserfunc" parameter to 30, because the 30th user-defined function corresponds to electron density ellipticity, see Section 2.7 for detail.

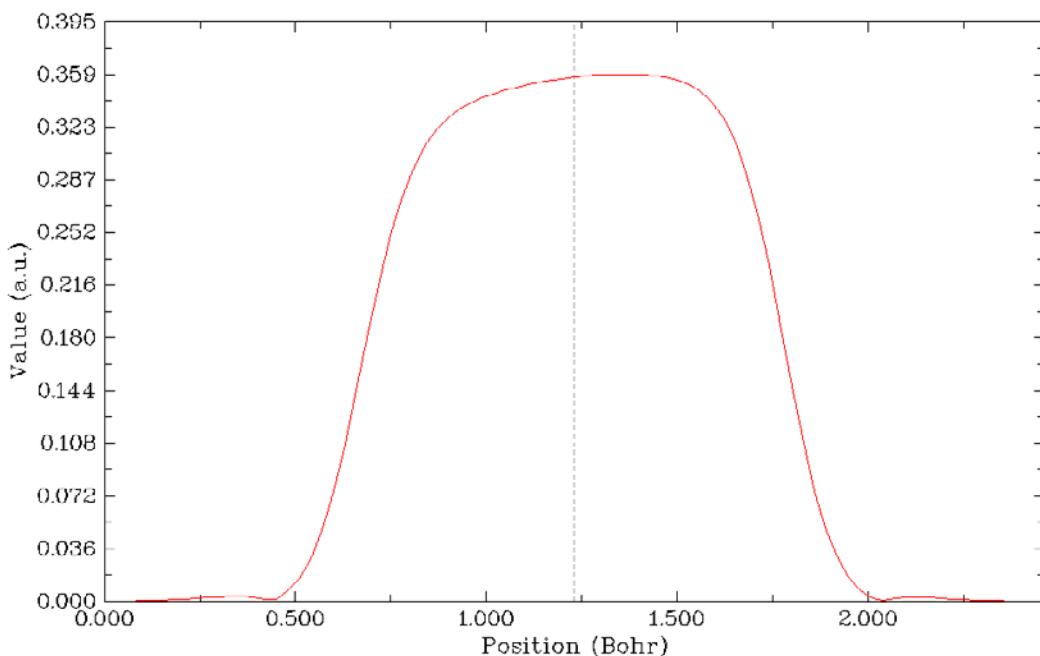
Then boot up Multiwfn and input below commands:

```
examples\butadiene.fch
2 // Topology analysis
2 // Search nuclear critical points from nuclear positions
3 // Search bond critical points from midpoint of atom pairs
8 // Generate bond path
0 // Enter GUI window to visualize result
```

In the GUI window, with the help of "Atom labels" and "Path labels" widgets at right side, we find paths 5 and 6 collectively constitute the bond path of boundary C-C bond. Clicking "RETURN" to close the window and input

```
-5
7 // Calculate specific real space funtion along a path
```

```
5,6 // The index of the paths
100 // User-defined function, which corresponds to ellipticity of electron density currently
```



The curve of electron density ellipticity along the boundary C-C bond path immediately shows on the screen, the dash line denotes the position of bond critical point. At the same time, the raw data of the curve are shown on the command-line window and you can copy them out, so that the map can be further analyzed or replotted in third-part plotting tools such as Origin.

From the graph it is clear that the electron density ellipticity is positive in the middle region of the bond path, exhibiting the double-bond character of the C-C bond.

You can also plot other real space functions such as ELF and kinetic energy density along bond paths, please have a try.

## 4.3 Plot properties in a line

### 4.3.1 Plot the spin density curve of triplet formamide along carbon and oxygen atoms

Boot up Multiwfn and input following commands

```
examples\formamide-m3.wfn // Assuming this input file is in current directory, so the path of directory is not needed to input
```

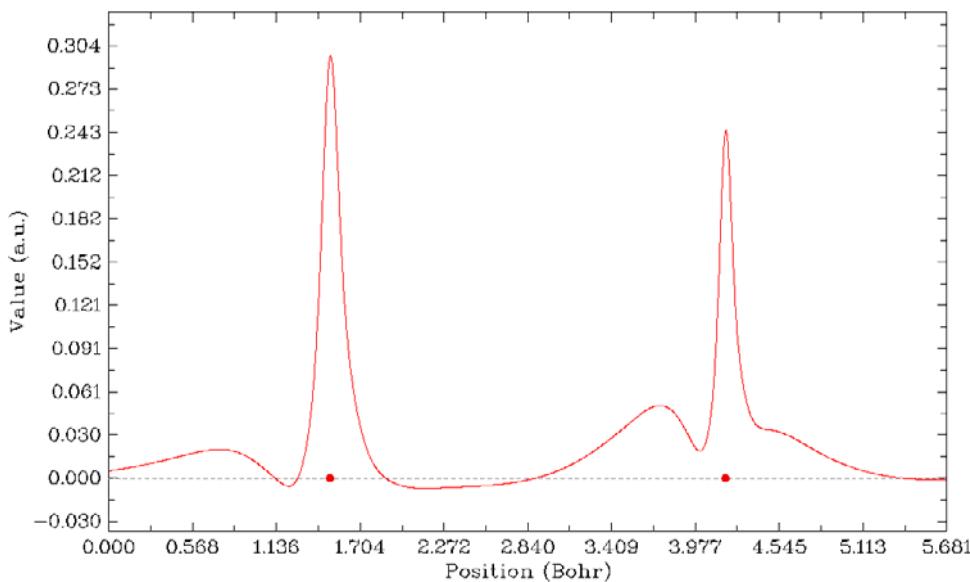
```
3 // Function 3, plot property in the line
```

```
5 // Spin density function
```

```
1 // Defining the line by nuclear coordinates of two atoms
```

```
1,6 // The indices of the two atoms, carbon and oxygen atoms correspond to 1 and 6 in present example
```

The graph shows up immediately:



The X-axis corresponds to the position in the line you defined, the dash line corresponds to the position of Y=0, two red circles denote the position of the two atom nuclei. After you click right mouse button on the graph to close it, a new menu appears on command-line interface, you can export the graph, adjust the range of Y-axis, export X-Y data set and replot the graph and so on by corresponding options. By selecting option 6, minimum and maximum positions can be located:

```

Local maximum X: 0.753677 Value: 0.20104903D-01
Local minimum X: 1.219518 Value: -0.55161276D-02
Local maximum X: 1.503567 Value: 0.29655008D+00
Local minimum X: 2.145518 Value: -0.70202704D-02
Local maximum X: 3.736194 Value: 0.51047629D-01
Local minimum X: 4.006988 Value: 0.18918295D-01
Local maximum X: 4.184992 Value: 0.24448996D+00
Totally found 3 local minimum, 4 local maximum

```

### 4.3.2 Study Fermi hole and Coulomb hole of H<sub>2</sub>

This is a relatively advanced example, you can skip this section if you are a newbie of quantum chemistry.

In this example we will plot correlation hole (Fermi hole and Coulomb hole) along the axis of H<sub>2</sub>. This is an advanced topic, if you are not familiar with the concept of correlation hole, please consult the discussion in part 17 of Section 2.6.

Hartree-Fock wavefunction is capable to exhibit Fermi correlation, but Coulomb correlation is completely omitted. In this case exact Fermi hole can be calculated and plotted by Multiwfn. If Coulomb hole is needed to be analyzed, then post-HF wavefunction must be employed. In current version, Multiwfn is able to evaluate and plot approximate Fermi hole and Coulomb hole for post-HF wavefunctions by Müller approximation, which makes use of natural orbitals to mimic exact pair density. Although the approximation is introduced, the results are generally at least qualitative correct. In the future version, I might try to make Multiwfn able to evaluate correlation hole for post-HF wavefunction exactly, but this is a nontrivial task, mainly because

## 4 Tutorials and Examples

two-particle density matrix (2PDM) has to be acquired in some ways.

First, we optimize and generate .wfn file for H<sub>2</sub> under CCSD/cc-pVTZ level. CCSD may be the highest level of wavefunction that can be generated by current Gaussian program. The file has been provided in "examples" folder as H2\_CCSD.wfn. The coordinate of H1 is 0.0, 0.0, 0.70160240 Bohr, the coordinate of H2 is 0.0, 0.0, -0.70160240 Bohr.

Correlation hole involves coordinates of two electrons, to study it visually we must determine coordinate of a reference electron. In this example, we set reference point at 0.0,0.0,-0.3 Bohr. So we open settings.ini, change "refxyz" parameter to 0.0,0.0,-0.3.

The correlation hole we first analyzed is Fermi hole (also known as exchange hole), so we change "paircorrtype" in settings.ini to 1. Since this is close-shell system, the results for  $\alpha$  or  $\beta$  electron are exactly the same, while for open-shell system, you should use "pairfunctype" in settings.ini to select which type of spin electrons will be studied, you can also choose to study exchange-correlation density or correlation factor by adjusting this parameter.

Now boot up Multiwfn, input following commands

```
examples\H2_CCSD.wfn
```

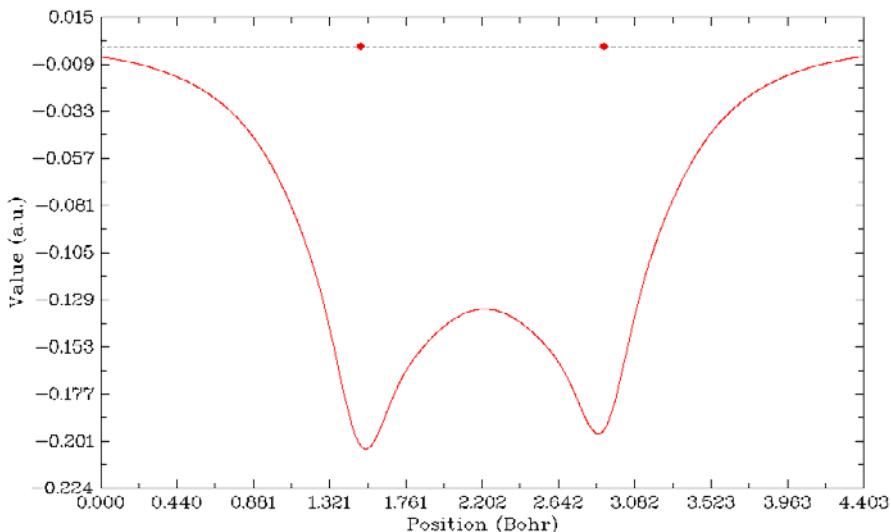
```
3
```

```
17
```

```
1
```

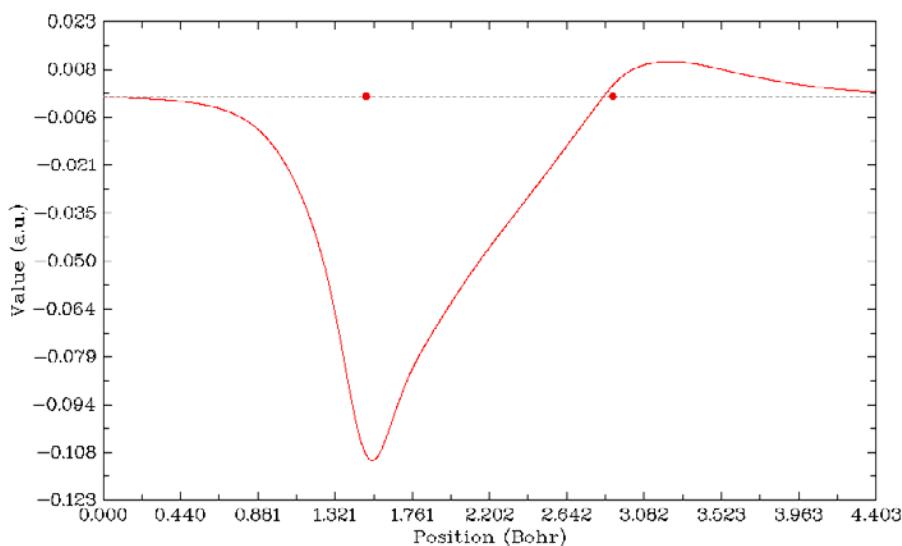
```
2,1 // Draw the line graph along H2 and H1
```

You will get below graph



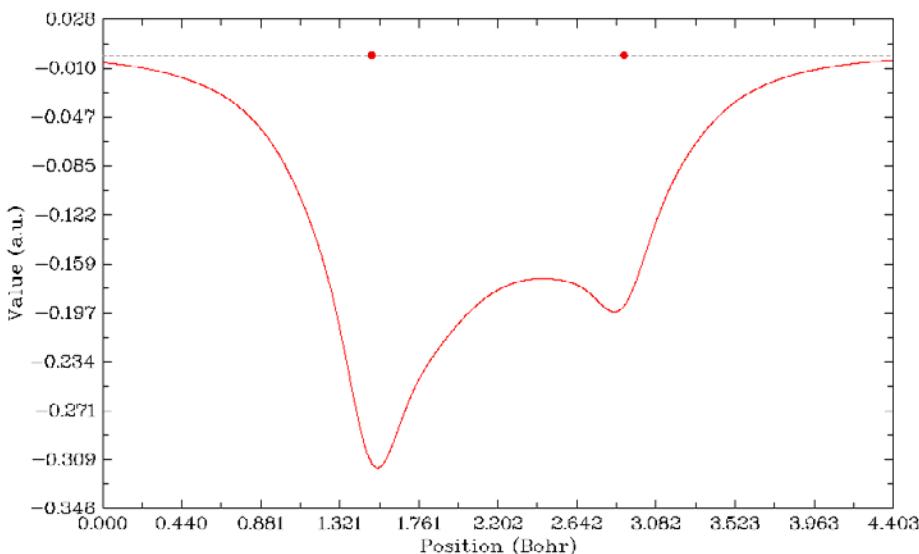
This graph suggests that if we place an  $\alpha$  electron at 0.0,0.0,-0.3, then the probability of finding another  $\alpha$  electron around the two nuclei will be significantly decreased by almost identical extent due to Pauli repulsion between like-spin electrons. In the bonding region, the probability decreased obviously too. According to Bader's statement "An electron can go where its hole goes and, if the Fermi hole is localized, then so is the electron" (p251 in *Atoms in molecules - A quantum theory*), we can say that if an  $\alpha$  electron can present at 0.0,0.0,-0.3, then it must be able to easily delocalize over the whole molecular space of H<sub>2</sub>.

Now we study Coulomb hole. Close Multiwfn, change "paircorrtype" to 2, reboot Multiwfn and then replot the line graph by using the same procedure, you will see



How can I infer the coordinate of the reference point on the graph? From the prompt "Set extension distance for mode 1, current: 1.500000 Bohr" we know that the plot range is extended by 1.5 Bohr to both sides relative to Z coordinates of H2 and H1, and we have already known that Z coordinate of reference point is larger than H2 by about 0.4016 Bohr, so the reference point on above graph is  $1.5+0.4016=1.9016$ . The graph reveals that owing to Coulomb repulsion, the probability of finding another electron ( $\alpha$  or  $\beta$ ) around the hydrogen closest to reference electron, namely H2, is largely decreased. While as a compensation, the probability is increased at backside of H1.

Finally, we study the collective effect of Fermi correlation and Coulomb correlation. Change "paircorrtype" to 3, and plot the line graph again, you will see



This graph is actually the sum of the first two graphs. From this graph it is clear that the probability decrease of finding an electron ( $\alpha$  or  $\beta$ ) around the hydrogen closest to reference electron is more severe than around another hydrogen.

### 4.3.3 Study interatomic interaction via PAEM-MO method

This is a relatively advanced example, you can skip this section if you are a newbie of quantum chemistry.

In *J. Comput. Chem.*, **35**, 965 (2014), the authors proposed a method named PAEM-MO to reveal the nature of interaction between two atoms (covalently or non-covalently bounded). In this example I will briefly introduce this method and show how to realize PAEM-MO analysis in Multiwfn.

PAEM (potential acting on one electron in a molecule) refers to the total potential acting on an electron at point  $\mathbf{r}$ , and can be written as  $V_{\text{PAEM}}(\mathbf{r}) = -V_{\text{ESP}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r})$ ; where  $V_{\text{ESP}}$  is molecular electrostatic potential and has been introduced in part 12 of Section 2.6.  $-V_{\text{ESP}}$  can be regarded as the classical potential acting on an electron in the system, while the exchange-correlation (XC) potential  $V_{\text{XC}}$  represents the important correction to the classical potential due to quantum effect.  $V_{\text{XC}}$  has two components, namely correlation potential ( $V_C$ ) and exchange potential ( $V_{\text{XC}}$ ); in fact only the latter is important, that means even the potential obtained at Hartree-Fock level is in general a good approximation to exact  $V_{\text{XC}}$ .

In wavefunction theory, the exchange-correlation potential can be explicitly written as

$$V_{\text{XC}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \int \frac{\Gamma_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \text{ where } \Gamma \text{ is known as exchange-correlation density, see part 17}$$

of Section 2.6 for detail. In DFT theory, the XC potential directly comes from the variation of

$$\text{exchange-correlation functional with respect to electron density, i.e. } V_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}.$$

The  $V_{\text{XC}}$  can be used in Multiwfn in terms of user-defined function. If parameter "iuserfunc" is set to **33**, then  $V_{\text{XC}}$  will be calculated based on  $\Gamma$ ; if it is set to **34**,  $V_{\text{XC}}$  will be evaluated in terms of DFT XC potential, in this case the computational cost is several times lower than **33**. For more information please check corresponding description in Section 2.7.

The core of HF and KS-DFT theories is the one-electron eigenvalue equation

$$\hat{h}\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r}) \quad \text{where } \hat{h} = -(1/2)\nabla^2 + V_{\text{PAEM}}(\mathbf{r})$$

Solving the equation results in a set of MOs  $\{\varphi\}$ , their eigenvalues correspond to the energy of the electrons running in the orbitals.

According to the viewpoint of PAEM-MO, if the energy of an occupied MO is higher than the barrier of  $V_{\text{PAEM}}$  between a pair of atoms, then the electrons in this MO will be able to freely delocalize over the two atoms, and thus have direct contribution to covalent bonding.

Below I present two very simple examples of using PAEM-MO method to judge the type of interatomic interaction. More examples and discussions can be found in *J. Comput. Chem.*, **35**, 965.

#### H-H interaction in hydrogen molecule

First set "iuserfunc" in settings.ini to 33, then user-defined function will be equivalent to the  $V_{\text{XC}}$  evaluated based on  $\Gamma$ . Boot up Multiwfn and input below commands

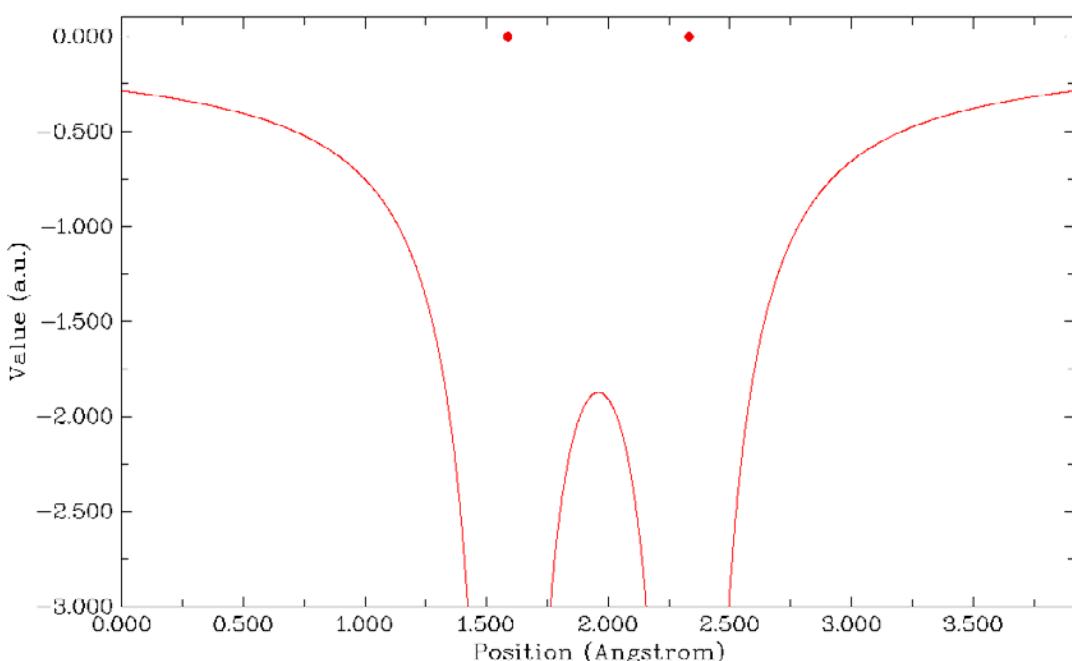
*examples\H2.fch* // Produced at HF/6-311++G\*\* level

```

3 // Plot real space function in a line
100 // User-defined function
0 // Adjust extension size in the plot
3 // 3 Bohr, which is larger than the default value
1 // Use two nuclei to define the line
1,2
Close the graph, then adjust some plotting parameters to make the graph better
11 // Change length unit of the graph to Angstrom
3 // Change range of Y axis
-3,0.1 // From -3.0 a.u. to 0.1 a.u.
10 // Set stepsize of X and Y axes
0.5,0.5
-1 // Replot

```

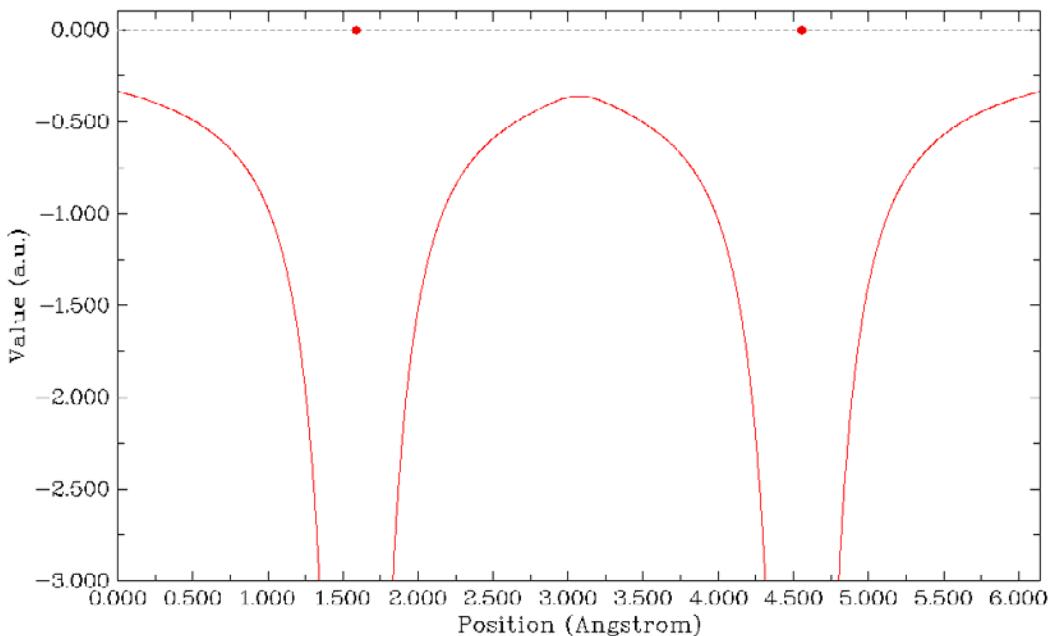
You will see below graph, which exhibits the PAEM curve along the H<sub>2</sub> axis



As you can see, there is a barrier of PAEM around the midpoint of H-H bond. In order to locate the exact value of the barrier, we close the graph and select 6. From the output we find the maximum of the curve is -1.873 a.u. (-50.96 eV). Present system only has one doubly occupied MOs, whose energy (-16.15eV) significantly exceeded the PAEM barrier, implying that the electron is not confined in any hydrogen atom but substantially contributes to the H-H binding, so the H-H bond must be covalent.

### He-He interaction in He<sub>2</sub>

Please plot PAEM curve along the He-He axis in He<sub>2</sub> with the same steps as above. The wavefunction file used here is *examples\He2.fch*. The resultant graph should look like below



Obviously, the PAEM barrier (-9.78 eV) is higher than that in the case of H<sub>2</sub>. The energy of the two doubly occupied MOs are -25.03 and -24.91 eV respectively, both of them are lower than the barrier, therefore the electrons in each He atom are difficult (but not completely impossible due to tunnel effect) to overcome the barrier to freely delocalize to another He. The He-He interaction thus should be regarded as non-covalent interaction.

Note that in the original paper of PAEM-MO the PAEM is evaluated based on the expensive CISD wavefunction, while we merely use HF wavefunction. However, our results are in good agreement with that at CISD level, showing that correlation potential can be safely neglected in the study of PAEM.

The interested users are suggested to replot the PAEM with iuserfunc=34 to employ DFT XC potential in PAEM, you will find the results are very similar to those we obtained earlier.

Worthnoting, although the PAEM-MO analysis method has clear physical meaning, its many limitations severely hinders it to be a universal method to distinguish covalent and non-covalent interactions like ELF or LOL: (1) PAEM-MO analysis does not always present reasonable conclusion in all cases. For example, PAEM-MO erroneously indicates that the H-bond in water dimer is covalent interaction. (2) PAEM-MO is difficult to be applied to polyatomic molecules, since there are often too many occupied orbitals with complex shape. (3) If the two atoms are placed too close to each other, then PAEM-MO almost always indicates that the interaction is covalent.

## 4.4 Plot properties in a plane

### 4.4.1 Color-filled map of electron density of hydrogen cyanide

In this example we plot slice map for electron density of hydrogen cyanide. Boot up Multiwfn and input following commands

*examples\HCN.wfn*

4 // Plot graph in a plane

1 // Electron density function

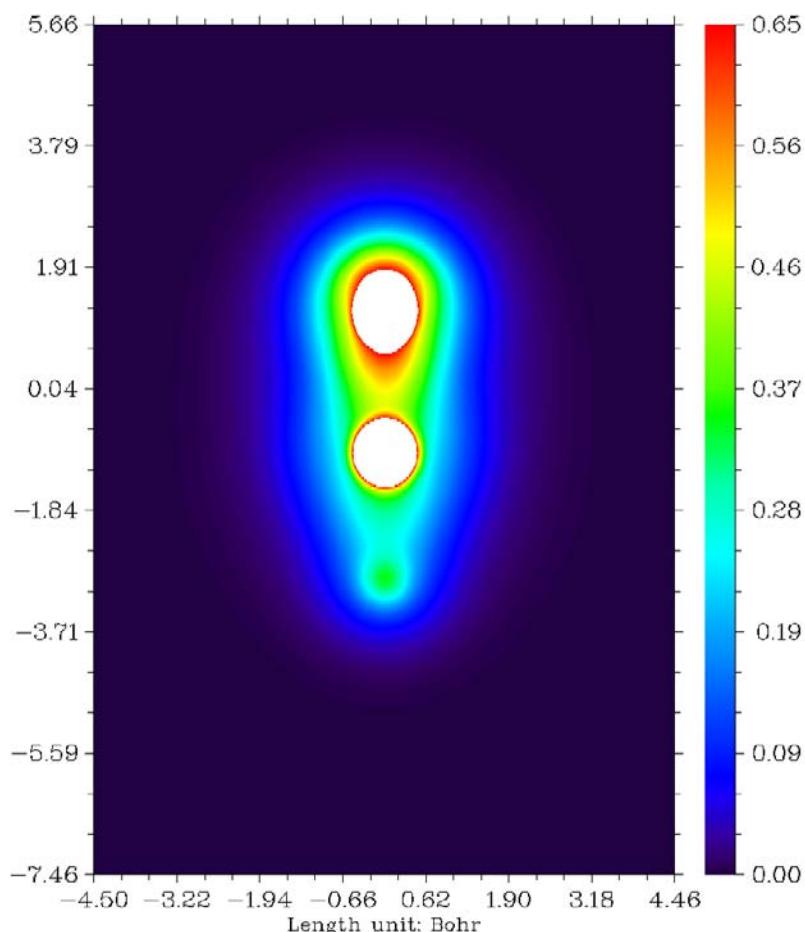
1 // Select color-filled map as graph type

Press ENTER button to use the recommended grid setting, namely 200,200. If you increase the number of grid points, graph will become finer, but you have to wait longer time for calculating data and plotting

2 // Select XZ plane (in hcn.wfn, Z-axis is molecular axis)

0 // The number of XZ planes is infinite, here we choose the only one with Y=0 Bohr

After a few seconds the graph pops up



The central regions of carbon and nitrogen are white, suggesting that electron density exceeds the upper limit of color scale (0.65). Close the graph, then a menu appears, you can choose corresponding options to adjust plotting parameters and then use -1 to replot again, or export X-Y data set to plain text file for replotting the graph by external data visualization software (sigmaplot, matlab, etc.), or save the picture in current directory (the graphical format can be controlled by "graphformat" in settings.ini) and so on.

#### **4.4.2 Shaded surface map with projection of localized orbital locator in a plane of monofluoroethane**

Boot up Multiwfn and input following commands

*examples\*C2H5F.wfn

#### 4 Tutorials and Examples

0 // Let's view the molecular structure first to find the plane we are interested in, suppose that the C-C-F plane is what we want, remember the indices of the three atoms: 1, 5, 8, and then press RETURN button

4 // Plot graph in a plane

10 // Localized orbital locator (LOL)

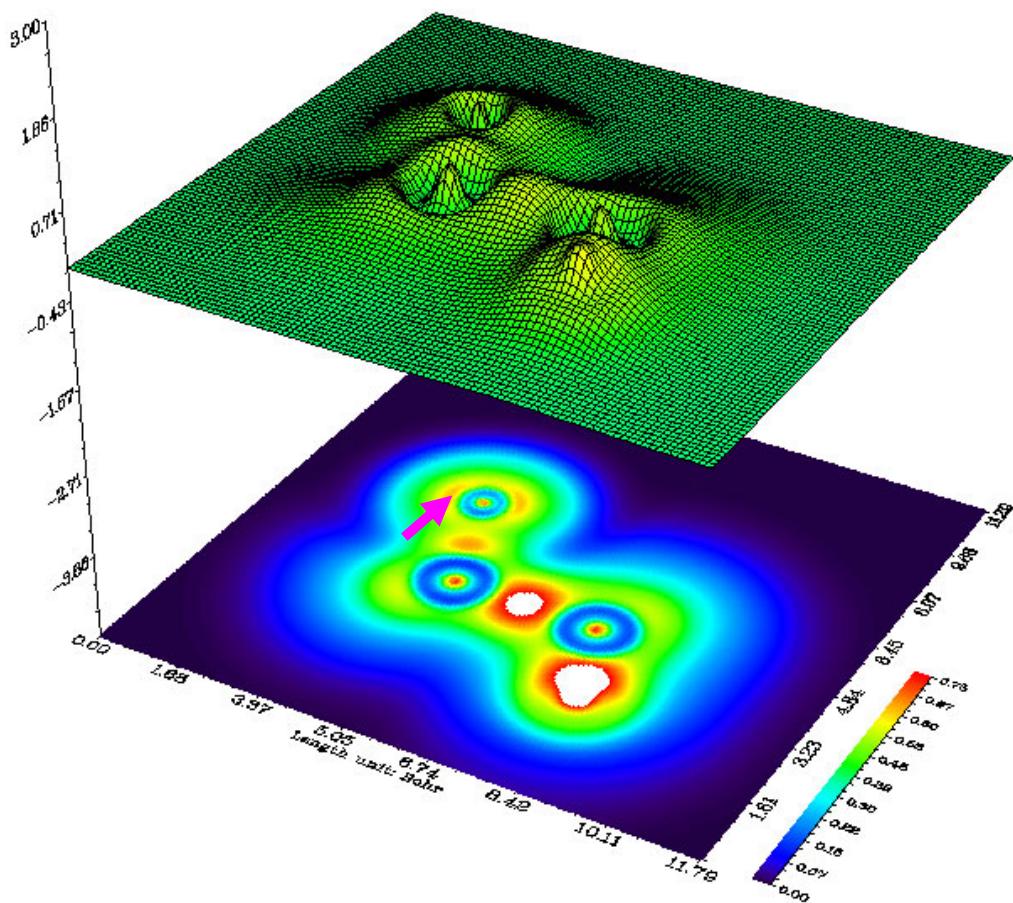
5 // Shaded surface map with projection

Press ENTER button to use recommended grid setting, namely 100,100

4 // Define the plane by three atoms. If you want to enlarge plotting region, select 0 first and input a larger value than the default one (4.5 Bohr)

1,5,8 // The indices of the three atoms

The graph immediately pops up:



We can see that covalent regions have high LOL value, the electron depletion regions between valence shell and inner shell are shown by the blue circles around nuclei. A lone pair of fluorine atom is pointed out by purple arrow.

The graph you have seen in the GUI can be saved to graph file by option 0 at post-process interface, if you found the exported picture is truncated at edge, select option -1 to reenter the GUI window, zoom out the graph and then export the picture again.

### 4.4.3 Contour map of electron density Laplacian of uracil without contributions from some atoms

Boot up Multiwfn and input following commands

*examples\Uracil.wfn*

-4 // Discard contribution of some atoms

3,4 // All GTFs in atom 3 and 4 will be discarded. In other words, atom 3 and 4 will be removed from current wavefunction

4 // Plot graph in a plane

3 // Laplacian function

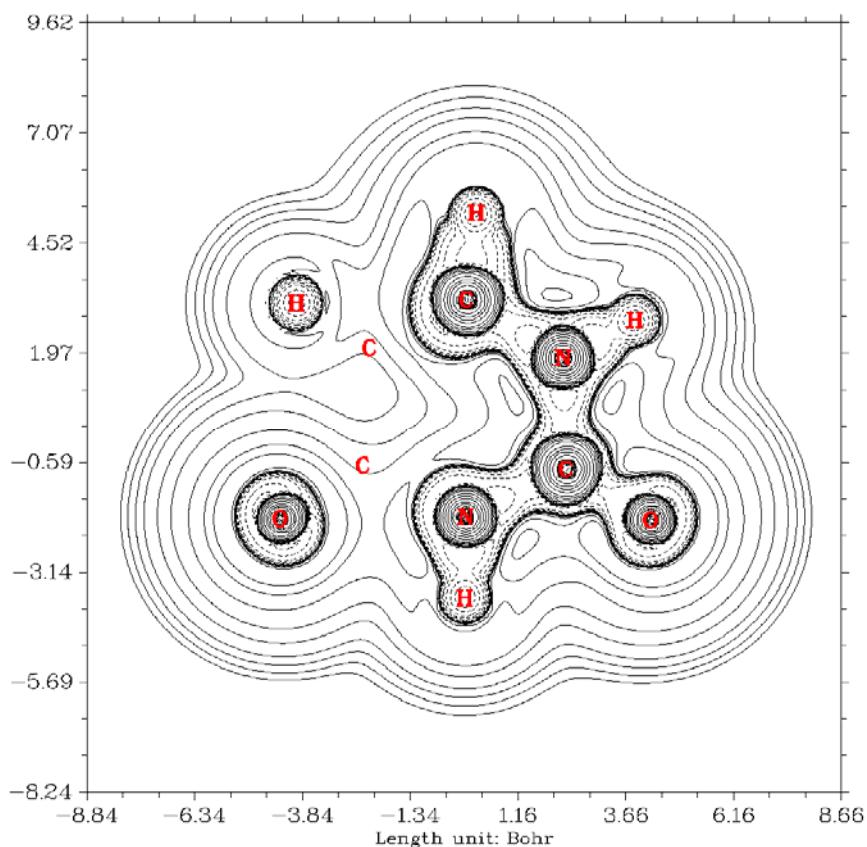
2 // Contour line map

Press ENTER button to use default grid setting

1 // XY plane will be plotted

0 // The Z-position of the XY plane is zero, that is molecular plane

Below is the resultant graph, solid and dash line correspond to positive and negative regions respectively.



From the graph you can see the contribution from the two carbons have been discarded as expected. By using the options shown on the command-line screen, you can save, export, redraw the picture, adjust plotting parameters, etc. If option 2 is chosen, the isovalue will be marked on corresponding contour lines. Once option 3 is chosen, you will enter an interface for setting up contour lines, please consult Section 3.5.4. For more about molecular fragment setting please consult Section 3.1.

#### 4.4.4 Contour map of electrostatic potential of chlorine trifluoride

This example we plot electrostatic potential (ESP) for chlorine trifluoride as contour map. Boot up Multiwfn and input following commands

*examples\ClF3.wfn* // ClF3.wfn was generated at B3LYP/6-31G\* level

4 // Plot graph in a plane

12 // Total electrostatic potential

2 // Draw contour line map

120,120

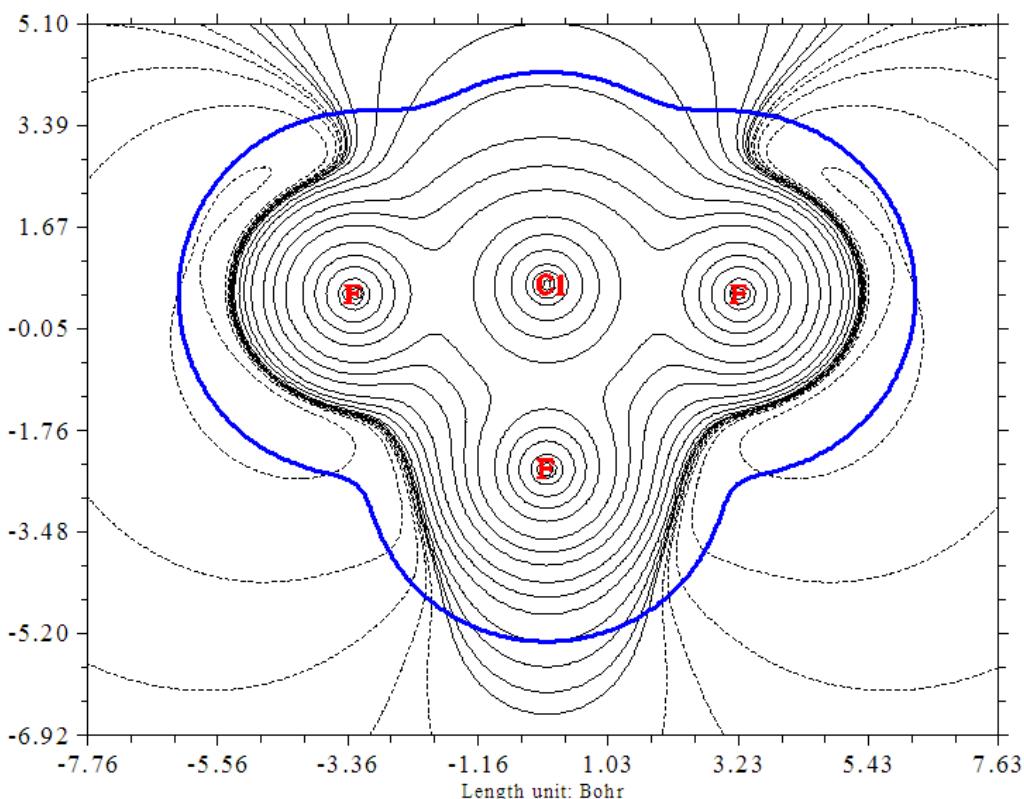
3 // YZ plane

0 // Set x coordinate of the YZ plane to 0

Because evaluation of ESP is evidently more time-consuming than other real space functions, you need to wait for a while.

PS: For very large system, the cost of plotting plane map for ESP may be prohibitively high. However, this task is still feasible if you make use the cubegen utility in Gaussian to generate ESP value at the plotting points, since cubegen calculates ESP much faster than Multiwfn for the case of large systems or high-quality basis-sets. See Part 2 of Section 4.12.7 on how to do this.

After the calculation is finished, ESP map will pop up. This map is inconvenient to be visually analyzed, since what we are interested in is often the ESP distributed on molecular vdW surface, so it is better to plot the vdW surface on this map simultaneously. In order to do this, we close the graph by clicking right mouse button, choose option 15, and then choose option -1 to replot the graph, you will see such a picture



The bold blue line corresponds to vdW surface (isosurface of electron density=0.001 a.u., as defined by R. F. W. Bader). From the graph it is clear that chlorine atom is positively charged, because the local vdW surface closed to chlorine atom largely intersected solid contour lines

(correspond to positive ESP). For the same reason, we can see that the equatorial fluorine atom possesses less electrons than the two axial fluorine atoms, this point can be further verified when we calculate Hirshfeld atomic charges for this molecule in section 4.7.1.

Plane map of the ESP derived from atomic charges can be directly plotted by Multiwfn too. First, you need to prepare a plain text file with .chg extension, the first column corresponds to element name, the 2th, 3th and 4th columns correspond to X,Y and Z cooredinates in Angstrom respectively, the last column is atomic charge. For example:

Cl	0. 000000	0. 000000	0. 359408	0. 529971
F	0. 000000	1. 726507	0. 294501	-0. 228394
F	0. 000000	0. 000000	-1. 267884	-0. 073185
F	0. 000000	-1. 726507	0. 294501	-0. 228394

Boot up Multiwfn as usual, and then use the .chg file as input. The plotting procedure is completely identical to the one given above, except that when the program prompts you to select real space function, you should select 8 (ESP from atomic charges) instead of 12.

#### 4.4.5 Contour map of two orbital wavefunctions

Multiwfn is capable to plot contour map for two orbitals simultaneously, in this section, we will draw contour map for NBO 12 and NBO 56 of NH<sub>2</sub>COH (recall Section 4.0.2). The plane we selected is perpendicular to molecular plane and passed through both carbon and nitrogen atoms.

Boot up Multiwfn and input:

*examples\NH2COH.31*

37 // Will load NH<sub>2</sub>COH.37

0 // This step prints all atom coordinates in Multiwfn console window, which will be used later. This step is not compulsory

4 // Plot plane graph

4 // Orbital wavefunction

12,56 // The two orbital indices. If you only input one index, then only one orbital will be plotted

Press ENTER to use default grid setting

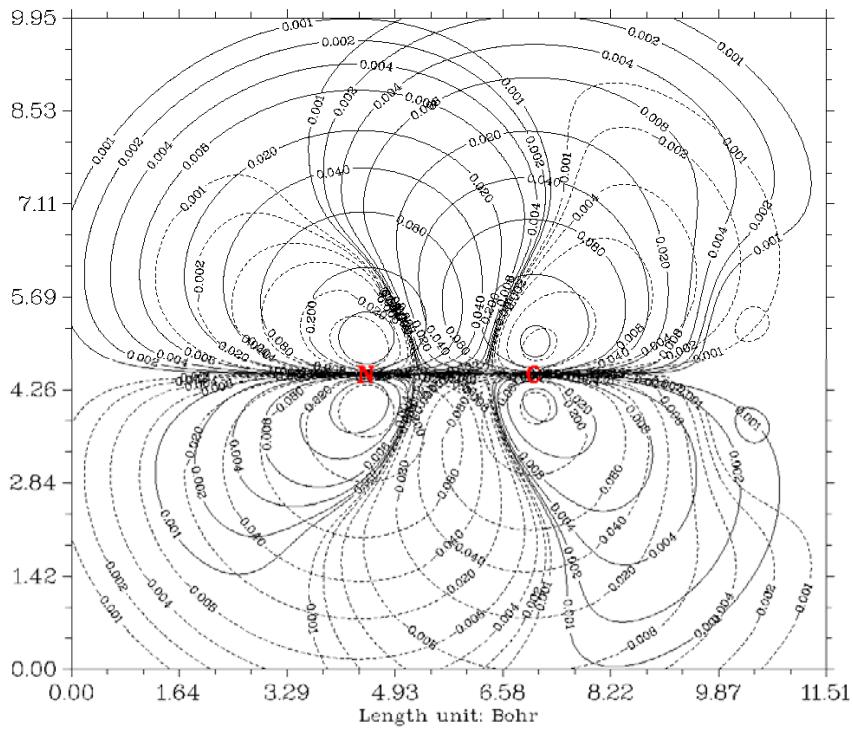
5 // The plane we want to plot is neither a XY/YZ/XZ plane nor a plane that can be defined by three atoms, the best way to define the plane is to input three points

0.000000 0.794089 0.000000 // The coordinate of the first point, this is just the coordinate of carbon atom, which has printed on screen when you selected main function 0

-1.778942 -1.064235 0.000000 // The coordinate of the second point, this is just the coordinate of nitrogen atom

-1.778942 -1.064235 1.000000 // The coordinate of the third point, X and Y coordinates are identical to the ones of nitrogen atoms, but Z value is suitably moved in Z-direction (you can use trial&error method to find the most suitable movement distance)

Immediately a graph pops up. We close it by clicking right mouse button, choose option 2 and input 25 to enable showing isovalue on contour lines, then choose -1 to redraw the graph, we will see:



This contour map is not ideal, there are too many contour lines intertwined together and confused us. The culprits are the contour lines with too small isovalue (i.e. magnitude smaller than 0.01), since they are not important, we can delete them to make the graph clearer. So, next we input

*3 // Change contour line setting*

*5 // Delete a range of contour lines*

*1,4 // Delete the four contour lines: 0.001, 0.002, 0.004, 0.008*

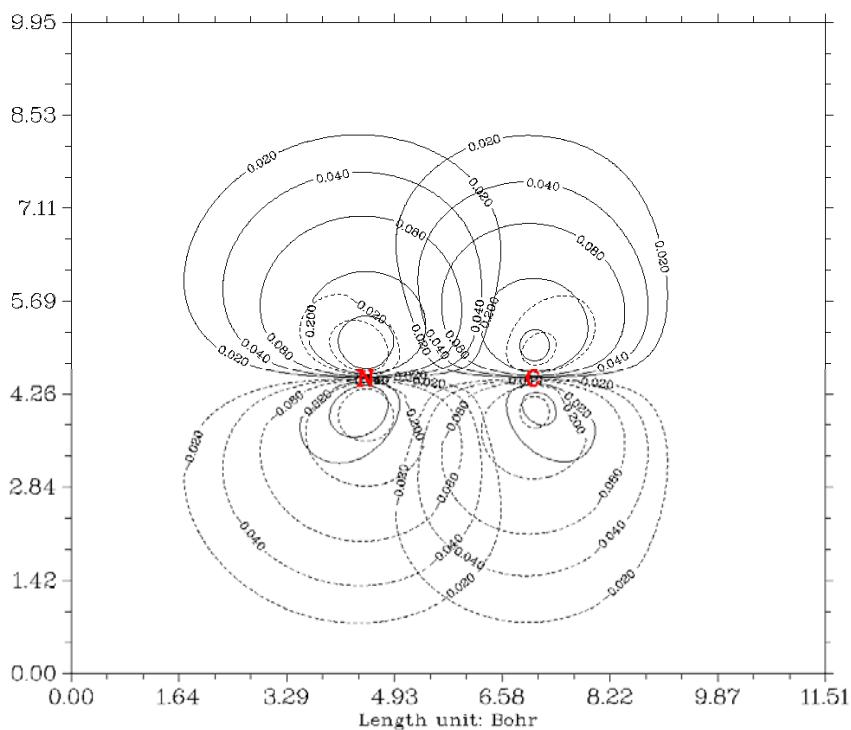
*5 // Delete a range of contour lines*

*28,31 // Delete the four contour lines: -0.001, -0.002, -0.004, -0.008.* For convenience, you can choose option 6 to export current contour line setting to an external file, when you use Multiwfn next time you can load present setting directly by choose option 7 in current interface

*I // Return to the upper menu*

*-1 // Replot the contour map*

Now the graph become informative, the overlapping regions of identical phases are quite distinct. Notice that only the labels of the atoms whose vertical distance to the plane are smaller than "disshowlabel" in settings.ini will be shown.



#### 4.4.6 Gradient+contour map with topology paths of electron density of hydrogen peroxide

As introduced in Section 3.5.5, critical points, bond paths and interbasin surfaces can also be plotted on plane map, here I give a very simple example.

Boot up Multiwfn and input following commands

`vb1510s\kabat\h2o2.fch` // Of course, you can also use .wfn file as input

`4`

`1` // Electron density

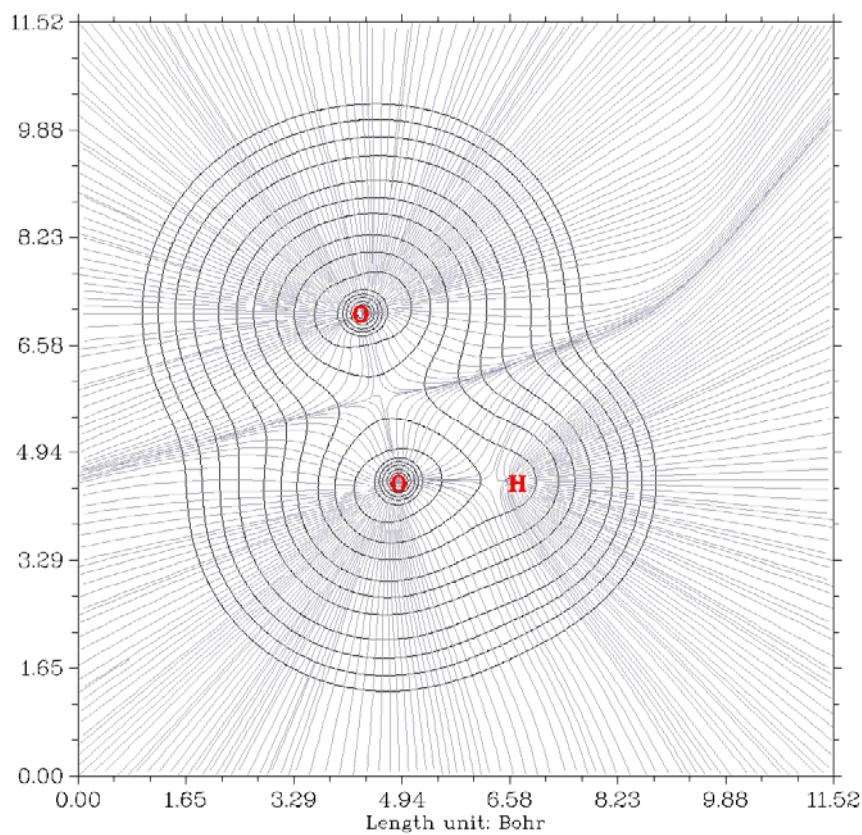
`6` // Gradient line with/without contour line map

Press ENTER to use default grid setting

`4`

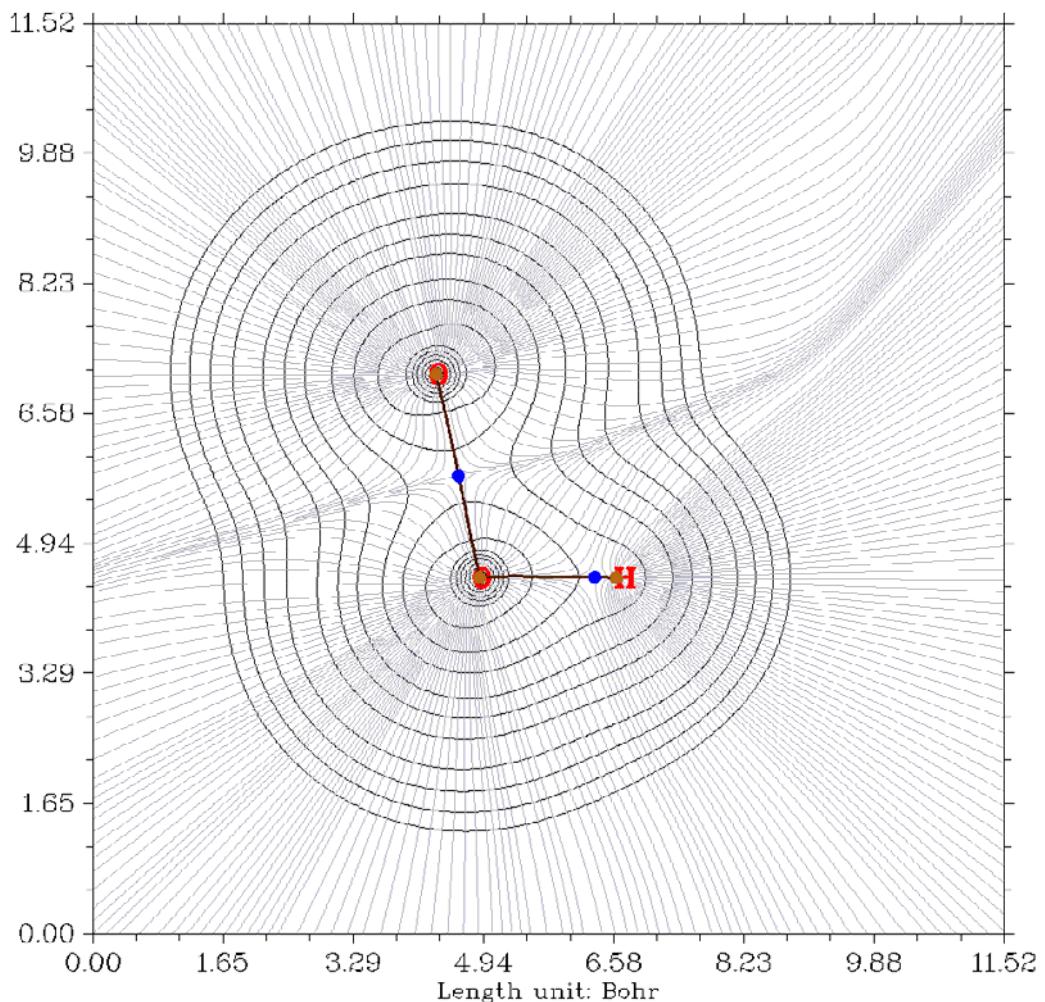
`2,1,3` // Define the plane by nuclear coordinates of atom 1, 2 and 3

Generating data and plotting gradient map take more computational time relative to other graph type, however since present system is small and basis-set is only 6-31G\*, resultant graph shows up immediately:

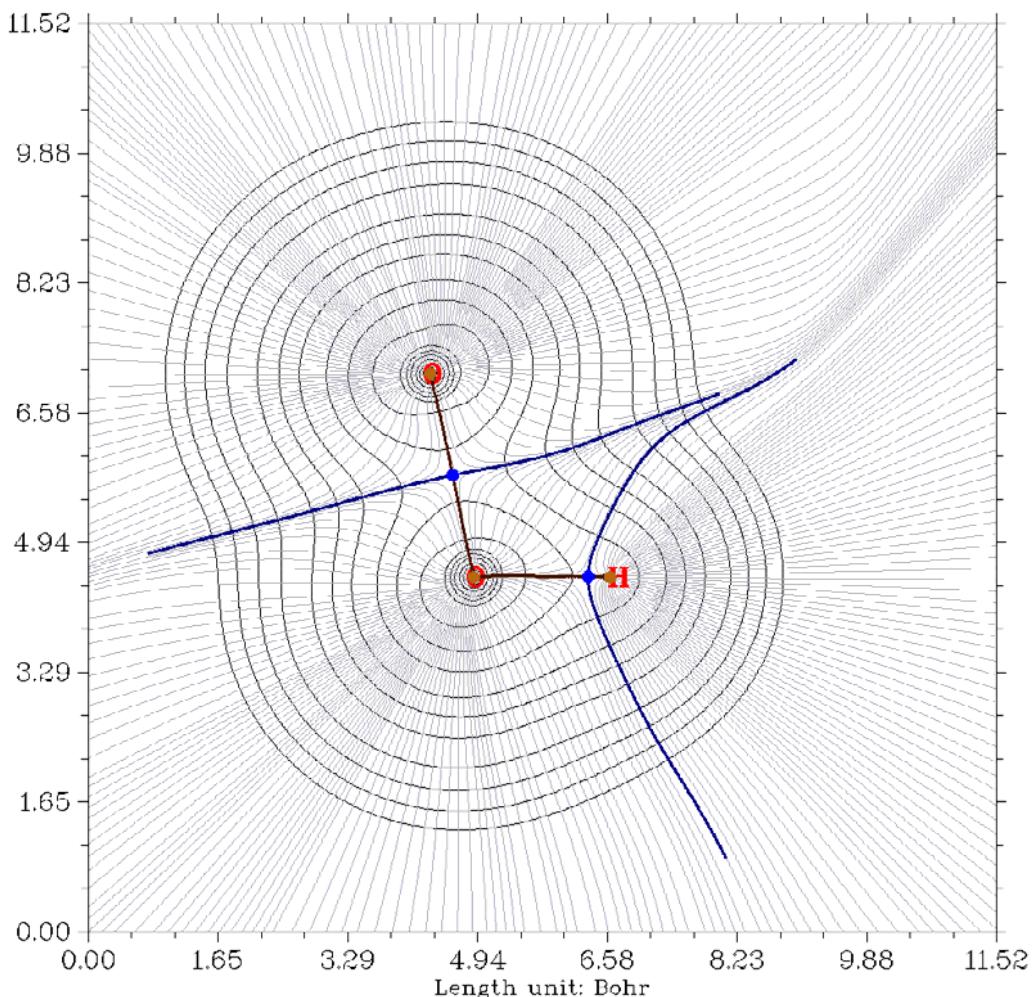


This type of graph is very useful in Bader's AIM analysis. You can also plot gradient+contour map for any other real space functions supported by Multiwfn.

If you want critical points and paths also to be portrayed on the graph, you need to do topology analysis as described in Section 4.2.1, then return to main menu, and then draw contour or gradient map as usual. The resultant graph looks like below. Brown, blue, and orange circles denote (3,-3), (3,-1) and (3,+1) critical points, respectively, bold dark-brown lines depict bond paths.



Interbasin paths can also be drawn on the graph. If you have finished the search of CPs in topology analysis module, after you draw contour/gradient/vector field map, you could find a option named "Generate and show interbasin paths" in post-process stage, select it, and show the graph again, the interbasin paths will be drawn on the graph by bold deep blue lines:



#### 4.4.7 Deformation map of electron density of acetyl chloride

Deformation map of electron density clearly shows you the electron density variation during formation of molecule, which is actually molecular electron density minus electron densities of each atom in free-state. It is a labor work to draw such a graph. However, with Multiwfn this task is very easy. Boot up Multiwfn and input following commands

*examples\CH3COCl.wfn*

4

-2 // Tell Multiwfn you want to draw deformation map, then Multiwfn prepares free-state atom wavefunctions

6-31G\* // The basis-set used to generate atom wavefunctions by Gaussian. Because the basis-set used for CH3COCl.wfn is 6-31G\*, here you'd better use 6-31G\* too

*d:\study\g09w\g09.exe* // The path of executable file of Gaussian (you can also use other Gaussian version). If you already set correct path in “gaupath” parameter in settings.ini, then Multiwfn will not ask you to input the path every time

Now Multiwfn starts to invoke Gaussian to calculate atom wavefunctions, then Multiwfn translates and sphericalizes them internally. These temporary wavefunction files are stored in “wfntmp” folder in current directory, after you get the expected graph you can delete the folder.

Let's continue to input the remain commands.

1 // Electron density function

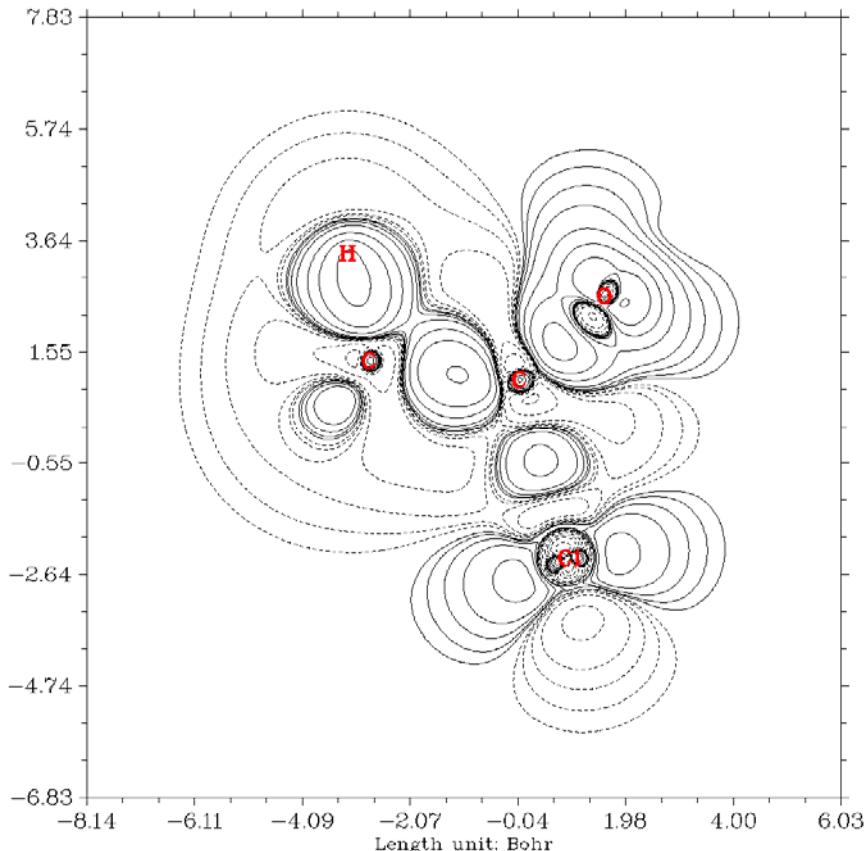
2 // Contour map

Press ENTER button to use default grid setting

1

0 // The XY plane with Z=0 is the plane of acyl chloride

Then the deformation map pops up:



As we expected, electron density concentrates towards bonding regions, we also find the density distribution around chlorine atom is largely desphericalized, satisfied with hybrid orbital theory, chlorine atom forms somewhat  $sp^3$  hybrid state.

You can also plot deformation maps for other functions by choosing corresponding real space function, however not all of them are meaningful.

If you want to avoid recalculating atom wavefunction files next time, you can copy the .wfn files without number suffix (such as “C.wfn”) from “wfntmp” folder to “atomwfn” folder in current directory, if Multiwfn finds all needed atom wavefunctions have already existed in “atomwfn” folder, then Multiwfn will not invoke Gaussian to calculate them again.

Hint: You can also use “genatmwfnpdb” in “examples” directory to generate all atom wavefunctions under specific basis-set in a single run, please consult Section 3.7.3.

The “atomwfn” folder in “examples” directory contains atom wavefunctions (by 6-31G\*) for all first-four row elements, you can directly copy this folder to current directory, after that you will not need Gaussian again during plotting deformation map.

If your system involves some elements heavier than Kr, you have to manually calculate the

corresponding atomic .wfn files and put them into "atomwfn" folder".

## 4.5 Generate grid data and view isosurface

### 4.5.1 Electron localization function of chlorine trifluoride

Boot up Multiwfn and input following commands

```
examples\ClF3.wfn // Chlorine trifluoride at B3LYP/6-31G*
```

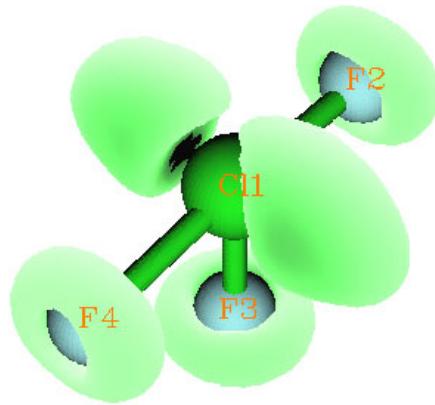
```
5 // Generate grid data and view isosurface
```

```
9 // Electron localization function (ELF)
```

2 // Medium quality grid, about 512000 points will be evaluated, this setting is fine enough for small system. Please consult Section 3.6 for more about grid setting information.

Now Multiwfn starts to calculate grid data, this is a time-consuming task, you have to wait for a while. Notice that if your computer have multiple CPU cores (SMP parallel architecture), I **strongly** suggest you enable the parallel mode, that is set “nthreads” parameter in settings.ini to the number of CPU cores, you will find calculation speed improved significantly! (By default, the parallel implementation is enabled for four cores)

When the calculation is finished, Multiwfn outputs some statistical information, in the new menu you can draw the isosurface by option -1, then a GUI window pops up, input isovalue of 0.85 in the text box and press “Enter” button on your keyboard, the isosurface would looks like this



The ELF isosurface clearly points out the lone electron pair regions of fluorine and chlorine atoms. After click “Return” button to close GUI window, you can use option 1 to save the graph in current directory (the effect is the same as clicking the button “save pic” in GUI), or use 2 and 3 to export grid data to Gaussian cube file and to plain text file in current directory respectively.

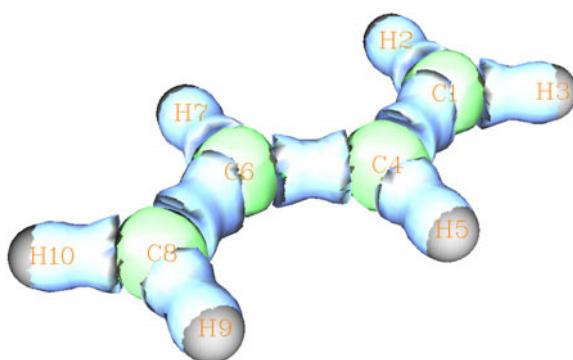
If you want to use different colors to shade different isosurfaces, you can download a mini tutorial named "Drawing ELF isosurfaces with different colors for different domains" from "Related resources and posts" section of Multiwfn website and then follow its steps.

### 4.5.2 Laplacian of electron density of 1,3-butadiene

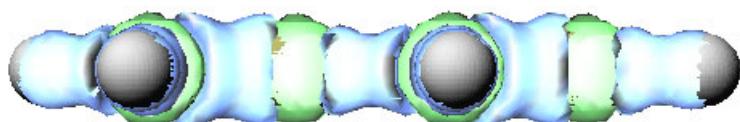
Electron density Laplacian is another localization indicator as ELF and LOL but with longer

history. Laplacian is not as good as ELF and LOL for highlighting localization region, its distinguishability is weak, for example, the shell structures of atoms heavier than krypton cannot be fully illustrated by Laplacian, and if you attempt to use Laplacian to analyze chlorine trifluoride, you will find the lone pair regions of fluorine atoms (circular isosurfaces) are hard to identify. Moreover, the value range of Laplacian is too large, which brings difficulties on analysis. However for most system Laplacian still works fine and now I illustrate its usefulness by an example. Boot up Multiwfn and input following commands

```
examples\butadiene.fch // Yielded under B3LYP/6-31G** level
5 // Generate grid data and view isosurface
3 // Electron density Laplacian
2 // Medium quality grid
-I // View isosurface
```



In the newly occurred window, change isosurface value from default value to 0.3, then the green and blue isosurfaces will correspond to isovalue of 0.3 and -0.3 respectively. The presence of blue isosurfaces between C-C and C-H suggests that valence-shell electrons are strongly concentrated on these regions, these are typical pattern of covalent bonding.



If you inspect the isosurfaces between carbon atoms carefully, you will find that the isosurface between C6-C8 or C1-C4 is wider than the isosurface between C4-C6, this phenomenon reflects that the two boundary C-C covalent bonds are stronger than the central one. This conclusion can also be verified by other wavefunction analysis schemes, for example, Mayer bond order (bond order between C6-C8 is 1.863, while the bond order between C4-C6 is only 1.136).

#### 4.5.3 Calculate ELF- $\alpha$ and ELF- $\pi$ to study aromaticity of benzene

ELF- $\alpha$  and ELF- $\pi$  are commonly used  $\alpha$  and  $\pi$  aromaticity indices. ELF- $\alpha$  (ELF- $\pi$ ) are defined as the ELF value at bifurcation point (that is (3,-1) CP) of ELF domain that only contributed from  $\alpha$  orbitals ( $\pi$  orbitals), see *J. Chem. Phys.*, **120**, 1670 (2004) and *J. Chem. Theory*

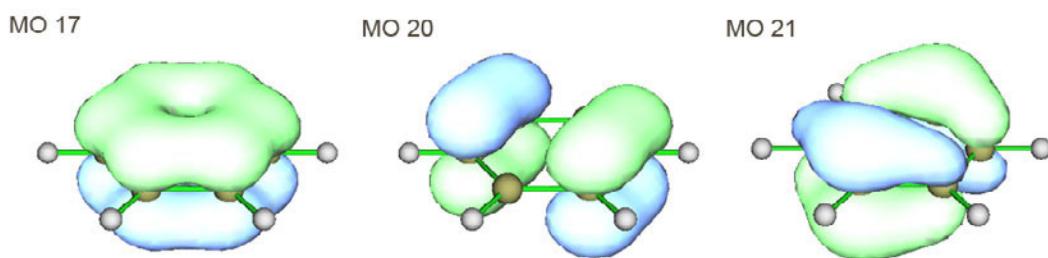
*Comput.*, **1**, 83 (2005) for detail. The theoretical basis of these indices is that the ELF value at bifurcation point measures interaction between adjoining ELF domains, the larger value means electrons have better delocalization between these domains, which is commonly recognized as the nature of aromaticity. It is argued that if ELF- $\pi$  is larger than 0.70, then the molecule has  $\pi$  aromaticity. While if the average of ELF- $\pi$  and ELF- $\alpha$  is larger than 0.70, one can say that the molecule is global aromatic. In present example, we will calculate ELF- $\alpha$  and ELF- $\pi$  for benzene.

In order to separate  $\alpha$  and  $\pi$  orbitals, we need to know which orbitals are  $\pi$  orbitals first. Boot up Multiwfn and input following commands

```
examples\benzene.wfn // Optimized at B3LYP/6-311G* level, the same level used in Chem. Phys. Lett., 443, 439
```

```
0 // View molecular orbitals (MO)
```

Now check orbital shape of each MO in turn, we found 17th, 20th and 21th MOs are  $\pi$  orbitals, as shown below. All other MOs are recognized as  $\alpha$  orbitals.



We first calculate ELF- $\pi$ . The contribution to ELF from  $\alpha$  orbitals should be omitted; **this can be realized by setting occupation number of all  $\sigma$  orbitals to zero.**

```
6 // Enter "Modify & Check wavefunction" interface
```

```
26 // Set occupation number for some orbitals
```

```
0 // 0 means selecting all orbitals
```

```
0 // Set occupation number of all orbitals to zero
```

```
17,20,21 // Select MO 17, 20 and 21
```

2 // Set occupation numbers of MO 17, 20 and 21 to 2.0, since they are close-shell system. If you want to check if occupation numbers have been correctly set, choose option 3. You will find occupation number of all  $\alpha$  orbitals have become zero, which means they will have no any contribution when we calculate any real space functions

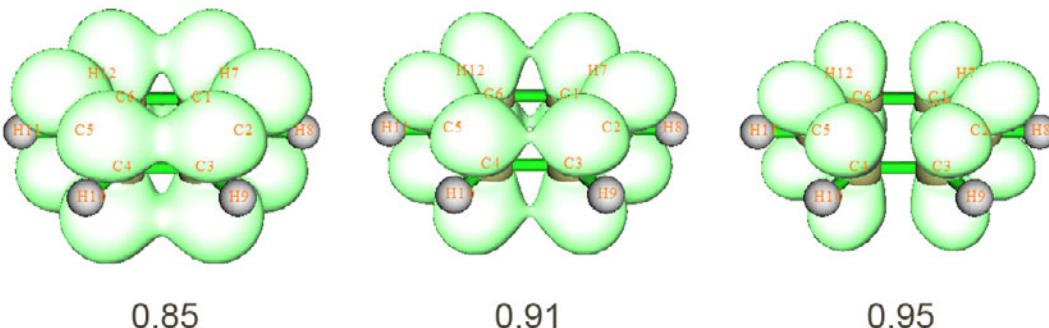
```
q // Return to last menu
```

```
-1 // Return to main menu
```

Note: There is a much more convenience way to set occupation number of  $\pi$  orbitals to zero. By this way you do not need to visually and manually find out the  $\pi$  orbitals, which will be rather laborious for large systems. The procedure is: Enter option 22 in main function 100, select molecular plane (in this example the one is XY), and then choose 1 (or may be 3, if heavier elements are involved), and finally choose 0 to return to main menu. If you want to

There are two ways to calculate ELF- $\pi$ , way 1 is to examine ELF isosurface directly, this way is more intuitive but less accurate than way 2, in which topology analysis technique is used. We use way 1 first. Generate and view isosurface for ELF by main function 5 as usual (likewise Section 4.5.1. High quality grid is recommended) This time the ELF isosurface only reflects  $\pi$

localization. Gradually increase isovalue, you will find the two circle-shape ELF domains are bifurcated to twelve spherical-like domains at about the isovalue of 0.91 (see below graph), which implies ELF- $\pi$  of benzene is about 0.91.

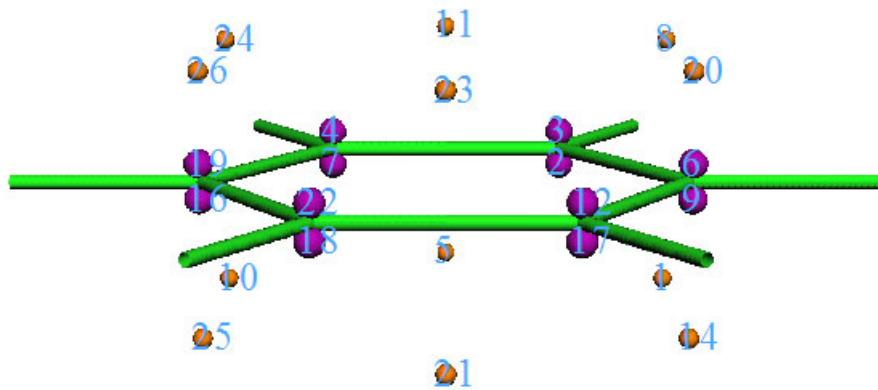


Let us use way 2 to calculate ELF- $\pi$  again, in principle this way is more rigorous than way 1. Choose 0 to return to main menu.

```

2 // Topology analysis
-11 // Select real space function
9 // Select ELF
6 // This searching mode is the most appropriate one for locating ELF CPs
-1 // Start the search. The guessing points will be scattered around each atom in turn.
-9 // Return to upper menu
0 // Visualize results. The resultant graph are shown below, two (3,+1) CPs are not shown

```



Compare this graph with ELF isosurface map, it clear that the (3,-1) CPs (orange) are bifurcation position of ELF domains. While (3,-3) CPs (purple) correspond to the maximal points of the twelves ELF domains. Now we check the ELF value at (3,-1) CPs, we can choose any one, since they are equivalent.

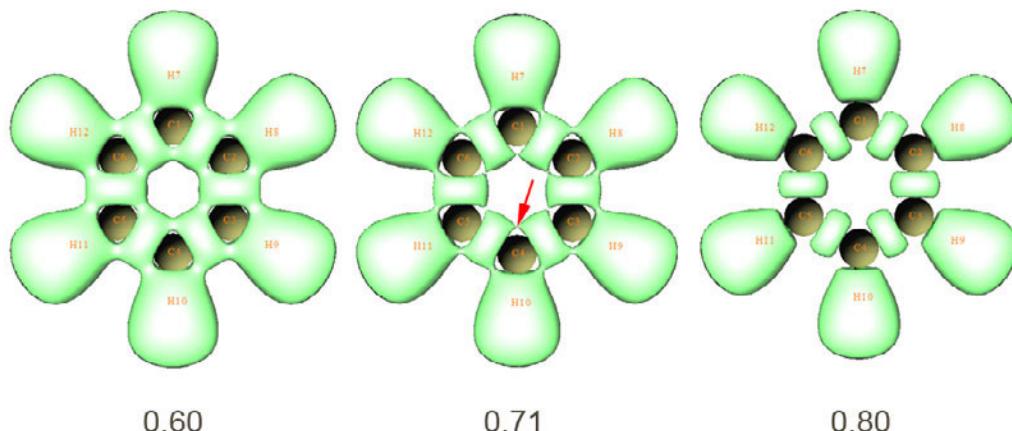
```

7 // Show all properties at a CP
23 // The CP with index of 23

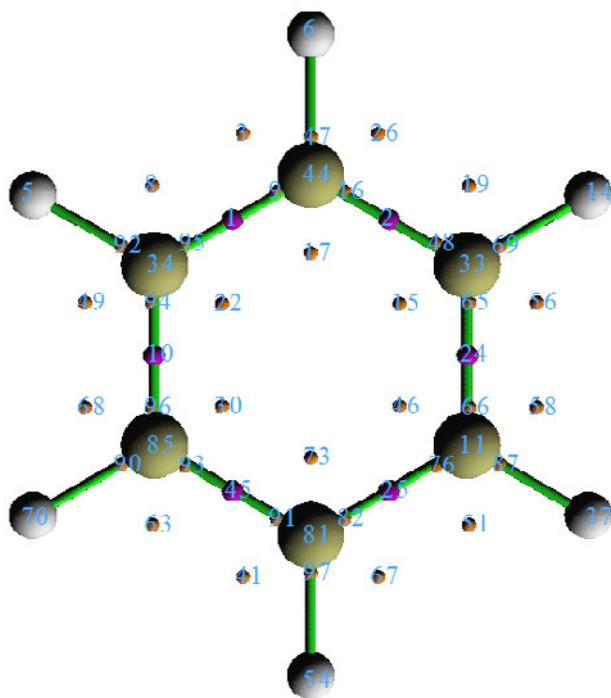
```

From the output, we find the ELF value at CP 23, namely ELF- $\pi$  of benzene is 0.91247, this result is in very good agreement with the value 0.913 given in *Chem. Phys. Lett.*, 443, 439. Evidently, this value exceeds the criteria (0.70) of  $\pi$  aromaticity, which implies that benzene has strong  $\pi$  aromaticity.

Now we calculate ELF- $\alpha$  for benzene. Reboot Multiwfn and load benzene.wfn, set occupation number of MO 17, 20 and 21 to zero (it is the most convenient to use option 22 in main function 100 to do this). Then generate isosurface for ELF as usual, gradually adjust isovalue, find out at which isovalue the domains correspond to the  $\alpha$ -bonds between carbon atoms are bifurcated. One can find at the isovalue equals to 0.71 the domain are bifurcated, suggesting that ELF- $\alpha$  is about 0.71, the bifurcation point is pointed by red arrow shown below:



Enter topology analysis module and search ELF CPs, like what we did in way 2 of ELF- $\pi$  analysis. You will obtain below graph. For clarity, (3,+1) and (3,+3) CPs are hidden.



Compare positions of CPs with ELF isosurface map, it is clear that the (3,-1) CPs such as CP 73 correspond to bifurcation points of the  $\alpha$ -bond domains between carbon atoms, check the ELF value at CP 73, we get 0.70907, this is the accurate ELF- $\alpha$  value. Our result agrees with the value 0.717 from *Chem. Phys. Lett.*, 443, 439.

The average of ELF- $\alpha$  and ELF- $\pi$  is  $(0.70907+0.91247)/2=0.81077$ , which is larger than the

criteria of global aromaticity. So benzene possesses global aromatic character.

#### 4.5.4 Use Fukui function and dual descriptor to study favorable site for electrophilic attack of phenol

##### Fukui function

Fukui function is an important concept in conceptual density functional theory, it has been widely used in prediction of reactive site. Fukui function is defined as (*J. Am. Chem. Soc.*, **106**, 4049)

$$f(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_{\nu}$$

where  $N$  is number of electrons in present system, the constant term  $\nu$  in the partial derivative is external potential. Generally the external potential only comes from nuclear charges, so  $\nu$  can be seen as nuclear coordinates for isolated chemical system. It is argued that reactive sites have larger value of Fukui function than other regions. We cannot directly evaluate the partial derivative due to the discontinuity when  $N$  is integer. In the finite difference approximation, Fukui function can be calculated unambiguously for three situations:

$$\text{Nucleophilic attack: } f^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \approx \rho^{\text{LUMO}}(\mathbf{r})$$

$$\text{Electrophilic attack: } f^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \approx \rho^{\text{HOMO}}(\mathbf{r})$$

$$\text{Radical attack: } f^0(\mathbf{r}) = \frac{f^+(\mathbf{r}) + f^-(\mathbf{r})}{2} = \frac{\rho_{N+1}(\mathbf{r}) - \rho_{N-1}(\mathbf{r})}{2} \approx \frac{\rho^{\text{HOMO}}(\mathbf{r}) + \rho^{\text{LUMO}}(\mathbf{r})}{2}$$

In this example, we first attempt to find out the reactive sites for electrophilic attack of phenol by means of Fukui function given above. The approximate form of Fukui function based on frontier orbitals will not be used here.

First of all, use quantum chemistry program to optimize structure and generate .wfn file for neutral state phenol, and then generate another .wfn file for phenol with charge of +1. Notice that at the second step you only need to change the charge and multiplicity to 1 and 2 respectively from 0 and 1, do not reoptimize molecule structure for +1 state phenol, because  $\nu$  (nuclear coordinates in this context) is defined as constant in the partial derivative of Fukui function. I assume that the two .wfn files are named as phenol.wfn and phenol+1.wfn, you can find them in “examples” directory.

For studying the isosurface of  $f^-$ , you can generate cube files for the two .wfn files separately by main function 5 of Multiwfn and then calculate the difference cube file by main function 13, and then visualize the cube file. However this work is more convenient to be achieved via “custom operation” function in Multiwfn (see Section 3.7.1 for detail), just boot up Multiwfn and input following commands:

*examples\phenol.wfn //Calculated at HF/6-31G\* level*

5

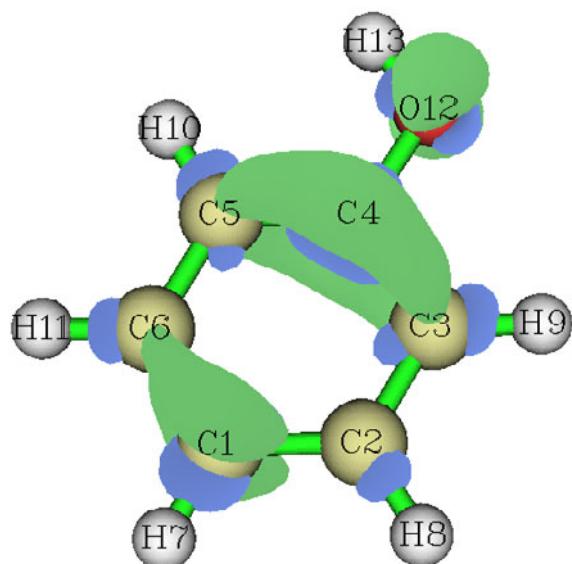
0 // Set custom operation

1 // Only 1 file will be operated with the file has been loaded (namely phenol.wfn)  
 $\text{-, examples}\backslash\text{phenol+1.wfn}$  // “-“ is minus operator, that means the property of phenol.wfn will minus corresponding property of phenol+1.wfn, which is the wavefunction of the phenol with +1 net charge (corresponds to  $N-1$  electron state)

1 // Electron density

2 // Medium quality grid

Now Multiwfn starts to calculate electron density grid data for phenol.wfn, and then calculate for phenol+1.wfn, finally the grid data of phenol.wfn, namely  $\rho_N$ , will minus the grid data of phenol+1.wfn, namely  $\rho_{N-1}$ , the result is  $f^-$ . Let's choose option -1 to check the isosurface, after adjusting the isovalue to a proper value (0.007), the graph will be



Clearly, most positive part of  $f^-$  function are localized in O12, C1, C3, C4 and C5, that means *para* and *ortho* positions of hydroxyl are favourite reactive sites for electrophilic attack, this conclusion is in agreement with empirical rule, that is hydroxyl is an *ortho-para-* director.

### Dual descriptor

Dual descriptor is another useful function used to reveal reactive sites, see *J. Phys. Chem. A*, **109**, 205 for detail. Formally, the definition of the dual descriptor  $\Delta f$  has close relationship with Fukui function:

$$\begin{aligned}\Delta f(\mathbf{r}) &= f^+(\mathbf{r}) - f^-(\mathbf{r}) \\ &= [\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})] - [\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] = \rho_{N+1}(\mathbf{r}) - 2\rho_N(\mathbf{r}) + \rho_{N-1}(\mathbf{r})\end{aligned}$$

Worthnotingly, dual descriptor can also be evaluated in terms of spin density  $\rho^s$ . Since  $\rho_{N+1} - \rho_N$  and  $\rho_N - \rho_{N-1}$  can be approximated as  $\rho_{N+1}^s$  and  $\rho_{N-1}^s$  respectively, it is clear

#### 4 Tutorials and Examples

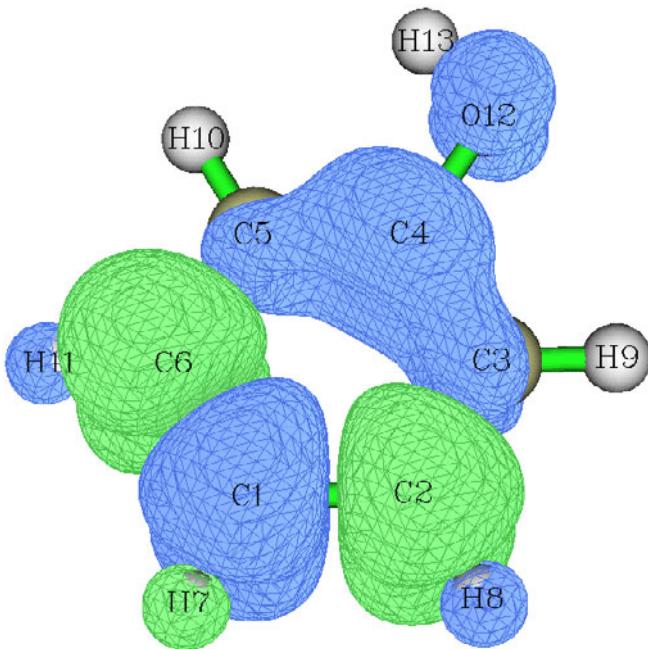
that  $\Delta f(\mathbf{r}) \approx \rho_{N+1}^s(\mathbf{r}) - \rho_{N-1}^s(\mathbf{r})$ . Commonly, there is no evident qualitative difference between the dual descriptor evaluated based on electron density of three states ( $N+1, N, N-1$ ) and the one based on spin density of two states ( $N+1, N-1$ ).

Unlike Fukui function, via  $\Delta f$  both types of reactive sites can be revealed simultaneously. It is argued that if  $\Delta f > 0$ , then the site is favorable for a nucleophilic attack, whereas if  $\Delta f < 0$ , then the site is favorable for an electrophilic attack. However, according to my experience, if your aim is to figure out which ones are more favorable among many potential sites, you do not need to concern the sign of  $\Delta f$ , you only need to study which sites have more positive or more negative of  $\Delta f$ . If the distribution of  $\Delta f$  around a site  $A$  is more positive than another site  $B$ , then one can say  $A$  is a more favorable site for nucleophilic attack than  $B$ , and meantime  $B$  is a more preferential site for electrophilic attack than  $A$ .

Here we calculate dual descriptor for phenol based on spin density of  $N+1$  and  $N-1$  states. Since we have calculated phenol+1.wfn earlier, now we only need to calculate phenol-1.wfn (this file has been provided in "example" folder). After that boot up Multiwfn and input:

```
examples\phenol-1.wfn // Corresponds to N+1 electron system
5
0 // Set custom operation
1 // Only one file will be operated with the file that has been loaded
-,examples\phenol+1.wfn // Corresponds to N-1 electron system
5 // Electron spin density
2 // Medium quality grid
4 // Change the isovalue
0.005
-1 // Visualize isosurface of dual descriptor
```

Change isosurface style to "solid face+mesh" from menu of the GUI, then you will see below graph. The region covered by negative isosurfaces (blue) suggests that only *para*- and *ortho*-carbons were activated for electrophilic attack by hydroxyl, this conclusion is in agreement with Fukui function.



If you would like to evaluate  $\Delta f$  in its exact form (based on  $\rho$  of three states), you can follow below steps:  
 examples\phenol-1.wfn // N+1 electron system

```

5
0 // Set custom operation
3 // Three files will be operated with the file that has been loaded
-examples\phenol.wfn // N electron system
-examples\phenol.wfn // N electron system
+examples\phenol+1.wfn // N-1 electron system
1 // Electron density
  
```

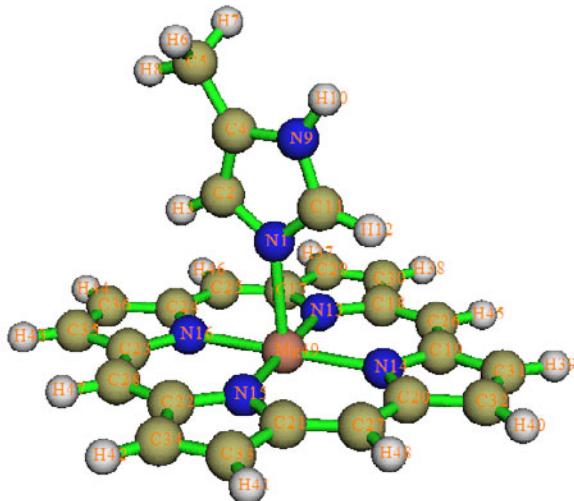
The remaining steps are identical as above. If you visualize the isosurface, you will find this time the ortho-carbons do not have negative value of  $\Delta f$ , they are only very slightly more negative than the para- carbons, that means this time  $\Delta f$  does not have good ability to discriminate preferential sites. So, using exact form to evaluate  $\Delta f$  does not necessarily give rise to better result than using spin density to approximately evaluate  $\Delta f$ !

Above we used visualization manner to examine Fukui function and dual descriptor and obtained the conclusion what we expected. However, visual analysis is somewhat ambiguous and the discussion is inconvenient to be given in literature. Therefore sometimes we hope that the discussions of Fukui function and dual descriptor can be quantified, namely using a value for each atom to indicate the probability that it can be acted as reactive site. To do so, one should calculate "condensed" version of Fukui function and dual descriptor based on population analysis techniques. Since population analysis is exemplified in Section 4.7, the method for calculating condensed Fukui function and condensed dual descriptor will be deferred to be introduced as Section 4.7.3. Another scheme to study Fukui function and dual descriptor is to first partition the whole molecular surface to local surface corresponding to each atom, and then examine the their average values on these local surfaces. Because this scheme relies on quantitative molecular surface analysis technique, it will be deferred to be illustrated in Section 4.12.4.

#### **4.5.5 Plot difference map of electron density to study electron transfer of imidazole coordinated magnesium porphyrin**

In this example, I will show you how to do fragmental electron density difference in

Multiwfn. It can be imagined that during the course of imidazole coordinating to magnesium porphyrin, electron density transfer occurs, the variation can be made clear by subtracting electron density of imidazole (referred to as NN below) and magnesium porphyrin (referred to as MN below) in standalone state from the whole system (referred to as MN-NN below). The geometry of MN-NN is shown below:

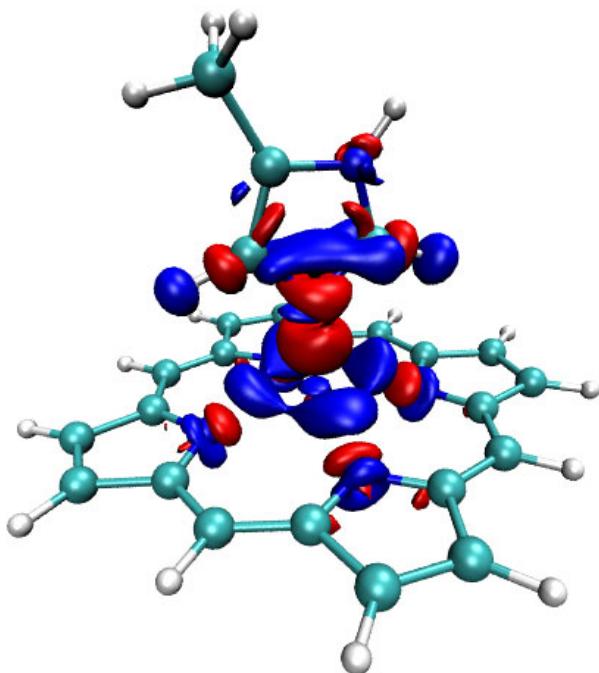


MN-NN.gjf in "examples" folder is Gaussian input file of MN-NN system (geometry has been optimized), run it by Gaussian after modifying the wfn output path at the last line, then MN-NN.wfn will be yielded. Next, respectively delete MN and NN parts from MN-NN.gjf and properly modify wfn output path and then save it as MN.gjf and NN.gjf (which have already been provided in "example" folder). Then run them by Gaussian to produce MN.wfn and NN.wfn. It should be paid attention that by default, Gaussian always puts input orientation to standard orientation, which will make the coordinates in MN.wfn and NN.wfn inconsistent with MN-NN.wfn, and thus the density difference will be meaningless. So "**"nosymm"**" keyword must be specified in route section to avoid the automatic adjustment of coordinates.

Now we generate grid data of fragmental electron density difference by Multiwfn. Boot up Multiwfn and input following commands

```
MN-NN.wfn
5
0 // Set custom operation
2 // Two files will be operated with MN-NN.wfn
-,MN.wfn // Subtract a property of MN.wfn from that of MN-NN.wfn
-,NN.wfn // Subtract a property of NN.wfn from that of MN-NN.wfn
1 // The property is selected as electron density
3 // Since present system is relative huge, we need more grid points than normal cases
```

After the calculation is finished, you can choose option -1 and then set isovalue to about 0.001 to visualize the isosurface of the grid data. However Multiwfn is not very professional at visualization of grid data, for large size of grid data the visualization speed is relatively slow; you can choose option 2 to export the grid data to cube file and then visualize it by external tools, such as VMD, ChemCraft, Molekel and GaussView. Below is the graph generated by VMD (<http://www.ks.uiuc.edu/Research/vmd/>), which is my favourite tool.



The red and blue isosurfaces (+0.0012 and -0.0012 a.u., respectively) represent the region in which electron density is increased and decreased after NN coordinated to MN, respectively. It is obvious that electron density is shifted from backside of nitrogen in NN toward magnesium atom to strengthen the coordination bond. Besides, the appearance of NN didn't perturb electron density distribution of porphyrin remarkably, only slight polarization effect occurs in the four coordination nitrogens of MN (by lowering iso value you may obtain richer information, but they can be ignored due to the small magnitude).

The detail step of drawing above graph in VMD: First drag the cube file density.cub into VMD main window. Select Graphics-Representations, create a new representation by clicking "Create Rep" button, change the "drawing method" to "isosurface", set "Draw" to "solid surface", set "Show" to "Isosurface", change the iso value to 0.0012, set "coloring method" to "ColorID" and choose red. Now the isosurface of positive part of density difference has been displayed. Then click "Create Rep" button again to create another representation, select blue in "ColorID" and change the iso value to -0.0012. If you would like to use white background instead of the default black background, select Graphics-Colors-Display-Background-8 white.

Next, let's generate contour map of fragmental electron density difference in the plane defined by atoms 16, 14, 9. Input following commands:

```

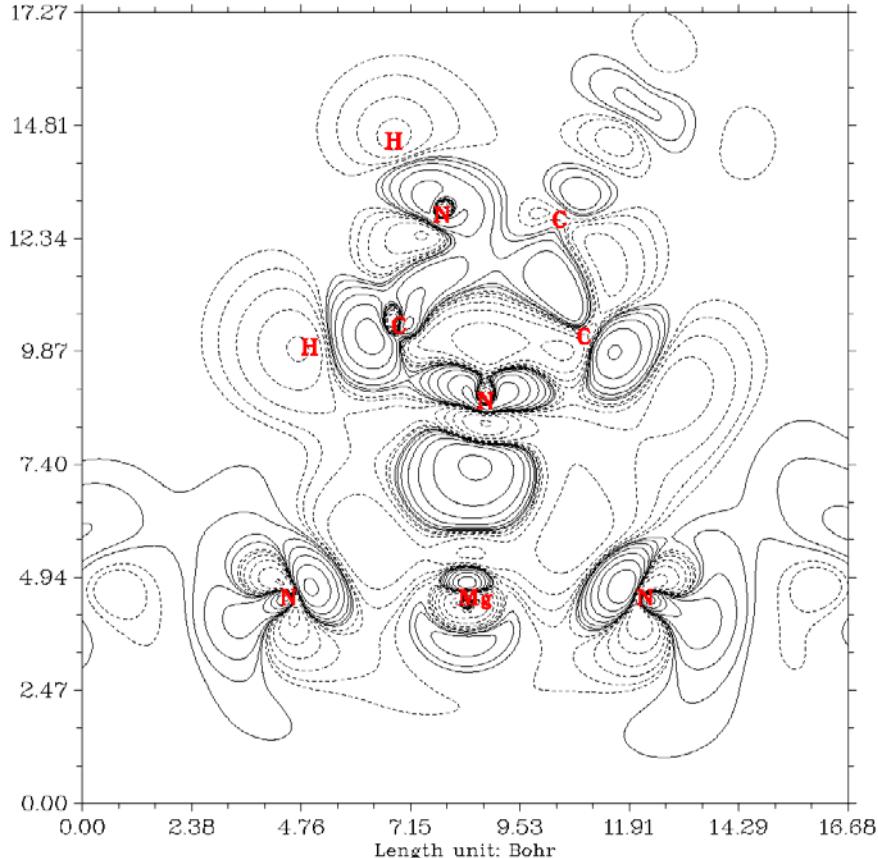
0 // Return to main menu
4 // Draw plane graph
0
2
-,MN.wfn
-,NN.wfn
1
2 // Contour line map
Press ENTER to use default setting
4 // Define the plane by three atoms
16,14,9

```

Immediately the contour map pops up. The solid and dashed contour lines exhibit where electron density is increased and decreased, respectively. The contour lines in the graph are a bit sparse; let's adjust contour line setting to make the graph look denser. Click right mouse button on the window to close it, and input

```
3 // Change contour line setting
9 // Generate contour value by geometric series
0.0001,2,30 // Start value, step size and the number of steps, respectively
y // Clean existed contour lines
9
-0.0001,2,30 // Set negative contour lines
n // Append the contour lines to existed ones
I // Save setting and return
-1 // Redraw the graph
```

Below is the final graph you will see, quite pretty!



Hint: After finished setting contour lines, you can choose option 6 to save the setting to external plain text file. Next time you can directly load the setting by option 7.

## 4.6 Modify wavefunction

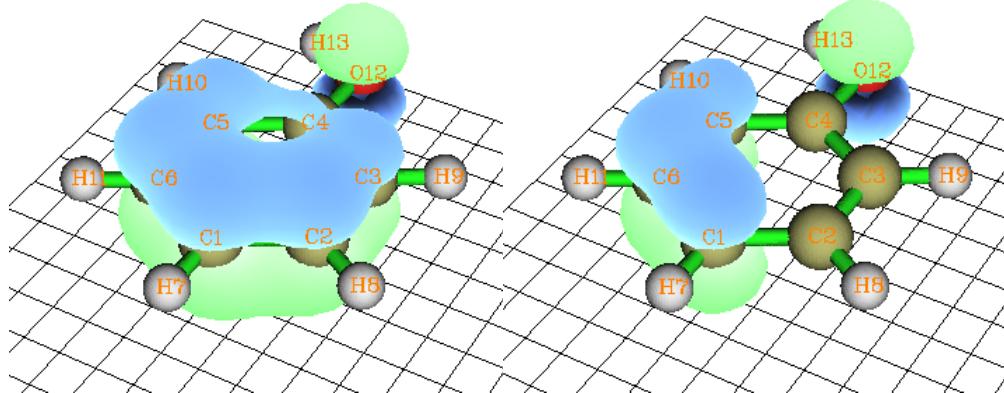
### 4.6.1 Delete certain Gauss functions

In subfunction 25 of main function 6, you can set orbital expansion coefficients of Gauss type

functions (GTFs) which satisfied certain conditions. If the coefficients are set to zero, that means the information of these GTFs are deleted. In this example, we delete all Z-type GTFs of atom 2,3 and 4 from orbital 23 of phenol and then plot isosurface for this molecular orbital. Boot up Multiwfn and input following commands

```
examples\phenol.wfn
6 // Modify wavefunction
25 // Set the coefficients of some GTFs that satisfied certain conditions
0,0 // Set the index range of GTFs, only the GTFs satisfied this condition will be reserved to next step. 0,0 tell Multiwfn the range is "ALL"
2,4 // Only the GTFs attributed to atom 2, 3, 4 will be reserved to next step
Z // Only reserve Z-type GTFs to next step
23,23 // Set lower and upper limit of orbital, if they are identical, then only one orbital is selected
0 // Set coefficients of selected GTFs in orbital 23 to zero, that is delete their information
0 // Save current wavefunction to new.wfn in current directory

You can choose option 4 and input 23 to check expansion coefficient of orbital 23 to verify if your operation is correct. Let's compare the isosurfaces of orbital 23 before and after modification. In order to plot the modified orbital 23, you can close Multiwfn and load new.wfn, or directly select option -1 to return main menu, and then enter main function 0 to plot the isosurface of orbital 23.
```



Left side is unmodified state, the molecular plane is parallel to XY plane, so if Z-type GTFs in some atoms are deleted, the corresponding part of isosurface should disappear, this is what we have seen at right side (modified state).

#### 4.6.2 Remove contributions from certain orbitals to real space functions

In Multiwfn, contributions from certain orbitals to real space functions can be removed. From formulae in Section 2.6 it is clear that if occupation numbers of certain orbitals are set to zero, they will have no contribution, as if they were not existed. Actually in Section 4.5.3 we have already used this trick to separate ELF as ELF- $\alpha$  and ELF- $\pi$ . Notice that some real space functions are not linear, such as ELF and LOL, so they cannot be computed as the sum of contributions from each occupied orbitals. In contrast, some real space functions are linear, such as electron density

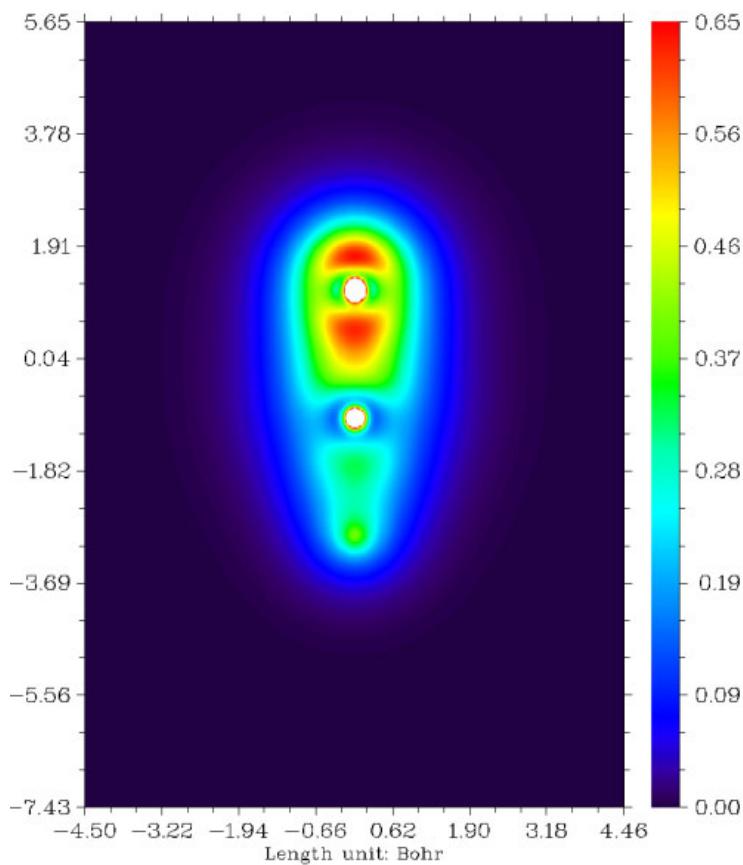
and kinetic energy density.

In this example, we will remove contributions from the MOs consist of inner-core atomic orbitals to electron density for hydrogen cyanide, so that we can obtained valence electron density map.

The principle is very sample. Inner-core atomic orbitals always have very low energies, so they can only compose MOs with the lowest energies. Hydrogen has no inner-core atomic orbital, both carbon and nitrogen have one inner-core atomic orbital, hence what we need to do is to set occupations numbers of the first two MOs to zero (assume that this is close-shell wavefunction). Now boot up Multiwfn, and input following commands

```
examples\HCN.wfn
6 //Modifying wavefunction
26 // Set occupation numbers
1,2 // Select MO 1 and 2
0 // Set their occupation numbers to zero
q // Return to last menu
-1 // Return to main manu
```

Then, if we redo the example in Section 4.4.1, we will get below graph



From the picture we find that the white circles in carbon and nitrogen center are largely contracted, this is because the contributions from their 1s atomic orbitals are removed. Electron structures are exhibited more clearly in this picture than in Secton 4.4.1.

For convenience consideration, Multiwfn provides function 34 in main function 6, one can directly choose it to set occupation numbers of the MOs that consist of inner-core atomic orbitals to zero.

### 4.6.3 Translate and duplicate graphene primitive cell wavefunction to periodic system

The .fch or .wfn file generated by periodic boundary condition (PBC) calculation of Gaussian only contains wavefunction of primitive cell, so the analysis results do not show any periodic character, of course you can enlarge your inputted system to multiple cells before PBC calculation, but you have to spend much more time for computation. Multiwfn provides a way to convert primitive cell wavefunction to a large supercell wavefunction, so that in the region you are interested the real space functions show periodic character.

Note: Beware that constructing supercell wavefunction in this manner is only a crude approximation! Since the orbital mix between neighbouring primitive cells is ignored, therefore the orbital wavefunctions of supercell cannot be faithfully reproduced.

In this section I use graphene as example. First, generate .fch (or .wfn) file of graphene primitive cell. The content of “molecular specification” field in the Gaussian input file is

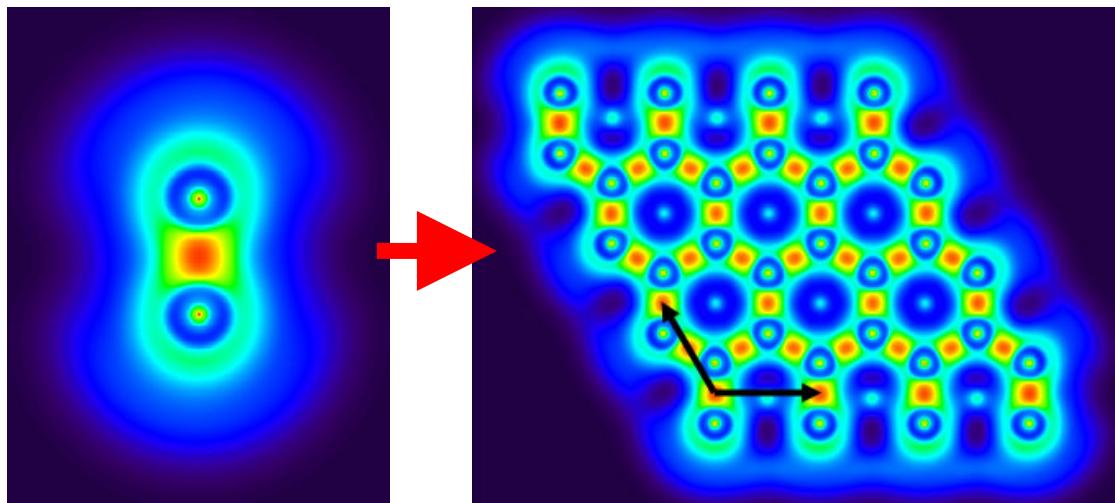
C	0. 000000	0. 000000	0. 000000
C	0. 000000	1. 429118	0. 000000
TV	2. 475315	0. 000000	0. 000000
TV	-1. 219952	2. 133447	0. 000000

In route section, fill “#P PBEPBE/3-21g/Auto SCF=Tight”. Use Gaussian to run this input file and then use formchk to convert the binary checkpoint file to graphene.fch. Then boot up Multiwfn and input:

```
examples\graphene.fch
6
32 // Translate and duplicate primitive cell wavefunction
2.475315    0.000000    0.000000 // Translation vector 1
2 // Unit is Angstrom
3 // Translate and duplicate present system three times in this direction
32 // Notice that current system already have four primitive cells, this time we will translate
and duplicate current system in another direction three times, so the final system will contain 16
primitive cells
-1.219952    2.133447    0.000000 // Translation vector 2
2 // Unit is Angstrom
3 // Translate and duplicate present system three times in this direction
```

The left part of the picture below is LOL function of primitive cell. After above manipulation, we recalculate LOL function and then the right graph is obtained (black arrows denote translation vectors). Apparently, the central region of the extended system shows correct periodic character, however the behavior of boundary region is still incorrect, you can extend the system further to enlarge “correct” region.

Notice that if “nosymm” keyword is not specified in PBC calculation, Gaussian may automatically put the system into standard orientation, at this time you should not use the translation vectors in Gaussian input file as the translation vectors for translating and duplicating system in Multiwfn, but should use the content in “Translation vectors” field of .fch file or “PBC vector” segment in Gaussian output file.



## 4.7 Population analysis

### 4.7.1 Calculate Hirshfeld and CHELPG charges for chlorine trifluoride

I have introduced the theory of Hirshfeld population in Section 3.9.1, to calculate Hirshfeld charges for  $\text{ClF}_3$ , input below commands in Multiwfn

```
examples\clf3.wfn
7 // Population analysis
1 // Hirshfeld population
```

Hirshfeld population analysis requires electron density of atoms in their free-states, you need to choose a method to calculate atomic densities. Selecting 1 to use built-in atomic densities is very convenient, see Appendix 3 for detail; alternatively, you can select 2 to evaluate atomic densities based on atomic .wfn files, see Section 3.7.3 for detail. Here we choose option 1.

From the result we find the charges of the three fluorine atoms are unequal, the equatorial one is -0.075 while the axial ones have more electrons, are -0.224.

Finally Multiwfn asks you if exporting the result, if you select ‘y’, the element names, atom coordinates and atomic charges will be outputted to a plain text file with .chg extension. You can use this file as Multiwfn input and select “Electrostatic potential from atomic charges” in main function 3, 4 or 5 to study the electrostatic potential distribution from Hirshfeld charges.

Next, we calculate CHELPG charge. CHELPG charge has been introduced in Section 3.9.10. First select option 12 in the population analysis module, you will see a new menu, in general you do not need to modify the default options, and you can directly select option 1 to start the calculation. Since calculation of ESP is time-consuming, for large system you may need to wait for a while. The result is 0.5772 for Cl, -0.2496 for axial F and -0.0779 for equatorial F. The conclusion of CHELPG charge is the same as Hirshfeld charge, namely axial F are more negatively charged than the equatorial one.

Fragment charge is defined as the sum of charge of atoms constituting a fragment, it is useful

to study net charge of local regions, such as a group. You can manually sum up atomic charges to derive fragment charge; however, for large systems this process may be laborious. In Multiwfn it is possible to directly calculate fragment charge, for doing this you should first enter main function 7, select option "-1 Define fragment" and then input atomic indices. After that, once atomic charges are calculated by a chosen method, the fragment charge will be shown together.

#### 4.7.2 Calculate and compare ADCH charges with Hirshfeld charges for acetamide

The ADCH (atomic dipole moment corrected Hirshfeld population) charge proposed by me is an improved version of Hirshfeld charge, which resolved many inherent drawbacks of Hirshfeld charge, such as poor dipole moment reproducibility, see Section 3.9.9 for brief introduction and *J. Theor. Comput. Chem.*, **11**, 163 (2012) for discussion and comparison. I highly recommend using ADCH charge to discuss charge distribution. The calculation process of ADCH charges is exactly identical to the one described in last section, the only difference is that you should select option 11 rather than option 1 in population analysis interface. For example, we calculate ADCH charge for CH<sub>3</sub>CONH<sub>2</sub>. Boot up Multiwfn and input

*examples\CH3CONH2.fch*

7

11

1

Multiwfn will calculate Hirshfeld charge first, and then perform atomic dipole moment correction for them to yield ADCH charges. The result is shown below

```
===== Summary of atomic dipole moment corrected (ADC) charges =====
Atom: 1C Corrected charge: -0.265810 Before: -0.090370
Atom: 2H Corrected charge: 0.096194 Before: 0.037254
Atom: 3H Corrected charge: 0.105928 Before: 0.043058
Atom: 4H Corrected charge: 0.117916 Before: 0.048339
Atom: 5C Corrected charge: 0.271667 Before: 0.170596
Atom: 6O Corrected charge: -0.364284 Before: -0.308866
Atom: 7N Corrected charge: -0.676238 Before: -0.159120
Atom: 8H Corrected charge: 0.355141 Before: 0.131920
Atom: 9H Corrected charge: 0.359404 Before: 0.127108

Note: The values shown after "Corrected charge" are ADCH charges, the ones after
      "Before" are Hirshfeld charges
```

Total dipole from ADC charge(a.u.) 1.4367898 Error: 0.0001153

X/Y/Z of dipole moment from the charge(a.u.) 0.0432323 -1.4253551 0.1756673

It is obvious that for all atoms, the magnitude of ADCH charge are evidently larger than Hirshfeld charges, the former are well in line with common chemical senses, while the latter turns out to be too small.

A remarkable feature of ADCH charges is that the molecular dipole moment can be exactly

reproduced by ADCH charges! The dipole moment derived from ADCH charges is 1.4368 a.u. (as shown above), which is exactly identical to the actual dipole moment, namely the one derived from present electron density distribution. (The error 0.0001153 comes from numerical accuracy aspects and is totally negligible).

If you scroll up the command-line window, you will find following information

Total dipole from atomic charges: 1.073849 a.u.

This is the dipole moment derived from Hirshfeld charges, which deviates to actual dipole moment (1.4368) apparently. In fact, for almost all small molecules, Hirshfeld charge always severally underestimates molecular dipole moments.

### 4.7.3 Calculate condensed Fukui function and condensed dual descriptor

In Section 4.5.4, I have introduced how to calculate and visualize Fukui function and dual descriptor. In this section, we will calculate "condensed" version of these two functions, so that the discussion of the possibility that an atom could act as a reactive site can be upgraded to quantitative level. Phenol will still be used as example case.

Before calculating phenol, we first derive the expression of condensed Fukui function and condensed dual descriptor. In the condensed version, atomic population number is used to represent the amount of electron density distribution around an atom. Recall the definition of Fukui function  $f^+$ :

$$f^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})$$

The definition of condensed Fukui function for an atom, say A, can be written as

$$f_A^+ = p_{N+1}^A - p_N^A$$

where  $p^A$  is the electron population number of atom A.

Since atomic charge is defined as  $q^A = Z^A - p^A$ , where Z is the charge of atomic nuclear, the  $f^+$  can be expressed as the difference of atomic charges in two states (note that the two Z terms are cancelled)

$$f_A^+ = q_N^A - q_{N+1}^A$$

By analogous treatment, one can easily formulate other types of condensed Fukui function

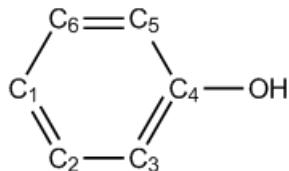
Nucleophilic attack : $f_A^+ = q_N^A - q_{N+1}^A$
Electrophilic attack : $f_A^- = q_{N-1}^A - q_N^A$
Radical attack : $f_A^0 = (q_{N-1}^A - q_{N+1}^A)/2$

Similarly, condensed dual descriptor can be written as

$\Delta f_A = f_A^+ - f_A^- = (q_N^A - q_{N+1}^A) - (q_{N-1}^A - q_N^A) = 2q_N^A - q_{N+1}^A - q_{N-1}^A$
---

There are numerous ways to calculate atomic charge, although currently there is no consensus that which method is the most suitable to calculate condensed Fukui function and dual descriptor, in my opinion, Hirshfeld charge and NPA charge are the ones most worth to be

recommended for this purpose. For example, *J. Phys. Chem. A*, **106**, 3885 illustrated how successfully is Hirshfeld charge used to study reactive site by means of condensed Fukui function.



According to the method introduced in Section 4.5.4, we calculate Hirshfeld charges for all carbons in phenol in its  $N$ ,  $N+1$  and  $N-1$  electrons states, respectively. The atomic charges are listed in below table as column 2, 3 and 4. The molecular wavefunction files used here are the same with the ones used in Section 4.5.4. By the formulae shown above, the condensed  $f^-$  and  $f^+$  and dual descriptor can be readily calculated, and they are listed below as the last three columns.

	$N$	$N-1$	$N+1$	$f^-$	$f^+$	$\Delta f$
C1	-0.0596	0.0725	-0.0992	0.1321	0.0396	-0.0925
C2	-0.0249	0.0297	-0.1620	0.0546	0.1371	0.0825
C3	-0.0597	0.0375	-0.2043	0.0973	0.1446	0.0473
C4	0.1017	0.2526	0.0619	0.1510	0.0397	-0.1112
C5	-0.0740	0.0153	-0.2112	0.0893	0.1372	0.0479
C6	-0.0276	0.0416	-0.1649	0.0691	0.1373	0.0682

Note: The Hirshfeld charges reported above were estimated based on build-in sphericalized atomic densities.

For  $f^-$ , the smallest two values occur at C2 and C6, therefore *meta* atoms are unfavorable sites for electrophilic attack.

For dual descriptor, the most positive values occur at C2 and C6, suggesting that they are the most unfavorable sites for electrophilic attack. C4 has a large negative value and hence favored by electrophilic reactant. Although the two *ortho* carbons (C3 and C5) have positive value, its magnitude is not as large as *meta* carbons, so dual descriptor indicates that *ortho* carbons are more possible than *meta* carbons to be reactive site for electrophilic attack. Our conclusion is completely in line with that of Section 4.5.4, in which we obtained the conclusion by visual inspecting isosurface of Fukui function and dual descriptor.

PS: In Section 4.5.4, when we calculate dual descriptor, we used spin density as approximation for electron density difference between two states. However, it seems that this approximation is not necessary for calculating condensed dual descriptor.

#### 4.7.4 Illustration of computing Hirshfeld-I charges

Hirshfeld-I (HI) is a more advanced technique to define atomic spaces than its predecessor (Hirshfeld). In this section I will illustrate how to compute HI charges using two systems as examples. Before reading this section please read Section 3.9.13 to gain basic knowledge of HI method and its implementation in Multiwfn.

##### (1) CH<sub>3</sub>COCl

Here we calculate HI charges for CH<sub>3</sub>COCl. Before calculation, you should properly set "gaupath" in settings.ini file to actual Gaussian executable file. Boot up Multiwfn and input

```
examples\CH3COCl.wfn // Generated at B3LYP/6-31G* level
```

```
7 // Population analysis
```

```
15 // Hirshfeld-I method
```

```
I // Start calculation with default settings
B3LYP/6-31G* // The keyword of Gaussian used to calculate atomic .wfn files
```

From the prompts shown on screen, you can find that Multiwfn invokes Gaussian to calculate atomic .wfn files for all elements involved in present molecule at various charge states. Then Multiwfn converts atomic .wfn files to .rad files, which record spherically averaged atomic radial density. The automatically generated Gaussian input file (.gjf), the resulting Gaussian output file (.out or .log) and the .rad files are all produced in "atmrad" subdirectory of current folder, you can manually inspect them if you have interesting.

Once all .rad files have been generated, Multiwfn initializes some data, and then starts to carry out HI iteration, the convergence status can be seen on the screen:

```
Cycl e 1
Cycl e 2 Maxi mum change: 0.215441
Cycl e 3 Maxi mum change: 0.154451
Cycl e 4 Maxi mum change: 0.105326
Cycl e 5 Maxi mum change: 0.080011
...

```

The "maximum change" denotes the maximum change of HI atomic charges, the iteration continues until "maximum change" is smaller than the given criterion. After convergence, Multiwfn prints final HI atomic charges:

```
Atom 1(C ): -0.667920
Atom 2(H ): 0.194766
Atom 3(H ): 0.188545
Atom 4(H ): 0.194766
Atom 5(C ): 0.755439
Atom 6(O ): -0.414041
Atom 7(Cl): -0.251555
```

Then you can choose if outputting these charges to .chg file in current folder. I suggest you compare above result with Hirshfeld charges, you will find the magnitude of HI charges is much higher than Hirshfeld charges. This phenomenon is expected, because HI atomic spaces properly contract or expand with respect to that of neutral state according to actual chemical environment, hence the difference of diffuse extent of atomic space between various atoms is greatly increased.

If you do not delete the "atmrad" folder or clean it up, then when you recalculate HI charges for CH<sub>3</sub>COCl, or calculate a molecule only consisting of C, H, O and Cl elements (or some of them), Multiwfn will directly perform HI calculation based on existing .rad files in "atmrad" folder rather than invokes Gaussian to calculate any new file.

## (2) Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>

The Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.wfn in "examples" folder was calculated by B3LYP functional, Lanl2DZ pseudopotential basis set was used to Pt, while 6-31G\* was applied to other atoms. To calculate HI charges for this system, two steps are needed since we are unable to specify calculation level using a single set of keywords. In the first step, we arbitrarily use a file solely containing Pt atom as input file, and specify B3LYP/Lanl2DZ keyword during HI charge calculation, so that .rad files of Pt can be generated at this level. In the second step, we use Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.wfn as input file to calculate HI charges as usual, in the meantime we specify B3LYP/6-31G\* keyword to

generate .rad files for all remaining elements. The .rad files of Pt will not be calculated in this step at B3LYP/6-31G\* level because they have existed in "atmrad" folder.

Notice that "atmrad" folder should be deleted if it has existed in current folder, otherwise Multiwfn may employs old files from it. Now let's start.

Firstly, we build a .xyz file containing only one Pt atom, namely editing a plain text file named "Pt.xyz" and fill below content into it:

```
1
test
Pt 0. 0. 0.
```

Now boot up Multiwfn and input

*Pt.xyz*

```
7
15
1
```

*B3LYP/lanl2DZ* // The level used to generate .wfn files for Pt

After generation of .rad files is finished, Multiwfn suddenly crashes, because the input file does not contain wavefunction information, and thus the HI charge cannot be computed. Then boot up Multiwfn again and input below commands:

*examples\Pt(NH3)2Cl2.wfn*

```
7
15
1
```

*B3LYP/6-31G\**

From the prompts on screen you can find the files corresponding to Pt are not calculated since they have already existed. The final HI charges are

Atom	1(Pt):	0. 410827
Atom	2(Cl):	-0. 414569
Atom	3(Cl):	-0. 414549
Atom	4(N ):	-0. 928921
Atom	5(H ):	0. 382603
Atom	6(H ):	0. 382600
Atom	7(N ):	-0. 928945
Atom	8(H ):	0. 382606
Atom	9(H ):	0. 382603
Atom	10(H ):	0. 372874
Atom	11(H ):	0. 372872

The result is in good agreement with our common chemical intuition.

Worthnotingly, the support of Hirshfeld-I in Multiwfn is never limited to population analysis, this partition manner can also be used to calculate orbital composition (main function 8), and be applied in fuzzy analysis module (main function 15).

## 4.8 Molecular orbital composition analysis

In this section, I will show how to use Mulliken, NAO and Hirshfeld/Becke methods to

analyze molecular orbital composition.

These methods are also applicable to other type of orbitals, e.g. natural orbitals and localized MO. The details about orbital composition analysis can be found in Section 3.10. The pros and cons of these methods are very detailedly discussed in my paper *Acta Chim. Sinica*, **69**, 2393 (in Chinese, [http://sioc-journal.cn/Jwk\\_hxxb/CN/abstract/abstract340458.shtml](http://sioc-journal.cn/Jwk_hxxb/CN/abstract/abstract340458.shtml)). Also you can consult my post <http://sobereva.com/131> (in Chinese).

Simply speaking, if your aim is merely obtaining atom composition in orbitals, Hirshfeld/Becke method may be the most robust and convenient way, see Section 4.8.3; if you also would like to obtain atomic orbital composition, then the NAO method exemplified in Section 4.8.2 is the best choice. The Mulliken method illustrated in Section 4.8.1 also generally works well but diffuse functions must not be used.

### 4.8.1 Analyze acetamide by Mulliken method

In this example we employ Mulliken method to first analyze the composition of the 6th molecular orbital of acetamide, and then analyze which orbitals have main contribution to the bonding between formamide part and methyl group. Beware that Mulliken method is incompatible with diffuse functions, if they are involved, you should either choose other orbital composition methods (e.g. NAO, Hirshfeld...) or remove them from your basis-set.

Boot up Multiwfn and input following commands

*examples\CH3CONH2.fch* // You have to use .fch/.molden/.gms file as input for this type of analysis

8 // Orbital composition analysis

1 // Use Mulliken partition

6 // The orbital index is 6

The composition of basis functions, shells and atoms are printed immediately, see below.

```
Threshold of absolute value: > 0.500000% // Only the basis functions with composition
larger than 0.5% will be printed, you can change the threshold by "comptresh" parameter in
settings.ini.

Orbital: 6 Energy(a.u.): -0.90528995 Occ: 2.00000000 Type: Al pha&Beta
Basis Type Atom Shell Local Cross term Total
23 S 5(C ) 14 0.44902% 0.67507% 1.12409%
24 X 5(C ) 15 0.31240% 0.50522% 0.81762%
25 Y 5(C ) 15 4.25271% 5.88221% 10.13493%
29 Y 5(C ) 17 0.00777% -0.61063% -0.60286%
38 S 6(O ) 20 3.50037% 2.65507% 6.15544%
42 S 6(O ) 22 3.29488% 1.71316% 5.00803%
53 S 7(N ) 26 15.20411% 15.32688% 30.53098%
57 S 7(N ) 28 16.89006% 17.40040% 34.29046%
61 XX 7(N ) 30 0.00774% 0.58279% 0.59053%
63 ZZ 7(N ) 30 0.02793% -0.98090% -0.95297%
67 S 8(H ) 31 1.27855% 3.03091% 4.30946%
69 S 9(H ) 33 1.52931% 3.60949% 5.13880%
Sum up listed above: 46.75484% 49.78967% 96.54451%
```

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Sum up all basis functions: 51.95605% 48.04395% 100.00000%

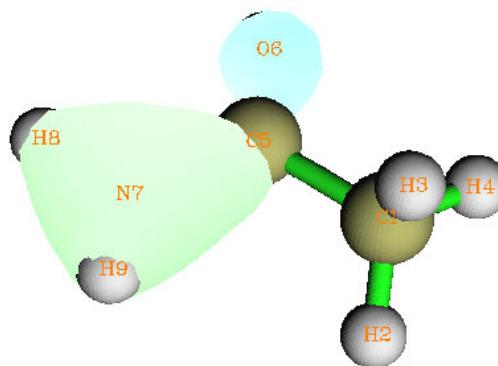
Composition of each shell, threshold of absolute value: > 0.500000%

Shell I	14	Type: S in atom	5(C ) :	1.12409%
Shell I	15	Type: P in atom	5(C ) :	10.95268%
Shell I	17	Type: P in atom	5(C ) :	-0.97156%
Shell I	20	Type: S in atom	6(O ) :	6.15544%
Shell I	22	Type: S in atom	6(O ) :	5.00803%
Shell I	26	Type: S in atom	7(N ) :	30.53098%
Shell I	28	Type: S in atom	7(N ) :	34.29046%
Shell I	31	Type: S in atom	8(H ) :	4.30946%
Shell I	33	Type: S in atom	9(H ) :	5.13880%

Composition of each atom:

Atom	1(C ) :	1.172494%
Atom	2(H ) :	0.054446%
Atom	3(H ) :	0.032119%
Atom	4(H ) :	0.008171%
Atom	5(C ) :	11.812452%
Atom	6(O ) :	11.632739%
Atom	7(N ) :	65.500850%
Atom	8(H ) :	4.470224%
Atom	9(H ) :	5.316506%

The result indicates that nitrogen has primary contribution (65.5%) to orbital 6, and the contribution consists of two S-shells (30.5% and 34.3%). P-shells of neighbour carbon and S-shells of oxygen have slight contribution too (both are about 12%). We can check if the result is reasonable by viewing isosurface (isovalue is set to 0.1 here):



From the graph, the region where the value of orbital wavefunction is large is mainly localized around nitrogen, and there is no nodal plane, so the orbital wavefunction in this region should be constructed from s-type orbitals. The isosurface also somewhat intrudes into the region of atom C5 and O6, so they should have small contribution to MO 6, moreover, because there is a

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nodal plane in C5, the atomic orbitals of C5 used to form MO 6 should be p-type. Obviously, these conclusions are in fairly agreement with composition analysis. The advantage of composition analysis is that the result can be quantified, while by visual study we can only draw qualitative conclusion, for some complex system we cannot draw even qualitative conclusion.

Now let's find which molecular orbitals have main contribution to the bonding between formamide part and methyl group.

*examples\CH3CONH2.fch*

8 // Orbital composition analysis

-1 // Define fragment 1

a 1-4 // Add all basis functions in atom 1, 2, 3, 4 (methyl group) into fragment1

q // Save fragment and return to upper menu

-2 // Define fragment 2

a 5-9 // Add all basis functions in atom 5, 6, 7, 8, 9 (formamide moiety) into fragment 2

q

4 // Print composition of fragment 1 and the cross term between fragment 1 and 2 in all orbitals by Mulliken analysis. If you only defined fragment 1, then only composition of fragment 1 will be printed

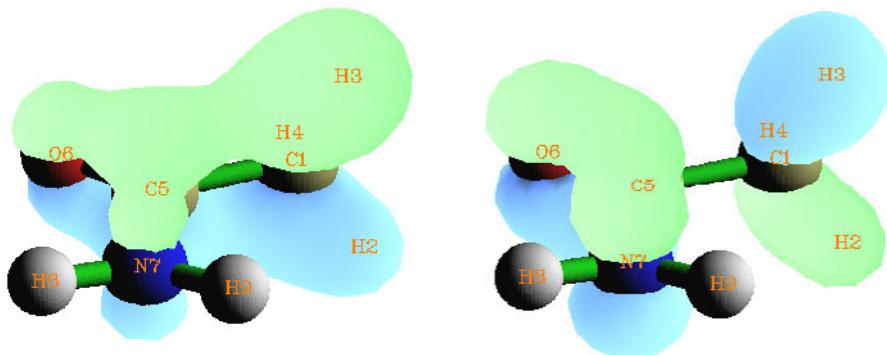
Amount of the information printed is huge, so I only extract cross term composition in all occupied orbitals:

Cross term between fragment 1 and 2 and individual parts:

Orb#	Type	Energy	Occ	Frag1 part	Frag2 part	Total
1	AB	-19. 104	2. 000	-0. 0013%	-0. 0013%	-0. 0026%
2	AB	-14. 349	2. 000	-0. 0001%	-0. 0001%	-0. 0003%
3	AB	-10. 282	2. 000	0. 0606%	0. 0606%	0. 1211%
4	AB	-10. 184	2. 000	0. 0604%	0. 0604%	0. 1209%
5	AB	-1. 038	2. 000	0. 3535%	0. 3535%	0. 7070%
6	AB	-0. 905	2. 000	0. 7295%	0. 7295%	1. 4590%
7	AB	-0. 739	2. 000	7. 9504%	7. 9504%	15. 9008%
8	AB	-0. 588	2. 000	-1. 8755%	-1. 8755%	-3. 7510%
9	AB	-0. 541	2. 000	-0. 7506%	-0. 7506%	-1. 5011%
10	AB	-0. 466	2. 000	3. 8098%	3. 8098%	7. 6197%
11	AB	-0. 447	2. 000	5. 5270%	5. 5270%	11. 0539%
12	AB	-0. 402	2. 000	-0. 3983%	-0. 3983%	-0. 7965%
13	AB	-0. 396	2. 000	-0. 4274%	-0. 4274%	-0. 8549%
14	AB	-0. 367	2. 000	-5. 8826%	-5. 8826%	-11. 7653%
15	AB	-0. 266	2. 000	0. 1192%	0. 1192%	0. 2383%
16	AB	-0. 244	2. 000	-6. 0931%	-6. 0931%	-12. 1863%

The product of the cross term composition between fragment 1 and 2 in orbital *i* and corresponding orbital occupation number is the total Mulliken bond order between them contributed from orbital *i*. From above information we can see MO 7 and 11 are helpful for bonding, because the composition are relative large, while MO 14 and 16 are not conducive for

bonding. The isosurfaces of MO 11 (left side) and 14 (right side) are shown below, it is clear that the result of composition analysis is reasonable.



As you have seen, using Mulliken method to analyze orbital composition is very convenient. However, the result of Mulliken method is sensitive to basis-set, and is not as robust as NAO method and Hirshfeld method discussed below. Especially, do not use Mulliken method when diffuse functions are involved in your calculation, otherwise the result will be meaningless!

### 4.8.2 Analysis on water by natural atomic orbital method

In this example we analyze molecular orbital composition of water by the natural atomic orbital (NAO) method discussed in Section 3.10.4. NAO method has much better basis-set stability (i.e. insensitive to the choice of basis-set) and stronger theoretical basis than Mulliken or Mulliken-like methods (such as SCPA and Stout-Politzer).

Performing NAO method requires MO coefficient matrix in NAO basis, this matrix cannot be generated by Multiwfn itself, but Multiwfn can utilize the output information containing this matrix by stand-alone NBO program or NBO module embedded in quantum chemistry softwares. The NBO 3.1 module embedded in Gaussian program is L607. Below is a Gaussian input file for water, which will output the matrix we needed. Notice that the Gaussian task should be single point task, do not perform geometry optimization together!

```
# HF/6-31g* pop=nboread
```

Title Card Required

```
O 1
O          0. 00000000  0. 00000000  0. 11472000
H          0. 00000000  0. 75403100 -0. 45888100
H          0. 00000000 -0. 75403100 -0. 45888100
```

\$NBO NAOMO \$END

[space line]

[space line]

where *pop=nboread* keyword indicates that the texts enclosed by \$NBO and \$END, namely *NAOMO*, will be passed to NBO module. *NAOMO* keyword tells NBO module to output MO

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coefficient matrix in NAO basis.

Assume that the Gaussian output file is named as H2O\_NAOMO.out (can be found in "example" folder), we start Multiwfn and input:

```
examples/H2O_NAOMO.out // Note that DO NOT use .fch as input file!
8 // Enter orbital composition analysis module
7 // Enter NAO analysis function
```

You will find the default output mode is "Only show core and valence NAOs". Core and valence NAOs have one-to-one relationship with actual atomic orbitals, if the MO to be analyzed is occupied, in general we only need to concern these NAOs, while Rydberg NAOs can be ignored. Assume that we want to analyze MO 4, we input

```
0 // Show orbital composition of specific MO
4 // Analyze MO 4
```

Below information will appear on screen

NAO#	Center	Label	Type	Composition
1	1(O)	S	Cor(1S)	0.03132%
2	1(O)	S	Val(2S)	8.573184%
5	1(O)	px	Val(2p)	0.000000%
7	1(O)	py	Val(2p)	0.000000%
9	1(O)	pz	Val(2p)	84.088900%
16	2(H)	S	Val(1S)	3.541924%
18	3(H)	S	Val(1S)	3.541924%

Summing up the compositions listed above: 99.777261%

Rydberg composition: 0.222739%

Condensed above result to atoms:

Center	Composition
1(O)	92.693413%
2(H)	3.541924%
3(H)	3.541924%

According to the result, we can say for example, 2pz atomic orbital of oxygen has 84.09% contribution to MO 4 in current geometry. The contribution from the NAOs listed above (Rydberg composition is not included in present example) are also summed up to atom contribution according to which center they are attributed to.

Note that the sum of non-Rydberg compositions, as shown above, is not 100% rather than 99.777%. To make the physical meaning more clear, I personally recommend to manually perform renormalization process for the result, for example, the composition of 2pz should be  $84.089\%/0.99777=84.277\%$ . Since before and after the renormalization the difference is only 0.188%, the renormalization is not necessary for current case. Only when the non-Rydberg composition is unmeasurable (e.g. larger than 2%), the renormalization is indispensable.

You can further analyze specific orbital composition by inputting corresponding MO number, but here we input 0 to return to last menu. We will analyze contribution from the NAOs centered on the two hydrogens to MO 1~10.

Input -1 to enter the interface for defining fragment, and then input all to check all NAOs, we

will see:

NAO#	Atom	Label	Type	Occupancy	Energy
14	0	1	dx2y2 Ryd( 3d)	0. 00073	2. 47969
... [ignored]					
15	0	1	dz2 Ryd( 3d)	0. 00254	2. 02361
16	H	2	S Val ( 1S)	0. 52321	0. 33308
17	H	2	S Ryd( 2S)	0. 00086	0. 70497
18	H	3	S Val ( 1S)	0. 52321	0. 33308
19	H	3	S Ryd( 2S)	0. 00086	0. 70497

We input *a* 2,3, that means all NAOs attributed to atom 2 and 3 will be added to current fragment. Then input *q* to save and quit. From the prompt printed on screen you will know NAO 16, 17, 18 and 19 have presented in this fragment.

Then select option 1 and input 1,8, the contribution from the four NAOs to MO 1~8 will be shown as below

Orb. #	Core	Val ence	Rydberg	Total
1	0. 000000%	0. 119072%	0. 001568%	0. 120640%
2	0. 000000%	18. 556232%	0. 054450%	18. 610682%
3	0. 000000%	26. 557472%	0. 018050%	26. 575522%
4	0. 000000%	7. 083848%	0. 012482%	7. 096330%
5	0. 000000%	0. 000000%	0. 000000%	0. 000000%
6	0. 000000%	35. 481888%	46. 831842%	82. 313730%
7	0. 000000%	27. 557888%	61. 538418%	89. 096306%
8	0. 000000%	32. 433458%	29. 568050%	62. 001508%

Since none of the four NAOs in the fragment is core-type, the Core term is 0% in all MOs. Valence and Rydberg terms correspond to the contribution from NAO 16, 18 and NAO 17, 19 respectively. The first five MOs are doubly occupied in present system. It is clear that Rydberg NAOs have very low contribution to occupied MOs, while their contribution to virtual MOs are significant and no longer can be ignored. NAO 16 and 18 directly correspond to 1s atomic orbital of H2 and H3, so we can say the two hydrogens collectively contribute 26.56% to MO 3.

The physical meaning of Rydberg NAOs is difficult to be interpreted, and these NAOs do not directly reflect atomic orbital characteristics. It is questionable to say the two hydrogens contributed either 32.43% or 62.00% to MO 8. Although seemingly one can employ renormalization process to "annihilate" the Rydberg composition, however when Rydberg composition is too large, for example larger than 10%, this treatment will make the result lack of reliability. So it is not generally recommended to use NAO method to analyze atomic contributions to virtual MOs; for this case, the Hirshfeld or Becke method introduced in Section 3.10.5 and exemplified in next section may be the best choice.

#### 4.8.3 Analyze acetamide by Hirshfeld and Becke method

In this section, we will first use Hirshfeld method and then Becke method to analyze the MO composition of acetamide and compare the result with the one obtained by Mulliken method in Section 4.8.1. Note that Hirshfeld and Becke methods are only capable of analyzing composition of atom or fragment in orbitals, while the composition of atomic orbitals are impossible to be obtained by these approaches.

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Boot up Multiwfn and input

*examples\CH3CONH2.fch* // You can also use such as .wfn and .wfx file as input. But .wfn and .wfx files do not contain virtual orbital information!

8 // Orbital composition analysis

8 // Use Hirshfeld partition

Hirshfeld analysis requires electron density of atoms in their free-states, you need to choose a method to calculate atomic densities. Selecting 1 to use built-in atomic densities is very convenient, see Appendix 3 for detail; alternatively, you can select 2 to evaluate atomic densities based on atomic .wfn files, see Section 3.7.3 for detail. Here we choose option 1.

Then Multiwfn initializes the data, for large system you may need to wait for a while. Assume that you want to analyze MO 6, then simply input 6, the result will be printed on screen, as shown below. (Because the integrals are evaluated numerically, the sum of all terms will be slightly deviated to 100%, so Multiwfn automatically normalizes the result.)

```
Atom 1(C) : 1.553970%
Atom 2(H) : 0.248499%
Atom 3(H) : 0.154527%
Atom 4(H) : 0.037207%
Atom 5(C) : 14.924962%
Atom 6(O) : 12.109412%
Atom 7(N) : 56.338603%
Atom 8(H) : 6.687609%
Atom 9(H) : 7.945211%
```

The composition of C5, O6 and N7 are 14.92%, 12.11% and 56.34%, respectively. This result is close to the one obtained by Mulliken method (Section 4.8.1), namely 11.81%, 11.63% and 65.50%, respectively. In fact, for occupied MOs, if diffuse basis functions are not employed, in general Mulliken, NAO and Hirshfeld methods give similar results.

Now let us check the composition of 7N in MO from 14 to 19. We input

-2

7 // Atomic index

14,19 // Orbital range

You will see:

Orb#	Type	Ene(a. u.)	Occ	Composition	Population
14	Alpha&Beta	-0.3674	2.000	16.075%	0.321499
15	Alpha&Beta	-0.2661	2.000	48.508%	0.970170
16	Alpha&Beta	-0.2438	2.000	6.794%	0.135870
17	Alpha&Beta	0.0410	0.000	12.390%	0.000000
18	Alpha&Beta	0.0762	0.000	21.757%	0.000000
19	Alpha&Beta	0.1252	0.000	14.516%	0.000000

Population of this atom in these orbitals: 1.427539

where 1.427539 (namely 0.321499+0.970170+0.135870) is the total population number of N7 in MO 14~19.

PS: If the orbital range you specified is 1~16, namely all occupied MO, then the outputted value 7.1586 will be the atomic population number of N7, and its Hirshfeld atomic charge is therefore  $7.0 - 7.1586 = -0.1586$ .

The steps of analyzing orbital composition by Becke method are completely identical to that

of Hirshfeld method. Here we calculate the composition of MO 6. Boot up Multiwfn and input

*examples\CH3CONH2.fch*

```
8 // Orbital composition analysis
9 // Use Becke partition
6 // The 6th orbital
```

The result is

```
Atom 1(C) : 1.229610%
Atom 2(H) : 0.085144%
Atom 3(H) : 0.048572%
Atom 4(H) : 0.002414%
Atom 5(C) : 14.901723%
Atom 6(O) : 12.069731%
Atom 7(N) : 60.741513%
Atom 8(H) : 4.929374%
Atom 9(H) : 5.991918%
```

As you can see, the result is highly close to that produced by Hirshfeld method.

In Multiwfn it is also possible to use Hirshfeld-I partition to calculate orbital composition, however this is not commonly employed, because generating Hirshfeld-I atomic space requires additional computational cost, while the result is not greatly improved (the orbital composition computed by Hirshfeld method is already reliable and meaningful enough).

#### 4.8.4 Calculate oxidation state by LOBA method

Please read Section 3.10.7 first to comprehend basic idea of LOBA method. This is a simple and useful method to evaluate oxidation state (OS). In this section I will use two examples to illustrate this function. Notice that the implementation of LOBA in Multiwfn is incompatible with diffuse functions, if basis set containing diffuse functions is used, the result may be meaningful.

(1)  $\text{Fe}(\text{CN})_6^{3-}$

First, we use Gaussian to perform regular calculation of this system, the input file is *example\Fe(CN)6\_3-.gjf*, please run it by yourself to get *Fe(CN)6\_3-.fch* file. LOBA analysis needs localized MO (LMO), thus we use Multiwfn to carry out Pipek-Mezey orbital localization. Boot up Multiwfn and input following commands:

```
Fe(CN)6_3-.fch
200
13 // Pipek-Mezey orbital localization
1 // Only localize occupied orbitals, this is enough for LOBA analysis
Now the orbitals recorded in memory has been updated to localized orbitals
0 // Return to main interface
8 // Orbital composition analysis
100 // LOBA analysis
50 // Percentage threshold for performing LOBA
Oxidation state of atom 1(Fe) : 3
Oxidation state of atom 2(C) : 2
Oxidation state of atom 3(C) : 2
Oxidation state of atom 4(C) : 2
```

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```
Oxidation state of atom 5(C) : 2
Oxidation state of atom 6(C) : 2
Oxidation state of atom 7(C) : 2
Oxidation state of atom 8(N) : -3
Oxidation state of atom 9(N) : -3
Oxidation state of atom 10(N) : -3
Oxidation state of atom 11(N) : -3
Oxidation state of atom 12(N) : -3
Oxidation state of atom 13(N) : -3
The sum of oxidation states: -3
```

The result looks reasonable and in good agreement with chemical intuition. The sum of all oxidation states just corresponds to the total net charge of -3. However, the LOBA is not free of ambiguity, the choice of the threshold is highly arbitrary. If we input 60 instead of 50, we will see oxidation state of carbon and oxygen become 4 and -1, respectively, and the sum of oxidation states become 21. Fortunately, the OS of transition metal is never so sensitive to the choice of threshold, the iron always keeps +3 oxidation state in present case as long as the threshold is not set to very small or very large. (In my viewpoint, the most appropriate threshold for evaluating OS of transition metal is 50~60%)

### (2) Ferrocene

For this system, we will not only check OS of iron, but also check OS of C<sub>5</sub>H<sub>5</sub> fragment. The corresponding regular Gaussian input file is *example\Ferrocene.gjf*, run it by yourself to obtain corresponding .fch file, then load it into Multiwfn and perform orbital localization first as shown above, after that enter LOBA analysis interface and input below commands:

```
-1 // Define fragment
1-5,7-11 // Index of the atoms constituting the C5H5 fragment
50 // Percentage threshold for performing LOBA
```

The result is

```
Oxidation state of atom 1(C) : 2
Oxidation state of atom 2(C) : 2
Oxidation state of atom 3(C) : 2
Oxidation state of atom 4(H) : 1
Oxidation state of atom 5(H) : 1
Oxidation state of atom 6(Fe) : 2
Oxidation state of atom 7(C) : 2
Oxidation state of atom 8(C) : 2
... [ignored]
```

The sum of oxidation state: 32

Oxidation state of the fragment: -1

In this system the OS of Fe is +2, which is again reasonable. From the output it is seen that the OS of individual carbons are not useful, however, the OS of the whole C<sub>5</sub>H<sub>5</sub> fragment is a meaningful value -1.

Above two examples exhibit usefulness of LOBA method. We should always focus on OS of transition metal or OS of whole ligands, while the OS of individual atom in ligand often does not make sense.

## 4.9 Bond order analysis

### 4.9.1 Mayer bond order and fuzzy bond order analysis on acetamide

In this instance we will calculate Mayer bond order and fuzzy bond order for acetamide. Related theories have been introduced in Section 3.11.1 and 3.11.6, respectively.

We first calculate Mayer bond order. Note that calculating Mayer bond order requires basis function information, thus currently .fch/.molden/.gms file must be used as input file.

Boot up Multiwfn and input:

*examples\ CH3CONH2.fch*

9 // Bond order analysis

I // Calculate Mayer bond order

Immediately you get below output:

```
The total bond order > 0.100000
# 1:      1(C )    2(H )   0. 93802674
# 2:      1(C )    3(H )   0. 93473972
# 3:      1(C )    4(H )   0. 94494566
# 4:      1(C )    5(C )   0. 96585484
# 5:      5(C )    6(O )   1. 90392771
# 6:      5(C )    7(N )   1. 11849509
# 7:      7(N )    8(H )   0. 83250273
# 8:      7(N )    9(H )   0. 83869874
```

Total valences and free valences defined by Mayer:

Atom	1(C ) :	3. 77555991	0. 00000000
Atom	2(H ) :	0. 93147308	0. 00000000
Atom	3(H ) :	0. 92778456	0. 00000000
Atom	4(H ) :	0. 93657474	0. 00000000
Atom	5(C ) :	3. 97788022	0. 00000000
Atom	6(O ) :	2. 05925868	0. 00000000
Atom	7(N ) :	2. 85041375	0. 00000000
Atom	8(H ) :	0. 86522064	0. 00000000
Atom	9(H ) :	0. 85875080	0. 00000000

By default, only the bond order terms larger than specific criteria will be outputted, the criteria can be adjusted in "bndordthres" in settings.ini. Mayer bond order often coincide with empirical bond order well. In this example, bond order between C5 and O6 is 1.9, which is very close to ideal value 2.0 (double bonds).

Total valence of an atom is the sum of Mayer bond orders that it formed. Free valence of a atom measures its remained capacity to form new bonds by sharing electron pairs, for close-shell this quantity is always zero.

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Then if you choose "y", entire bond order matrix will be outputted to bndmat.txt in current folder.

Next, we want to try to find which orbitals have main contributions to Mayer bond order between C5 and O6, calculating the so-called "Orbital occupancy-perturbed Mayer bond order" is useful for realizing this goal. Hence, we select option 6 in bond order analysis module, and then input 5,6. Below information will be outputted:

Mayer bond order before orbital occupancy-perturbation: 1. 903928

Orbital	Occ	Energy	Bond order	Variance
1	2. 00000	-19. 10356	1. 906089	0. 002162
2	2. 00000	-14. 34920	1. 903934	0. 000006
3	2. 00000	-10. 28192	1. 905514	0. 001586
4	2. 00000	-10. 18447	1. 903939	0. 000011
5	2. 00000	-1. 03758	1. 606912	-0. 297016
6	2. 00000	-0. 90529	1. 825661	-0. 078267
7	2. 00000	-0. 73868	1. 872011	-0. 031917
8	2. 00000	-0. 58838	1. 896333	-0. 007594
9	2. 00000	-0. 54103	1. 868127	-0. 035801
10	2. 00000	-0. 46630	1. 799351	-0. 104576
11	2. 00000	-0. 44722	1. 512533	-0. 391394
12	2. 00000	-0. 40158	1. 830827	-0. 073101
13	2. 00000	-0. 39610	1. 659075	-0. 244853
14	2. 00000	-0. 36742	1. 393122	-0. 510805
15	2. 00000	-0. 26611	1. 743383	-0. 160545
16	2. 00000	-0. 24383	1. 796157	-0. 107770

Summing up occupancy perturbation from all orbitals: -2. 03987

From the output we can know that, for example, if the two electrons are removed from orbital 15, then Mayer bond order between C5 and O6 will decreased from 1.903928 to 1.743383, we can also say that the contribution from orbital 15 is 0.160545. The sum of contributions from all occupied MOs is 2.03987, the reason that this value is not equal to 1.903928 is that Mayer bond order is not a linear function of density matrix, we needn't to concern this.

Orbital 14 has the largest negative value of orbital occupancy-perturbed Mayer bond order, therefore this orbital must be greatly beneficial to the bonding. This conclusion can be further testified by visual inspection of the orbital isosurface, see the graph given at the end of Section 4.8.1. As expected, this orbital shows strong character of  $\pi$ -bonding between C5 and O6.

Now we calculate fuzzy bond order. Unlike Mayer bond order, fuzzy bond order does not rely on basis function, therefore you can also use such as .wfn/.wfx as input file. Calculating fuzzy bond order is more time consuming than Mayer bond order, its advantage over Mayer bond order is that the basis-set sensitivity is greatly reduced, and using diffuse basis functions will never deteriorate result.

In the bond order analysis menu, we select "7 Fuzzy bond order analysis", the result will be

printed, as shown below

```
The total bond order >= 0.050000
# 1:      1(C )    2(H )    0. 89666213
# 2:      1(C )    3(H )    0. 89075146
# 3:      1(C )    4(H )    0. 88888051
# 4:      1(C )    5(C )    1. 08050669
# 5:      1(C )    6(O )    0. 13600686
# 6:      1(C )    7(N )    0. 11096284
# 7:      3(H )    5(C )    0. 05357850
# 8:      5(C )    6(O )    2. 00411901
# 9:      5(C )    7(N )    1. 40339002
# 10:     6(O )    7(N )    0. 24523041
# 11:     7(N )    8(H )    0. 87233783
# 12:     7(N )    9(H )    0. 88243512
```

Comparing the result with that of Mayer bond order, you will find the results of both types of bond orders are very similar, in fact this is the common case. However, for highly polar bonds their results may deviate with each other relatively evidently.

#### 4.9.2 Three-center bond order analysis on Li<sub>6</sub> cluster

The electron structure character of complex system, such as cluster is hard to predict by simple empirical rules, we have to resort to wavefunction analysis methods. In this section we use three-center bond order to study which type of three-membered ring in Li<sub>6</sub> cluster is the most stable. We will calculate the three-member ring consisting of Li1, Li4 and Li3 first.

Notice that multi-center bond order analysis requires basis function information, therefore in current Multiwfn version, you have to use .fch/.molden/.gms file as input file.

Boot up Multiwfn and input following commands

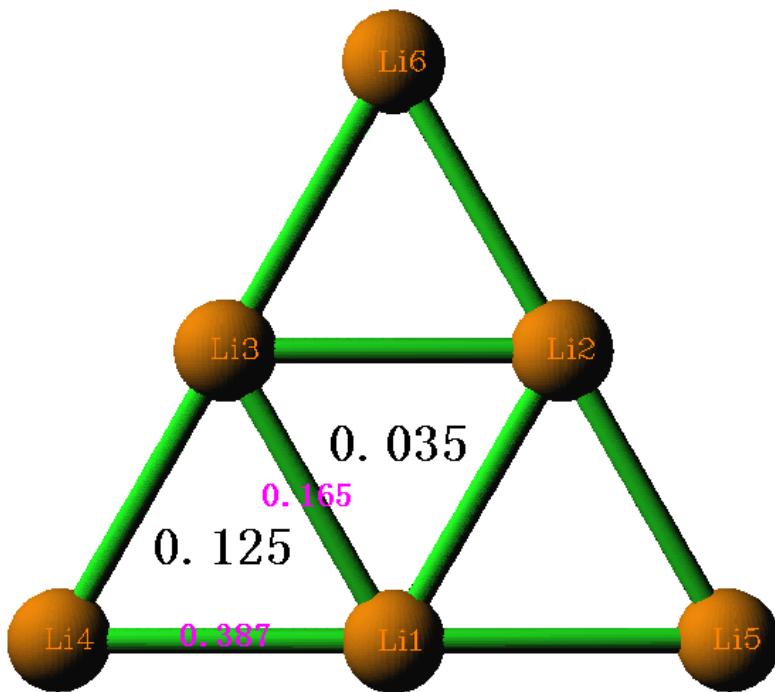
*examples\Li6.fch*

9 // Bond order analysis

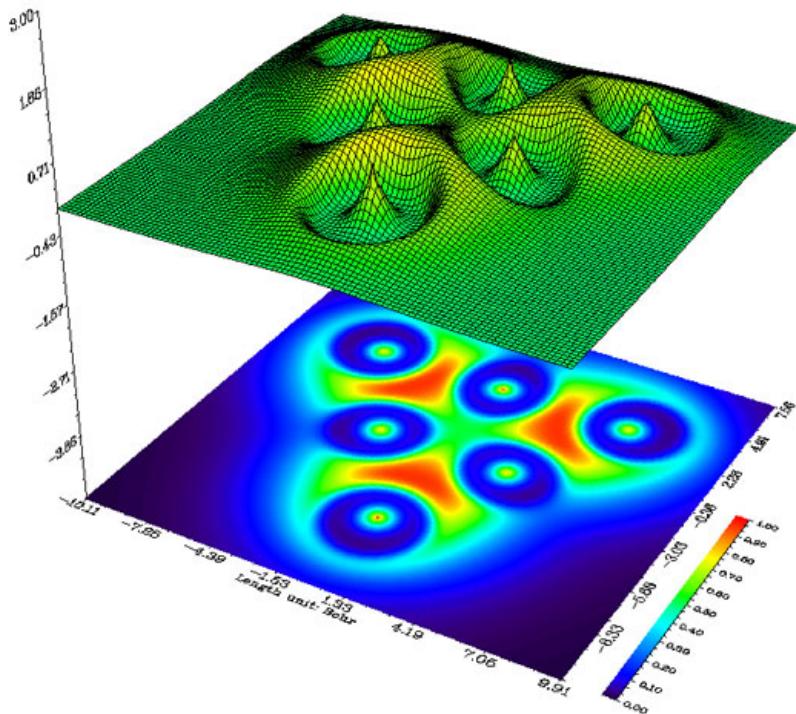
2 // Multi-center bond order analysis

1,4,3 // Input the indices of the atoms constituted the three-member ring

The result is 0.12478846. Then repeat above procedure to calculate three-center bond order of central three-member ring, the result is 0.03517822. I marked the results in the graph below. The pink texts denote two-center Mayer bond orders, you can calculate them by subfunction 1.



Evidently, the outer-side three-member rings are more stable than the central one, even with two-center bond order this conclusion can be drawn too. We can further demonstrate this viewpoint by LOL graph in molecular plane



It is clearly that electrons tend to localized in the outer-side three-member rings to stabilize them, the conclusion of real space function analysis is in fairly agreement with bond order analysis. By checking Laplacian map, ELF map and electron density deformation map, you will draw the

same conclusion.

The *Li6.fch* used in this example was produced at B3LYP/6-31G\* level. Sometimes diffuse functions must be employed for properly describing a system (in particular, anions), in this case you should evaluate the multi-center bond order based on natural atomic orbitals (NAO) rather than based on original basis functions as illustrated above, otherwise the result may be even completely useless, see Section 3.11.2 for detail.

### 4.9.3 Calculate Laplacian bond order (LBO)

Laplacian bond order (LBO) was proposed by me in *J. Phys. Chem. A*, **117**, 3100, see Section 3.11.7 for detail. LBO is very suitable for organic system and has close correlation with bonding strength. Let's calculate LBO for C-C bond of ethane, ethene and acetylene.

Boot up Multiwfn and input following commands

```
examples\ethane.wfn // Optimized and produced at B3LYP/6-31G**
9 // Bond order analysis
8 // Laplacian bond order
```

You will see the result:

```
The bond order >= 0.050000
# 1: 1(C ) 2(H ): 0.887111
# 2: 1(C ) 3(H ): 0.889492
# 3: 1(C ) 4(H ): 0.889492
# 4: 1(C ) 5(C ): 1.059879
# 5: 5(C ) 6(H ): 0.887111
# 6: 5(C ) 7(H ): 0.889492
# 7: 5(C ) 8(H ): 0.889492
```

As you can see, LBO is very close to formal bond order (1.0) for C-C and C-H. LBO only reflects covalent bonding character, due to C-H is a weakly polar bond, the value is slightly smaller than 1.0.

Then use "examples\ethene.wfn" to calculate LBO for ethene

```
# 1: 1(C ) 2(H ): 0.919443
# 2: 1(C ) 3(H ): 0.919443
# 3: 1(C ) 4(C ): 2.022583
# 4: 4(C ) 5(H ): 0.919443
# 5: 4(C ) 6(H ): 0.919443
```

Then calculate LBO for acetylene by using "examples\C2H2.wfn"

```
# 1: 1(C ) 2(H ): 0.958393
# 2: 1(C ) 3(C ): 2.767449
# 3: 3(C ) 4(H ): 0.958393
```

The LBO of the C-C bonds in the three systems are 1.060, 2.022 and 2.767, the ratio is 1:1.907:2.61. It is known that the ratio of the bond dissociation energy (BDE) of the three bonds is 1:1.85:2.61. Clearly, LBO has surprisingly good correlation with BDE, in other words, LBO exhibits bonding strength fairly well (no other bond order definitions have so close relationship with BDE in comparison with LBO)

Moreover, LBO predicts that the sequence of the C-H bonding strength in the three systems

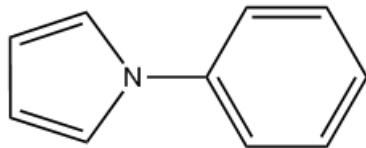
is acetylene (0.958) > ethene (0.919) > ethane (0.889), this is completely in agreement with the experimental BDE sequence! (Other bond order definitions, such as Mayer bond order, fail to reproduce this sequence)

Finally, calculate LBO for O-H bond in water by using "examples\H2O.fch", the result is 0.585. This value is significantly smaller than the C-H bond order, reflecting that O-H bond is much more polar than C-H bond.

## 4.10 Plot density of states (DOS)

### 4.10.1 Plot total, partial and overlap DOS for N-phenylpyrrole

In this example, we will plot total, partial and overlap density-of-states (TDOS, PDOS and OPDOS) for N-phenylpyrrole. Please read Section 3.12.1 first if you are not familiar with DOS.



Because basis function information is required in plotting PDOS and OPDOS, we use .fch as input file in this example; .molden and .gms files are also OK, but .wfn/.wfx are not supported, since which do not contain information of basis function and virtual MOs. If you only need to obtain TDOS, you can also simply use a plain text file recording MO energy levels or the Gaussian output file with pop=full keyword as input file, see Section 3.12.1 for file format.

Worthnotingly, if you intend to plot PDOS and OPDOS, employing diffuse basis functions in the basis-set is highly deprecated, because they lack of chemical meaning and thus always worsen the reliability of the results. The wavefunction of present system was generated at B3LYP/6-31G\* level.

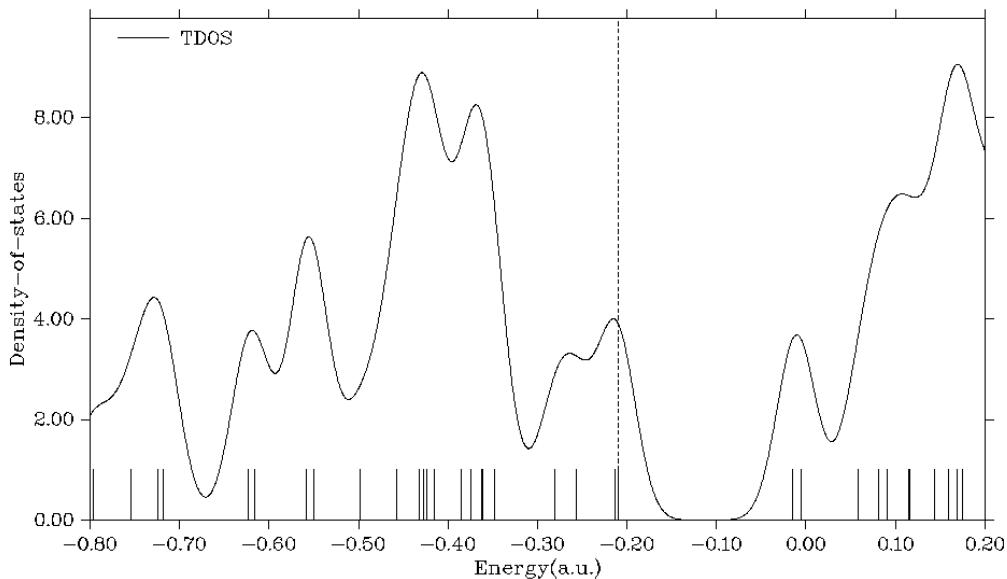
Boot up Multiwfn and input below commands

*examples\N-phenylpyrrole\_6-31Gx.fch*

10

0 // Plot DOS

Since currently no fragment is defined, only TDOS is plotted. The TDOS map pops up immediately, see below



In the TDOS map, each discrete vertical line correspond to a molecular orbital (MO), the dashed line highlights the position of HOMO. The curve is the TDOS simulated based on the distribution of MO energy levels. In the negative part, the region around -0.40 a.u. has obviously larger state density than other regions.

Clicking mouse right button on the graph to close it, and select option 0 to return to last menu.

Next, we define the heavy atoms of pyrrole moiety as fragment 1 and that of the phenyl moiety as fragment 2 to check their PDOS and OPDOS. In addition, we define all hydrogens as fragment 3.

-1 // Enter the interface for defining fragments. You can define up to 10 fragments. PDOS will be plotted for all of them but OPDOS will only be drawn between fragment 1 and 2

```

1 // Define fragment 1
a 1-5 // Add carbons and nitrogen of pyrrole moiety (atoms 1~5) to the fragment
q // Save fragment 1
2 // Define fragment 2
a 10-13,15,17 // Add phenyl moiety (atoms 10~13, 15 and 17) to the fragment
q // Save fragment 2
3 // Define fragment 3
a 6-9,14,16,18-20 // Add all hydrogens to the fragment
q // Save fragment 3
0 // Return to last menu
2 // Set X-axis

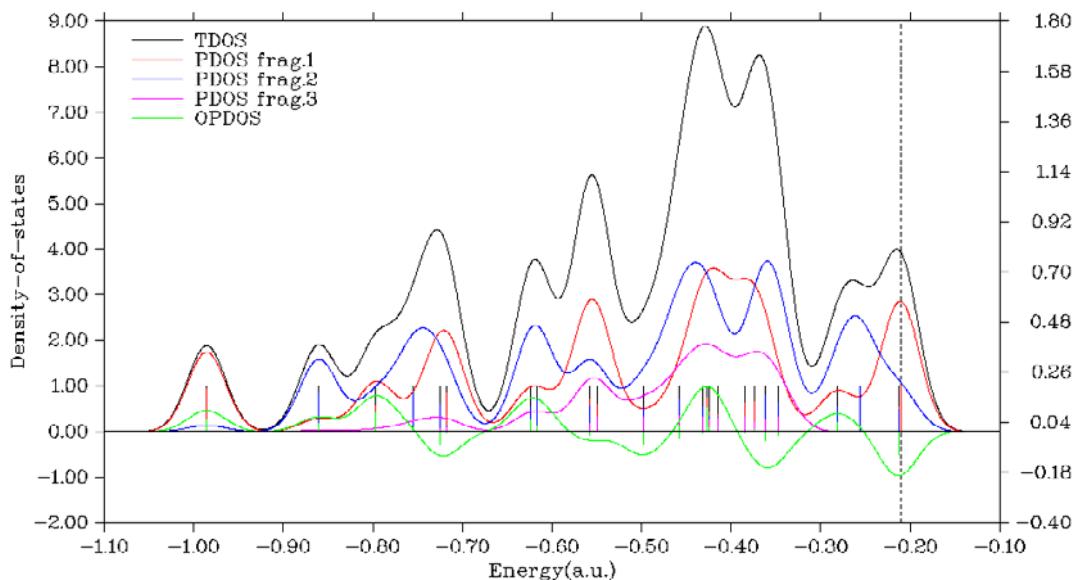
```

-1,-0.1,0.1 // Set the range of X-axis to -1.2 ~ -0.1 a.u., so that all valence MOs can be shown in the graph. The step between labels is set to 0.1 a.u..

0 // Draw TDOS+PDOS+OPDOS

Current graph is not very ideal. Close the graph, you can see many options used to customize the graph, such as setting curve colors, setting legend texts. Try to play with them and if you are confused you can consult Section 3.12.3. Here we select option 4 and input -2,9,1 to set lower,

upper limits and stepsize of Y-axis as -2.0, 9.0 and 1.0, respectively. Select 14 and input the scale factor 0.2, then the range of the Y-axis corresponding to OPDOS are set to -0.4, 1.8 (because  $-2.0*0.2=-0.4$  and  $9.0*0.2=1.8$ ). Shrinking the range of the Y-axis at right side is equivalent to enhancing the amplitude of OPDOS curve, which makes the variation of OPDOS in the map more clear. Then select 1 to replot the DOS map, you will see



The axis at left side corresponds to TDOS and PDOS, while the one at right side corresponds to OPDOS. The red, blue and magenta curves and discrete lines represent PDOS of fragment 1, 2 and 3, respectively. It can be seen that in most valence MOs, the fragments 1 and 2 have comparable amount of contribution. The fragment 3 (hydrogens) mainly contributes to the MOs between -0.60~0.35 a.u. Green curve is the OPDOS between fragments 1 and 2, its positive part implies that the MOs in corresponding energy range show bonding character between the two fragments (e.g. the one at -0.8 a.u., which corresponds to MO14); there are also regions where OPDOS is negative, e.g. the HOMO-1 (-0.213 a.u.) behave as antibonding orbitals between the two fragments.

Current molecule is in YZ plane, let's check the PDOS of px atomic orbital of the nitrogen atom. Select 0 to return to last menu and then input

```

-1 // Define fragments
-2 // Fragment 2 is not needed, so we input corresponding negative value to unset it
-3 // Unset fragment 3
1 // Redefine fragment 1
clean // Clean the content of the fragment
all // Print out information of all basis functions

```

The information corresponding to nitrogen atom is extracted and shown below

Basis:	61	Shell:	25	Center:	5(N)	Type:	S
Basis:	62	Shell:	26	Center:	5(N)	Type:	S
Basis:	63	Shell:	27	Center:	5(N)	Type:	X
Basis:	64	Shell:	27	Center:	5(N)	Type:	Y

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```
Basis: 65 Shel I: 27 Center: 5(N ) Type: Z
Basis: 66 Shel I: 28 Center: 5(N ) Type: S
Basis: 67 Shel I: 29 Center: 5(N ) Type: X
Basis: 68 Shel I: 29 Center: 5(N ) Type: Y
Basis: 69 Shel I: 29 Center: 5(N ) Type: Z
Basis: 70 Shel I: 30 Center: 5(N ) Type: XX
Basis: 71 Shel I: 30 Center: 5(N ) Type: YY
Basis: 72 Shel I: 30 Center: 5(N ) Type: ZZ
Basis: 73 Shel I: 30 Center: 5(N ) Type: XY
Basis: 74 Shel I: 30 Center: 5(N ) Type: XZ
Basis: 75 Shel I: 30 Center: 5(N ) Type: YZ
```

Current system is calculated under 6-31G\* basis set, according to the basis-set definition, each valence atomic orbital is represented by two basis functions of corresponding type. Therefore, what we should do is to put basis functions 63 and 67 into the fragment, they collectively represent the px orbital of nitrogen. Input below commands

*b* 63,67 // Then you can input command *all* again, the basis functions added to present fragment are marked by asterisks

```
q // Save fragment
0 // Return
0 // Plot TDOS and PDOS
```

Please analyze the resulting graph by yourself.

This molecule is in YZ plane, assume that we only intend to study PDOS/OPDOS of  $\pi$  orbitals of pyrrole and phenyl moieties and want to get rid of effect of all other MOs, although in the fragment definition interface we can choose each PX basis function in turn, because there are too many atoms, this process will take you a lot of time and is very boring. A much better way is to use the condition selection command. Select 0 to return to last menu and then input

```
-1 // Define fragments
1 // Redefine fragment 1
clean // Clean the content of the fragment
```

*cond* // Use conditions to select basis functions. You will be prompted to input three conditions, the basis functions simultaneously satisfying the three conditions will be added to current fragment

*1-5* // The first condition is that the basis functions must belong to the heavy atoms in pyrrole moiety (atoms 1~5)

*a* // The second condition is the index range of basis functions. Inputting *a* means any basis function is OK (in other words, do not employ this condition)

*X* // The third condition is that the type of basis function should be PX

*q* // Save fragment 1

*2* // Define fragment 2

*cond*

*10-13,15,17* // Atom index of the carbons in phenyl moiety

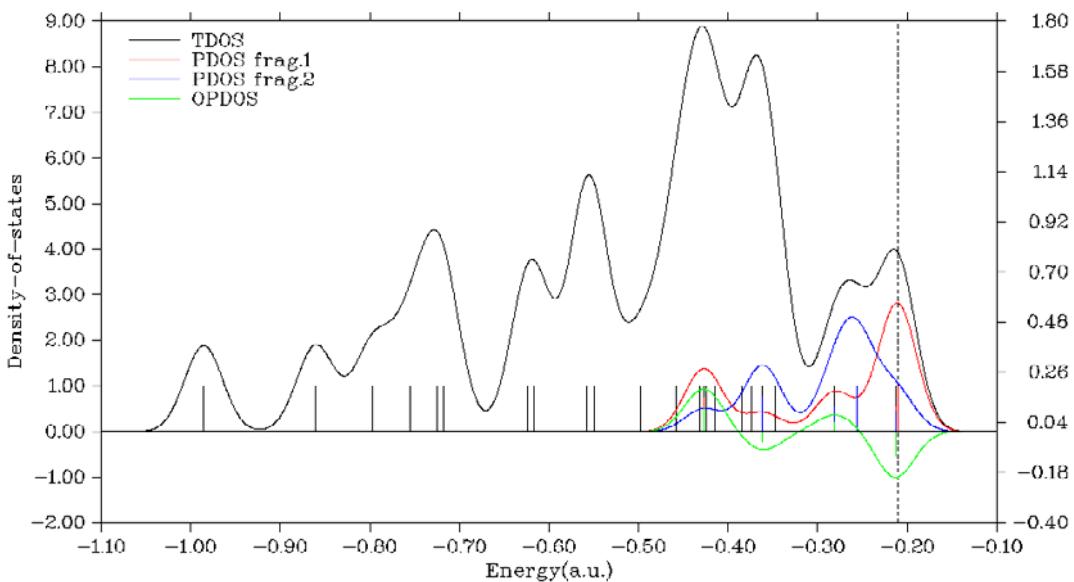
*a*

*X*

```

q // Save fragment 2
0 // Return to last menu
0 // Plot DOS

```



This time the PDOS curves only cover high-energy regions, implying that most  $\pi$  MOs in present system have higher energy than  $\sigma$  MOs. Please use main function 0 of Multiwfn to visualize corresponding MO isosurfaces.

PS: If you only need to obtain TDOS, you can simply use a plain text file recording MO energy levels or Gaussian output file with pop=full keyword as input file, see Section 3.12.1 for file format.

#### 4.10.2 Plot local DOS for butadiene

If you don't know what is local DOS (LDOS), please check Section 3.12.4 first. Briefly speaking, TDOS represents DOS curve for the whole system, PDOS describes DOS curve for an atom (or fragment), while LDOS exhibits DOS curve for a point (i.e. space-resolved). In addition, we can plot LDOS for a set of point constituting a line as color-filled map, the X-axis corresponds to energy while the Y-axis shows position in the line. LDOS is useful when interpreting the data from an scanning tunneling microscope (STM), you can find relating experimental data in for example, *J. Phys. Chem. Lett.*, **5**, 3701 (2014).

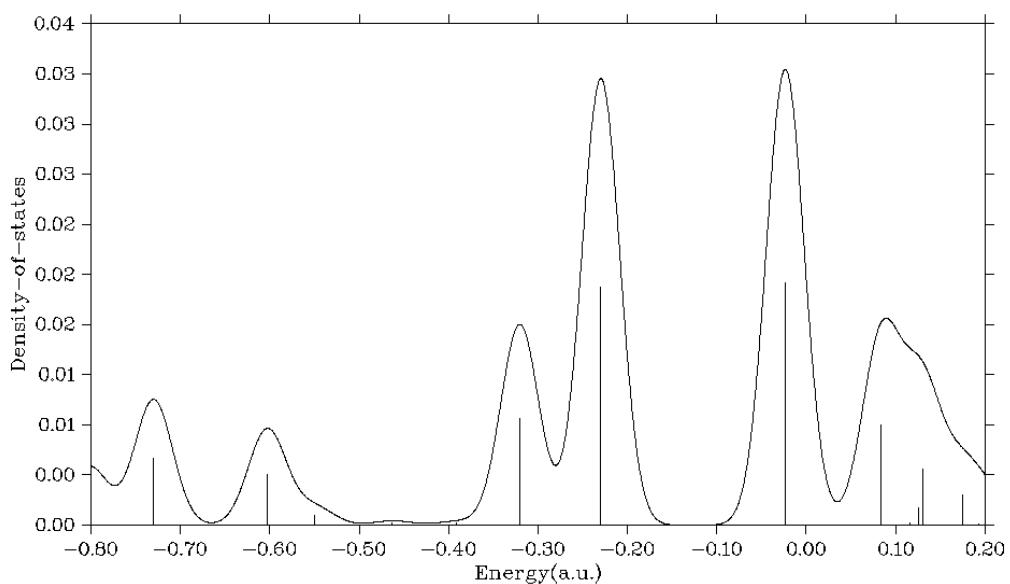
In the current example, we plot LDOS for butadiene at selected points. First, we plot LDOS for the point over 1.5 Bohr of terminal carbon of butadiene. Boot up Multiwfn and input following commands:

```

examples\butadiene.fch
0 // From output in command-line we can find the expected point should be 1.137 3.308
1.5 (1.5 Bohr above C1)
10 // DOS plotting module
10 // Draw local DOS for a point
1.137 3.308 1.5

```

Then you will see (you can compare it with TDOS map)

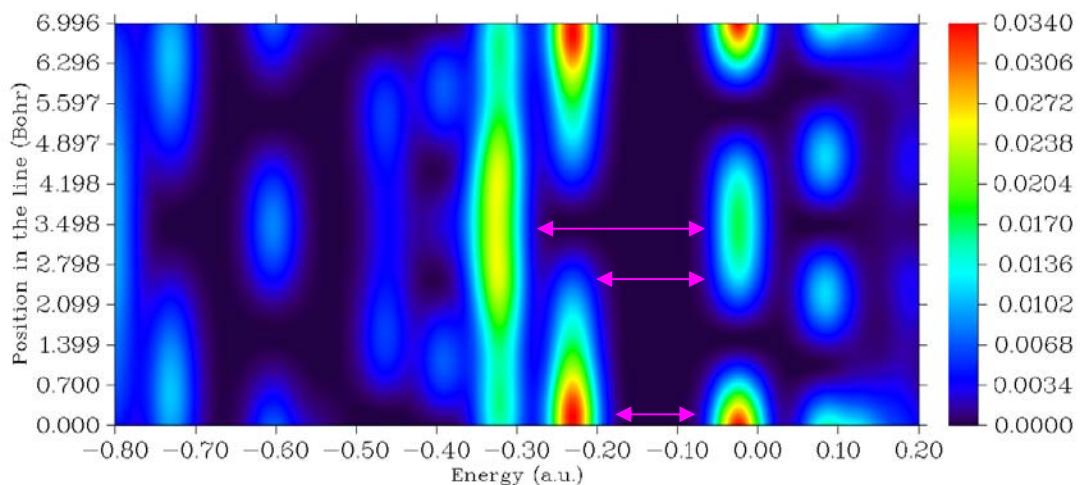


Close the graph and select 0 to return to the last menu.

Next, we plot color-filled map along the line connecting the two points above 1.5 Bohr of the two terminal carbons (C1 and C8):

```
1.137 3.308 1.5
-1.137 -3.308 1.5
200 // Evenly taking 200 points along line
Then close the graph that pops up and input
4 // Modify the ratio between Y and X axes
0.5 // The length of Y-axis will be half of X-axis
1 // Replot
```

Then you can see



The lowermost part of the graph (viz. Y=0, standing for the point 1.5 Bohr above C1) corresponds to the LDOS curve map we have obtained. The pink arrows highlight the gaps at three different positions in the line.

## 4.11 Plot spectrums

Multiwfn has a very powerful spectrum plotting module. The basic principles, supported input files and all options of this module have been detailedly introduced in Section 3.13, below sections will briefly exemplify the usage of this module.

### 4.11.1 Plot infrared spectrum for $\text{NH}_3\text{BF}_3$

This example plots infrared (IR) spectrum for  $\text{NH}_3\text{BF}_3$ . Multiwfn can read in frequencies and intensities from output file of Gaussian or ORCA vibration analysis task (“freq” keywords). Boot up Multiwfn and input following commands

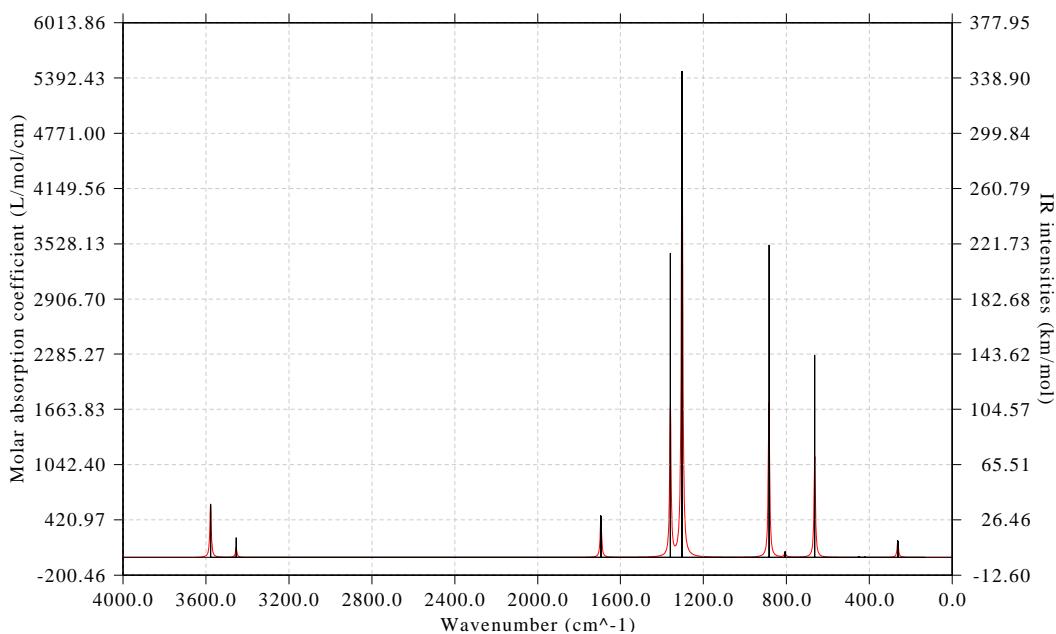
`examples\spectra\NH3BF3_freq.out //` The output file of optimization and vibrational analysis task of Gaussian at B3LYP/6-31G\* level

`11 // Plot spectrum`

`1 // The type of the spectrum is IR`

`0 // Plot spectrum right now`

You will get below graph



The left axis corresponds to curve (broadened data), the right axis corresponds to discrete lines (original transition data). Plotting parameters such as full width at half maximum (FWHM), broadening function, unit and range of the axes can be adjusted by corresponding options in the interface. The graph and X-Y data set of discrete lines/curve can be exported by option 1 and 2, respectively.

It is well known that the frequencies produced under harmonic approximation deviate to experimental vibrational frequencies systematically. In order to correct this problem, fundamental frequency scale factor should be applied, this can be done easily in Multiwfn. We close the spectrum and then choose "14 Multiply the vibrational frequencies by a factor", then input *all* to choose all vibrational modes, then input the scale factor fitted for B3LYP/6-31G\* level, namely 0.9614, which can be found in Table 1 of *J. Phys. Chem.*, **100**, 16502 (1996). After that, if you plot

the spectrum again, the resulting spectrum will be the scaled corrected one.

The procedure of plotting Raman, UV-Vis, electronic/vibrational circular dichroism (ECD/VCD) spectra are very similar with plotting IR spectrum. If the quantum chemistry program you used for spectrum calculation is not Gaussian, ORCA or sTDA, you can manually extract data from corresponding output file and then write them into a plain text file according to the format shown in Section 3.13.2, then the file can be used as input file of Multiwfn for plotting spectrum.

#### 4.11.2 Plot UV-Vis spectrum and the contributions from individual transitions for acetic acid

The spectrum plotting module of Multiwfn is quite flexible, not only the total spectrum but also the contribution from individual transitions can be exported. This feature is particularly useful when you want to identify nature of spectrum. In this section I will show how to realize this analysis, UV-Vis spectrum of acetic acid is taken as example.

Boot up Multiwfn and input

*examples\spectra\acetic\_acid\_TDDFT.out* // Calculated at TD-B3LYP/cc-pVDZ level by Gaussian

*11 // Plot spectrum*

*3 // The type of the spectrum is UV-Vis*

*15 // Output the spectrum including the contributions from certain individual transitions*

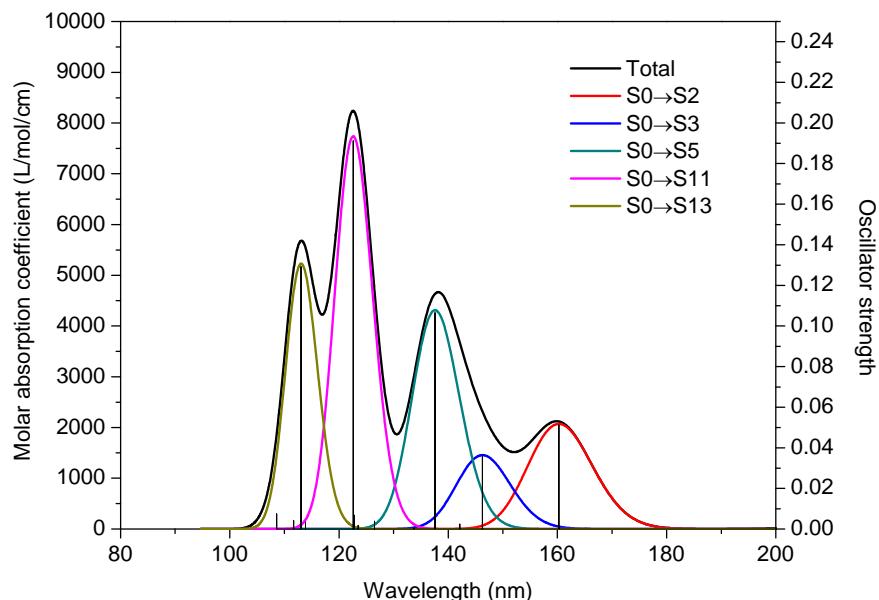
*0.01 // The criterion of selecting transitions is oscillator strength > 0.01*

The curve of the UV-Vis spectrum together with the contributions from the transitions whose strength are larger than 0.01 have been outputted to "spectrum\_curve.txt" in current folder. The first two columns correspond to energies and molar absorption coefficients, the correspondence between the other columns and transition modes are clearly indicated on screen:

Column#	Transition#	
3	2	// i.e. transition S0→S2
4	3	// i.e. transition S0→S3
5	5	// i.e. transition S0→S5
6	11	// i.e. transition S0→S11
7	13	// i.e. transition S0→S13

The discrete line data are outputted to "spectrum\_line.txt" in current folder.

Now you can plot the data in the two files as curves in a single graph by your favourite program (if you use Origin to plot, you can directly drag these two files into Origin window to import them). In the two files, the first column should be taken as X-axis data, while the other columns should be taken as Y-axis data. The spectrum plotted by Origin is shown below, if you are confused about the procedure, you can consult "acetic\_acid\_TDDFT.opj" provided in "examples\spectra" folder, which is the corresponding .opj file of Origin 8.



From the graph the underlying character of the total UV-Vis spectrum (black curve) is now very clear. Although the  $S_0 \rightarrow S_3$  transition (146.28nm) does not have very small oscillator strength (0.036), no absorption peak directly corresponds to this transition, since its absorption curve (blue curve) has been completely merged into the neighboring large absorption peak due to  $S_0 \rightarrow S_5$  transition (cyan curve).

Multiwfn is able to locate minima and maxima of spectrum curve. Select option 16, then you will see their positions and values. This feature is quite useful for pointing out the exact position of the peaks

Local maximum X:	113. 1515	Value:	5680. 8733
Local maximum X:	122. 6050	Value:	8239. 3520
Local maximum X:	138. 1754	Value:	4667. 8074
Local maximum X:	159. 8627	Value:	2123. 3503
Local maximum X:	213. 9266	Value:	48. 5312
Local minimum X:	116. 9205	Value:	4222. 4896
Local minimum X:	130. 5755	Value:	1866. 1290
Local minimum X:	152. 0775	Value:	1515. 6418
Local minimum X:	187. 9759	Value:	1. 5107

Total ly found 4 local minimum, 5 local maximum

Based on above outputs, we can calculate the contributions from different transitions to a peak. For example, we want to study the composition of the peak at 138.1754 nm. In spectrum\_line.txt, move to the line corresponding to 138.17536 nm, you can find the total value is 4667.80738, while the values in column 4 and 5 are 310.33658 and 4272.69585, respectively. Therefore, the contribution from  $S_0 \rightarrow S_3$  and  $S_0 \rightarrow S_5$  can be respectively calculated as  $310.33658/4667.80738*100\% = 6.65\%$  and  $4272.69585/4667.80738*100\% = 91.53\%$ .

### 4.11.3 Plot electronic circular dichroism spectrum for asparagine

In this example we plot electronic circular dichroism (ECD) spectrum for asparagine. Boot up Multiwfn and input

```
examples\spectra\Asn_TDDFT.out // Gaussian TDDFT task at PBE1PBE/6-311G* level, 30
lowest states were calculated
```

```
11
4 // ECD
```

```
2 // Use the rotatory oscillator in velocity representation
0 // Plot spectrum
```

From the resulting spectrum, you will find the labels of X-axis and Y-axis are decimal. In order to make the graph more beautiful, it is suggested to modify the scale so that label of each tick is integer. Therefore, we close current graph and input below commands:

```
3 // Set X-axis
```

```
120,280,20 // Lower and upper limits, as well as spacing between ticks of X-axis
```

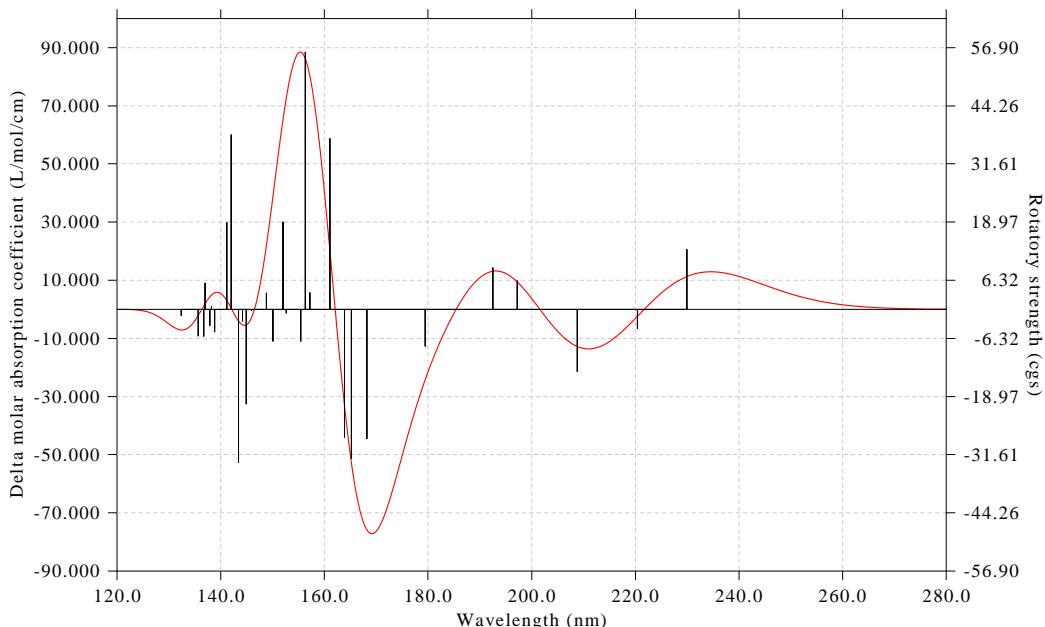
```
4 // Set left Y-axis
```

```
-90,100,20 // Lower and upper limits, as well as spacing between ticks of left Y-axis
```

```
y // Let program properly adjust right Y-axis to guarantee that zero point of left and right
axes are in the same horizontal line
```

```
0 // Plot spectrum
```

Then you will see below graph



### 4.11.4 Plot conformational weighted spectrum for plumericin

For a flexible system with many thermally accessible conformation (or configurations), when plotting its spectrum, it is crucial to take weighting average of various conformations into account, otherwise the resulting spectrum is impossible to be compared well with experimental spectrum. Fortunately, weighted spectrum can be very conveniently plotted by Multiwfn, I will show how to do this in present section. Plotting conformationally weighted UV-Vis and ECD spectra of

plumericin are taken as instances.

### (1) Preparation

Before calculating conformationally weighted spectrum, we need to evaluate population of these conformations, commonly Boltzmann's weight is used. We assume that plumericin has four accessible conformations, and properly construct their initial geometries, then optimize them and perform frequency analysis at B3LYP/6-31G\* level with zero-point energy scale factor of 0.9806. Based on optimized geometries, high-accuracy single point energies at M06-2X/def2-TZVP level were calculated. Finally, we add the Gibbs thermal corrections produced by frequency analysis to the single point energies to yield relatively accurate Gibbs energy of various conformations. After that, according to Boltzmann's formula and relative Gibbs energy among these conformations, we calculate their weights at 298.15K. Then, using TD-PBE0/TZVP level we calculate the lowest 20 excited states for these conformations. The output file of the TDDFT tasks have been provided in "examples\spectra\weighted" folder as a.out, b.out, c.out and d.out (the names are arbitrary, you can also use other file names).

Now we write a plain text file named "multiple.txt" with below content (the name "multiple.txt" should not be changed, otherwise Multiwfn will unable to properly recognize it):

```
examples\spectra\weighted\ a.out 0.6046
examples\spectra\weighted\ b.out 0.1950
examples\spectra\weighted\ c.out 0.1686
examples\spectra\weighted\ d.out 0.0317
```

The first column records path of Multiwfn input file for various conformations, the second column is the Boltzmann weights we calculated above. Below the four conformations will be called as *a*, *b*, *c* and *d*, respectively.

### (2) Plot conformationally weighted UV-Vis spectrum

Boot up Multiwfn and input

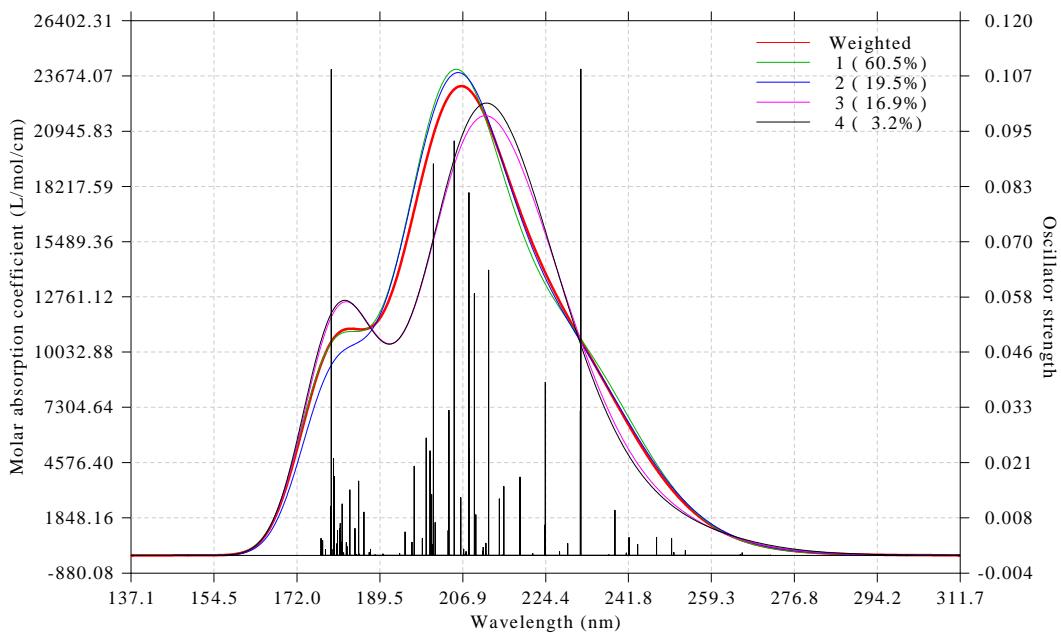
```
examples\spectra\weighted\multiple.txt // The file mentioned in last section
```

```
11
```

```
3 // Plot UV-Vis
```

```
0
```

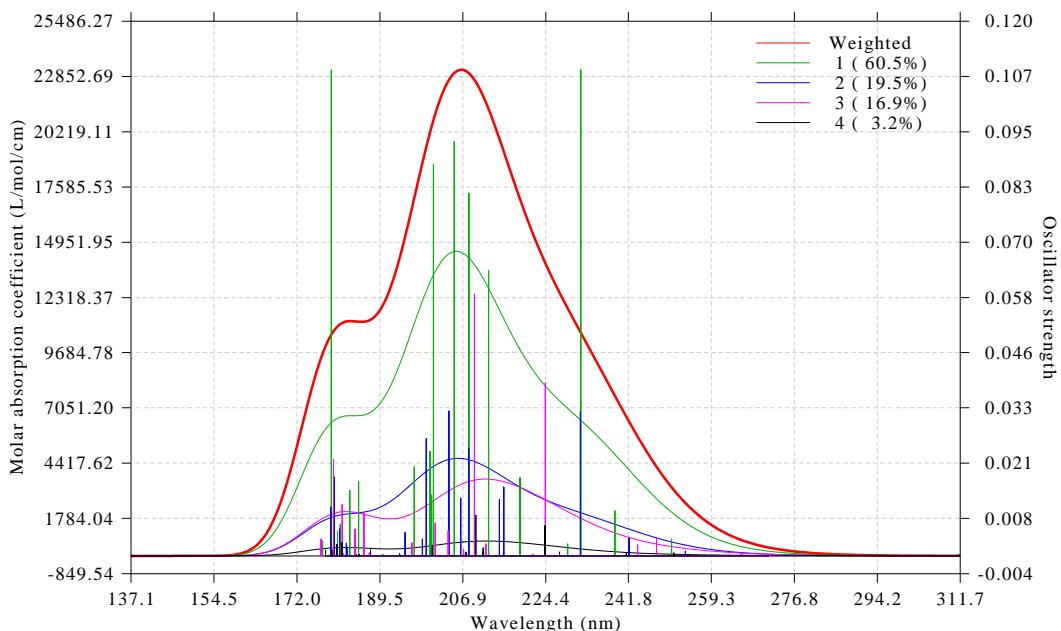
The resulting graph is shown below



The thick red curve corresponds to conformationally weighted UV-Vis spectrum, while the green, blue, purple and black curves correspond to UV-Vis spectrum of conformation *a*, *b*, *c* and *d*, respectively. The weight of each conformation is also shown in the legend. From this graph we can very conveniently compare the character of weighted spectrum and spectra of individual conformations.

The black discrete lines on the graph represent all transition data of the four conformations, their heights have already been scaled by conformational weight. Hence, the thick red curve can be regarded as broadened by all discrete lines shown on the graph.

Multiwfn provides another mode to plot spectrum of individual conformations. We close above graph and choose "18 Toggle weighting spectrum of each system" once, then choose option 0 to view the spectrum again, we will see



The spectrum curve of each conformation shown on this graph has already been multiplied by

corresponding weight. Obviously, what this graph represents is contribution of each conformation to the conformationally weighted spectrum. In other words, the height of thick red curve is simply the sum of height of all other curves. It can be seen that conformation *a* (green line) has major contribution to the conformationally weighted spectrum, their profiles are rather similar, this is because *a* has as high as 60.5% population.

The discrete lines in above graph now have different colors, the color correspond to legend shown at right-top side. For each conformation, since both discrete lines and curve currently have identical color, we can say for example, green curve can be directly yielded by broadening the green discrete lines.

### (3) Plot conformationally weighted ECD spectrum

Using the same procedure illustrated in the last section, we plot conformationally weighted ECD spectrum and ECD spectrum for all the four conformations.

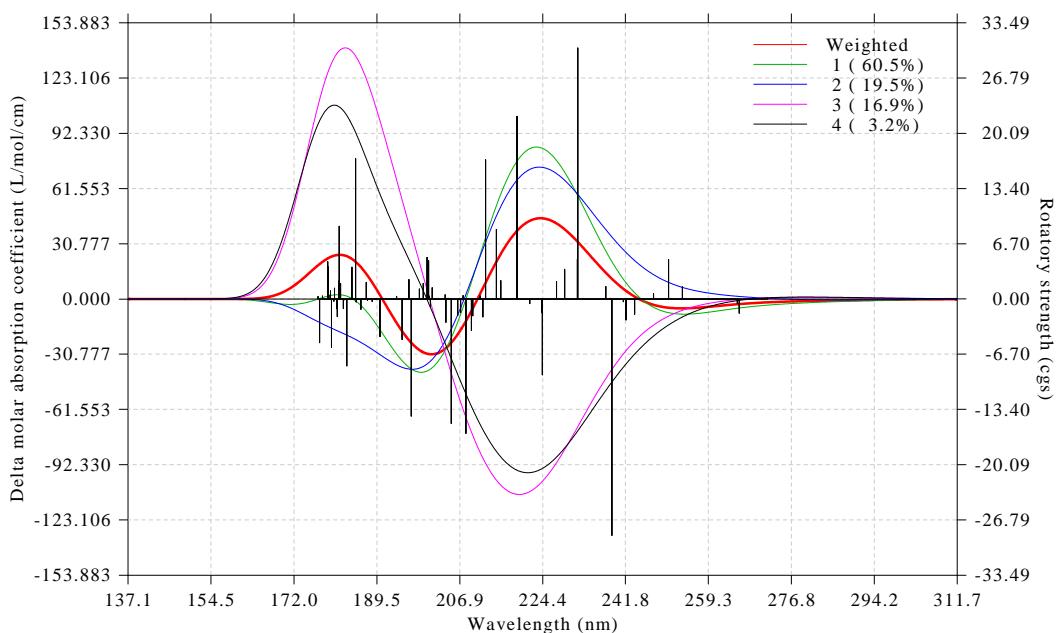
Boot up Multiwfn and input

*examples\spectra\weighted\multiple.txt*

11

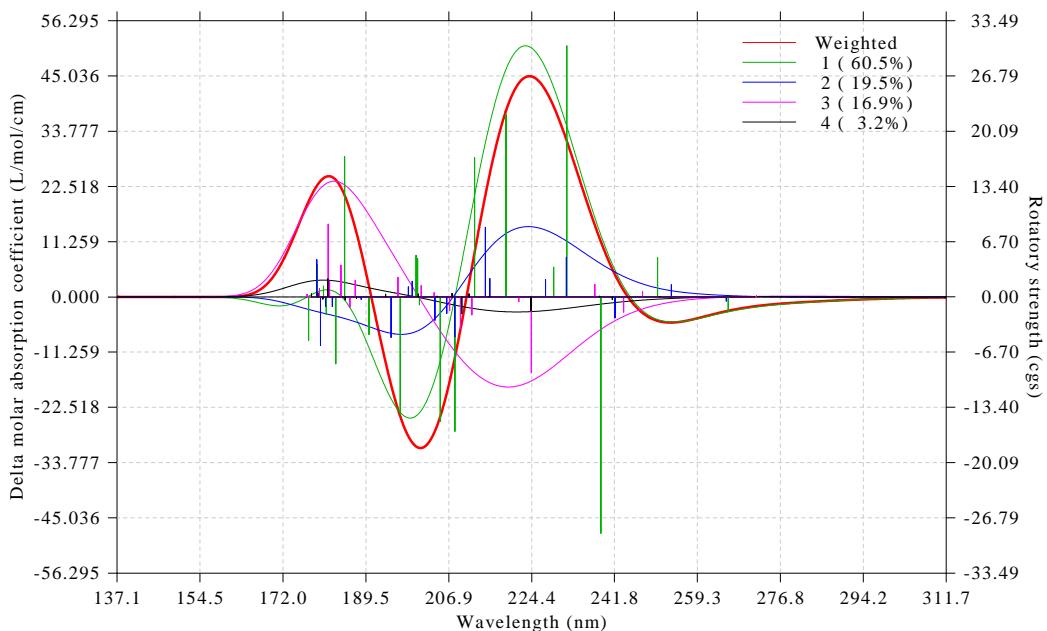
```
4 // Plot ECD
2 // Read rotatory strength in velocity representation from the 1st file in multiple.txt
2 // ibid, but for the 2nd file
2 // ibid, but for the 3rd file
2 // ibid, but for the 4th file
0 // Plot spectrum
```

You will see



From this graph you can see conformationally weighted ECD spectrum (thick red curve) as well as ECD spectrum of individual conformations (other curves).

Then choose "18 Toggle weighting spectrum of each system" option once and plot spectrum again, you will see



This graph decomposes the final weighted ECD spectrum to contribution of individual conformation. Again, since conformation *a* (green) has very high population and thus dominates the final weighted curve, most characters of these two curves are similar. However, influence from other conformations cannot be simply ignored. From the graph it is easy to find that if conformation *c* (purple) is missing, then there will not be an evident ECD peak at approximately 180 nm, since only ECD of *c* at this wavelength has significant signal.

#### 4.11.5 Plot Raman spectrum for 2-methyloxirane based on Raman intensity

The procedure of plotting Raman spectrum is very similar with plotting IR spectrum, the only additional step you would better do is to convert the Raman activities directly outputted by Raman task of quantum chemistry codes to Raman intensities before plotting the spectrum, so that the resulting spectrum can be comparable with the experimental one. The Raman intensities are dependent of wavelength of excitation light source and ambient temperature, while Raman activities are not. This point has been emphasized in Section 3.13.1. In this section, I illustrate how to properly plot Raman spectrum using (2S)-2-methyloxirane as example.

Boot up Multiwfn and input

`examples\spectra\2-methyloxirane_Raman.out // Output file of Raman task calculated at B3LYP/6-31G* level by Gaussian09`

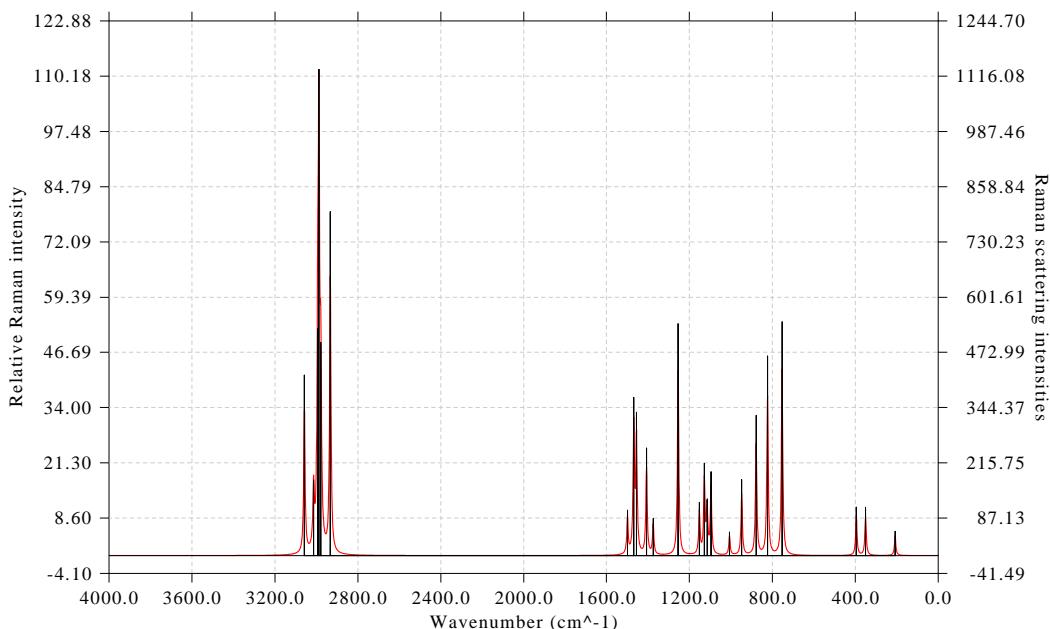
```

11
2 // Raman spectrum
14 // Apply frequency scale factor
all
0.9614 // Scale factor suitable for fundamental frequencies at B3LYP/6-31G* level
19 // Convert Raman activities to intensities
15000 // Wavenumber (cm-1) of excitation light source. This value should be consistent
with actual experimental condition, the value we inputted here is arbitrarily chosen

```

298.15 // Assume that experimental temperature is 298.15K

Then input 0 to plot spectrum, you will see below Raman spectrum



## 4.12 Quantitative analysis of molecular surface

### 4.12.1 Electrostatic potential analysis on phenol molecular surface

Below I will introduce quantitative analysis of molecular surface by case study of phenol. The theoretical basis has been documented in Section 3.15.1 and thus will not be repeated here. In this section we only analyze electrostatic potential (ESP) on phenol vdW surface, in next section we will then analyze average local ionization energy on the phenol surface.

Boot up Multiwfn and input following commands

`examples\phenol_DFT.wfn` // phenol wavefunction produced at B3PW91/6-31G\*\* level. For most systems this level can give satisfactory result. Hartree-Fock wavefunction is not recommended to use, since HF completely ignored electron correlation and hence lead to unreliable ESP distribution

`12 // Quantitative analysis of molecular surface`

`0 // Start the analysis under default settings. By default the mapped function is ESP`

Now the calculation starts. Since computing ESP is time consuming, you need to wait for a while. During the calculation some intermediate information are printed, ordinary users do not need to concern them. Below results will be printed on screen once the calculation has been finally finished:

```
Global surface minimum: -0.041203 a.u. at 1.455097 3.343708 -0.007902 Ang.
Global surface maximum: 0.085761 a.u. at -1.936645 3.093464 0.021360 Ang.
```

Number of surface minima: 3

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#	a. u.	eV	kcal /mol	X/Y/Z coordinate(Angstrom)		
1	-0.03046066	-0.828877	-19.112843	0.150202	-1.011077	-1.882004
2	-0.03045989	-0.828856	-19.112362	0.192185	-0.985412	1.877656
*	3 -0.04120321	-1.121196	-25.853368	1.455097	3.343708	-0.007902

Number of surface maxima: 5

#	a. u.	eV	kcal /mol	X/Y/Z coordinate(Angstrom)		
1	0.02275520	0.619200	14.277975	-3.344441	-2.281045	0.047286
*	2 0.08576096	2.333674	53.811572	-1.936645	3.093464	0.021360
3	0.01935782	0.526753	12.146259	0.066223	-4.286661	0.040555
4	0.01980285	0.538863	12.425498	3.340574	-2.325727	0.021485
5	0.01583741	0.430958	9.937340	3.419218	1.225375	-0.019326

===== Summary of surface analysis =====

Volume: 835.71041 Bohr^3 ( 123.83953 Angstrom^3)

Overall surface area: 476.05682 Bohr^2 ( 133.30951 Angstrom^2)

Positive surface area: 231.09186 Bohr^2 ( 64.71232 Angstrom^2)

Negative surface area: 244.96497 Bohr^2 ( 68.59719 Angstrom^2)

Overall average value: -0.00020233 a. u. ( -0.12695332 kcal/mol )

Positive average value: 0.01877643 a. u. ( 11.78145591 kcal/mol )

Negative average value: -0.01810626 a. u. ( -11.36095315 kcal/mol )

Overall variance (sigma^2\_tot): 0.00041488 a. u.^2 ( 163.34165024 (kcal/mol)^2 )

Positive variance: 0.00031106 a. u.^2 ( 122.46642148 (kcal/mol)^2 )

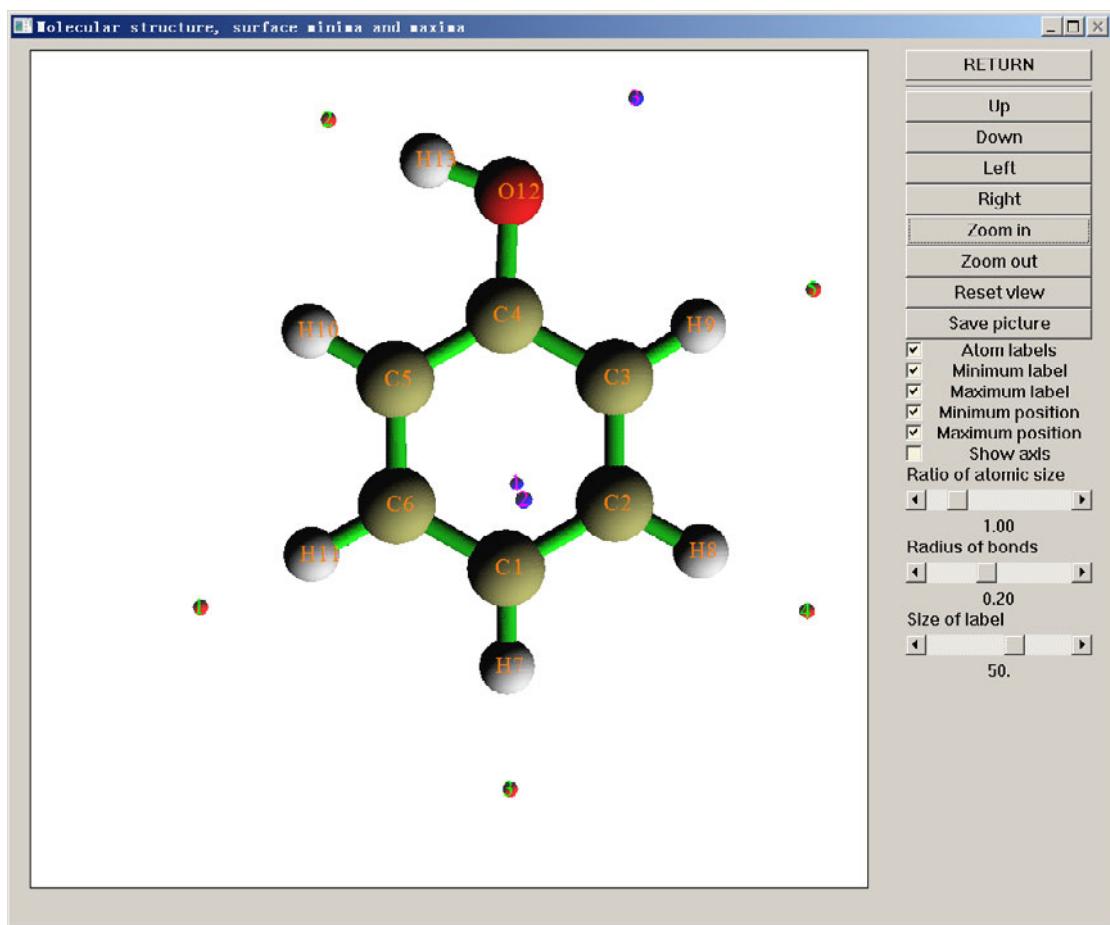
Negative variance: 0.00010382 a. u.^2 ( 40.87522876 (kcal/mol)^2 )

Balance of charges (miu): 0.18762182

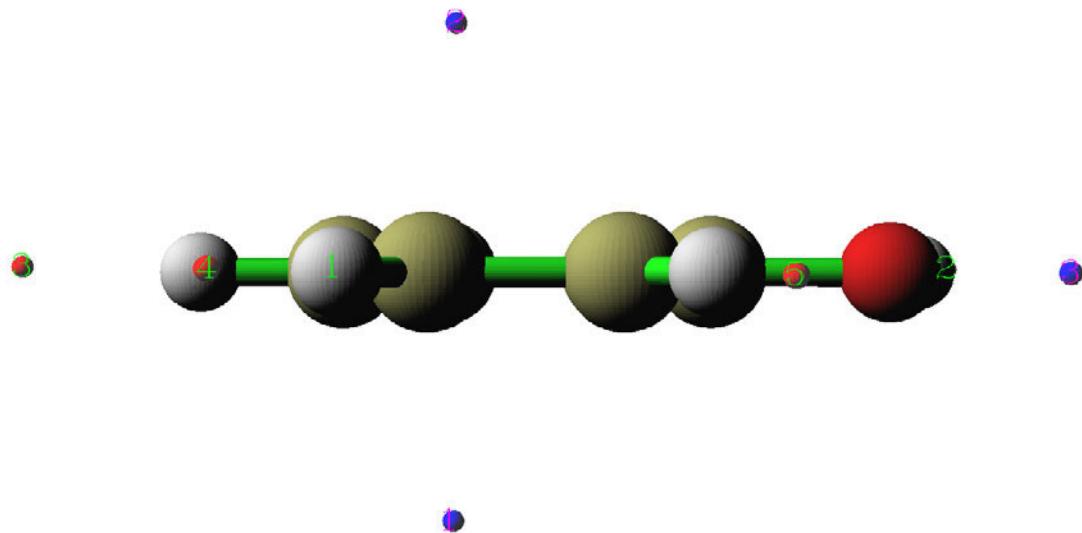
Product of sigma^2\_tot and miu: 0.00007784 a. u.^2 ( 30.6464578 (kcal/mol)^2 )

Internal charge separation (Pi): 0.01842642 a. u. ( 11.56183883 kcal/mol )

Above information includes all quantities that involving ESP mentioned in Section 3.15.1. In Multiwfn, the vdW volume can also be computed by Monte Carlo method through subfunction 3 of main function 100, see Section 3.100.3, the results match fairly well. Now select option 0 in the post-process interface to view molecular structure and surface extrema (red and blue spheres correspond to maxima and minima, respectively):

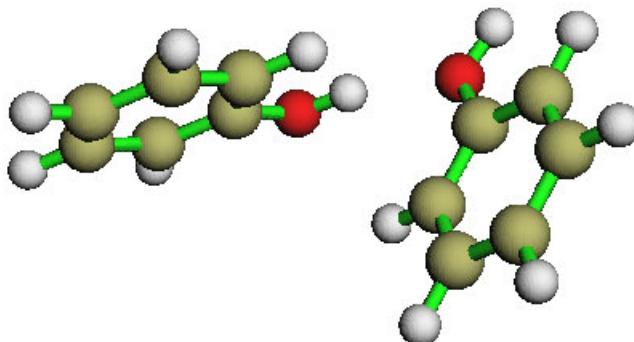


In side view:



Minimum 3 (-25.85kcal/mol) is global minimum on the surface, its large negative value is owing to the lone pair of oxygen. Maximum 2 (53.81kcal/mol) is global maximum arising from the positively charged H13, the ESP at this point is much larger than that at other maxima (where the ESP ranges from 10 to 15kcal/mol). This is because the presence of oxygen, which attracted a great deal of electrons from H13. In complex, assume that only electrostatic interaction exists,

monomers always contact each other in maximally ESP complementary manner. So we can expect that in phenol dimer, H13 and maximum 2 in a monomer, and O12 and minimum 3 in neighbour monomer will be in a straight line (resulting hydrogen bonding), this is the exactly situation in actual geometry of phenol dimer, see below graph. Notice that in the dimer, maximum 2 and minimum 3 shown above have cancelled each other out.



Minimum 1 and 2 (both are -19.11kcal/mol) are local minimum on the surface, mainly arise from the abundant  $\pi$  electrons above and below the ring. It is well known that electrophiles always prefer to attack the atom which has very low ESP around it, so C1 should be an ideal reaction site for electrophilic reaction. This conclusion is partially consistent with the general knowledge that hydroxyl is an ortho-para directing group. However, although the global minimum is closest to O12, O12 is not the electrophilic reaction site; this contradiction reveals the inherent limitation of ESP analysis method.

Note: Since the molecule has Cs symmetry, in principle, minimum 1 and 2 should have identical X and Y coordinates. However, this cannot be exactly fulfilled in numerical process, because the points scattered on molecular surface do not have the molecular symmetry, see Section 3.15.1 for detail. So X and Y coordinates of minimum 1 and 2 are slightly deviated to each other. If you want to refine the result, choose option 3 "Spacing of grid data for generating molecular surface" and input a smaller value than default value. Smaller spacing of grid points yields more accurate result, but bring higher computational burden.

The non-bonded radius defined in the framework of atoms in molecule (AIM) theory is the shortest distance between a nucleus and  $\rho=0.001$  isosurface. Let's calculate the non-bonded radius for O12 and H13. Select option 10 in the post-process interface and input 12, we can see that the non-bonded radius of O12 is 1.701 Angstrom. Select 10 and input 13, the non-bonded radius of H13 is 1.172 Angstrom. In the phenol dimer, the H---O of the H-bond is 1.937 Angstrom, therefore the so-called mutual penetration distance is  $1.701+1.172-1.937=0.936$  Angstrom. This is a nontrivial value, indicating the H-bond is strong.

As the final part of ESP analysis, we examine the molecular surface area in each ESP range, this is useful to quantitatively discuss ESP distribution on the whole molecular surface. We choose option 9 in the post-process interface, and then input:

*all // All atoms are taken into the statistics (alternatively, if you input for example 2-4, then only the local surfaces corresponding to atom 2, 3 and 4 will be taken into account, see Section 4.12.3 for illustration of the concept of local molecular surface)*

*-30,55 // The ESP range you are interested in. Since we have already known that the minimum and the maximum ESP on the surface are -25.85 and 53.81 kcal/mol respectively, here we input a slightly larger range to enclose them*

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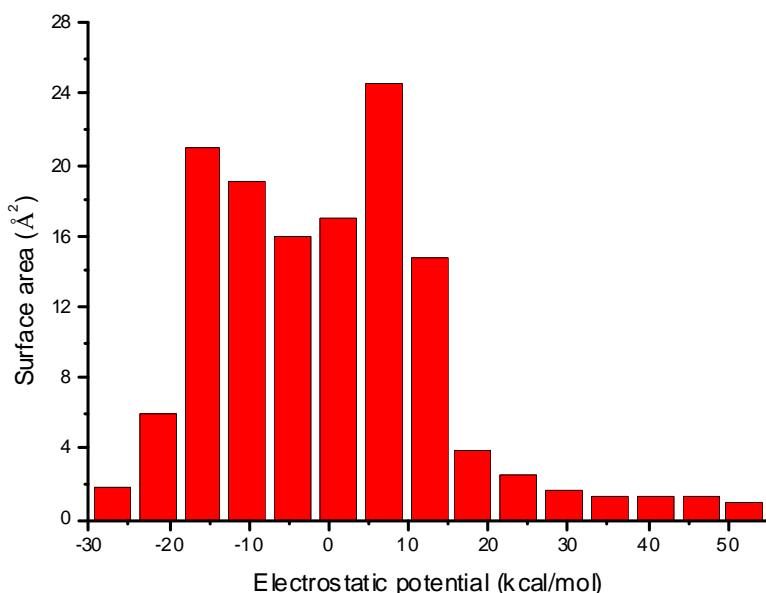
15 // The number of intervals

3 // Both the inputted and outputted units are in kcal/mol

Then you will see surface area (in  $\text{\AA}^2$ ) and corresponding percentage in the whole surface area in each successive ESP range.

Begin	End	Center	Area	%
-30. 0000	-24. 3333	-27. 1667	1. 8192	1. 3647
-24. 3333	-18. 6667	-21. 5000	6. 0284	4. 5221
-18. 6667	-13. 0000	-15. 8333	20. 9732	15. 7327
-13. 0000	-7. 3333	-10. 1667	19. 0390	14. 2818
...				
43. 6667	49. 3333	46. 5000	1. 2690	0. 9519
49. 3333	55. 0000	52. 1667	1. 0457	0. 7844
Sum:			133. 3095	100. 0000

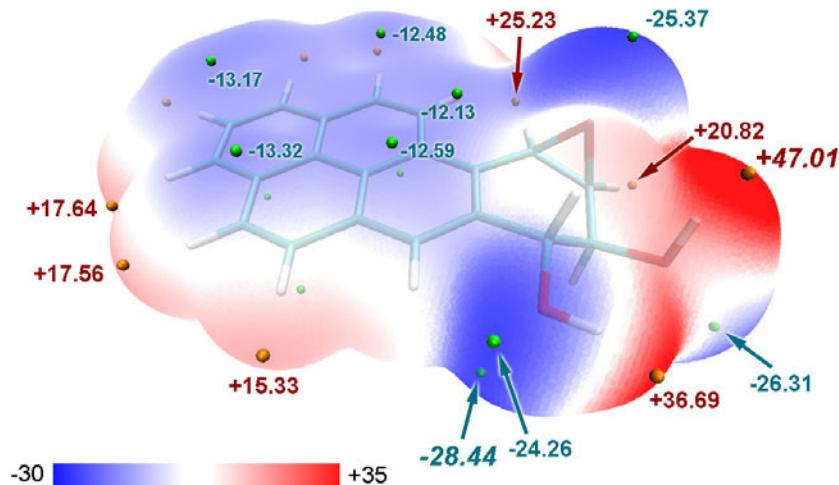
By using these data you can use your favourite program to draw a histogram graph. For example, we choose "center" column as X-axis and "Area" column as Y-axis to plot below graph



From the graph it can be seen that there is a large portion of molecular surface having small ESP value, namely from -20 to 20 kcal/mol. Among these areas, the negative part mainly corresponds to the surface above and below the six-membered ring and shows the effect of the abundant  $\pi$ -electron cloud; the positive part mainly arises from the positive charged C-H hydrogens; the near-neutral part represents the border area between the negative and positive parts. There are also small areas having remarkable positive and negative ESP value, corresponding to the regions closed to the global ESP minimum and maximum, respectively.

With the help of VMD program, one can plot very nice color-filled molecular surface map with surface extrema for various real space functions based on the output of Multiwfn. Below is such a plot for ESP, which was presented in my study of benzoapyprene diol epoxide, see *Struct. Chem.*, **25**, 1521 (2014). In which blue, white and red correspond to ESP varying from -30 to 35

kcal/mol, the green and orange spheres correspond to ESP surface minima and maxima, respectively



If you would like to plot similar graphs, please download and follow the tutorial "Plotting electrostatic potential colored molecular surface map with ESP surface extrema via Multiwfn and VMD" in "Related resources and posts" section of Multiwfn website.

#### 4.12.2 Average local ionization energy analysis on phenol molecular surface

This example is a continuation of the last example, please finish the last example first if you haven't. Below we will analyze average local ionization energy  $\bar{I}$  on phenol vdW surface.

-1 // Return to the parameter setting interface from post-process stage

2 // Reselect mapped function

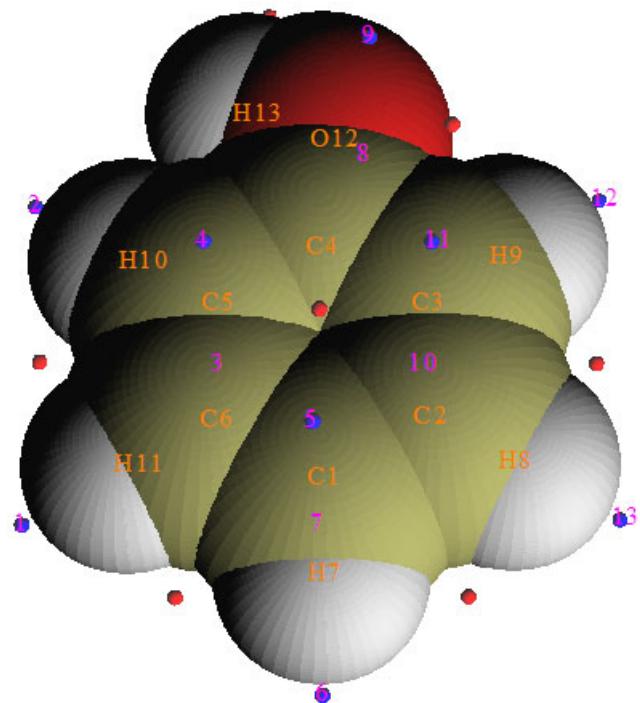
2 // Choose  $\bar{I}$  as mapped function

0 // Start the surface analysis.

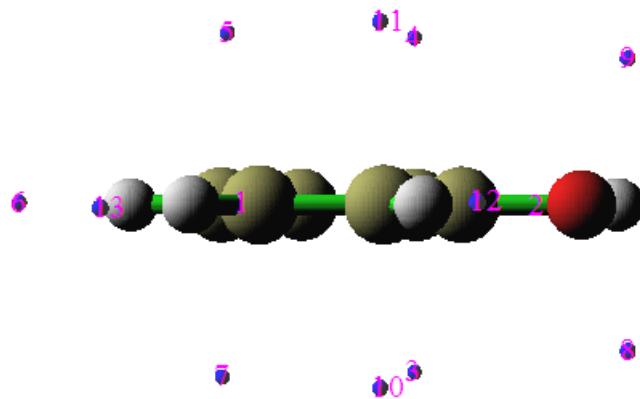
Since calculation of  $\bar{I}$  is much simpler than ESP, the calculation will be finished soon. Unlike surface analysis for ESP, at this time only vdW volume, surface area, average and variance of  $\bar{I}$  on vdW surface are outputted alongside extrema information.

**Hint:** If you only want to use Multiwfn to obtain molecular volume and surface area, you can simply perform quantitative molecular surface analysis for average local ionization energy. As you have seen, this task can be finished rather quickly.

Choose 0 to visualize extrema, in order to make the correspondence between extrema and atoms clearer, we can drag the "Ratio of atomic size" scale bar to 4.0, which correspond to vdW surface, we will see:



In side view (For clarity, only minima are shown)

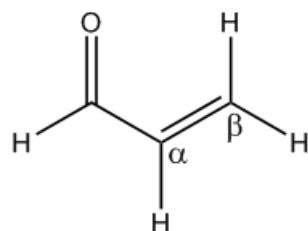


Low value of  $\bar{I}$  suggests the electron at this position is not tightly bounded, the site with lowest  $\bar{I}$  on vdW surface is usually recognized as the most vulnerable site to electrophilic or to free radical attack. The regions easy to be polarized such as  $\pi$  electron and lone pair generally have corresponding surface minima of  $\bar{I}$ . In present instance, minimum 8 and 9 correspond to lone pair of O12, both the  $\bar{I}$  value are 10.59eV. Minimum 4,5,11, and 3,7,10 correspond to  $\pi$  electrons, all of them the  $\bar{I}$  values are about 8.9eV and can be viewed as degenerate global minima. Worthnotingly, the minima above and below the conjugated ring only present at ortho- and para-carbon. These observations perfectly explained the effect of hydroxyl as an ortho-para

directing group. Since  $\bar{I}$  at minimum 8 and 9 are obviously larger than the  $\bar{I}$  at the minima surrounding the carbon ring, oxygen is not a vulnerable site for electrophilic reaction.

### 4.12.3 Local molecular surface analysis for acrolein

It is well known that acrolein (see below) tends to undergo nucleophilic attack at carbonyl carbon and  $\beta$  carbon; in particular, the former is the primary site for hard nucleophilic reagent. The so-called hard means the electron cloud of the nucleophilic reagent is difficult to be polarized; the selectivity of reactive site for this case is usually dominated by ESP.



In this example, we will try to interpret the site-selectivity of acrolein by analyzing ESP on its vdW surface. Note that average local ionization energy is only useful for studying electrophilic attack, but completely useless for analyzing nucleophilic attack.

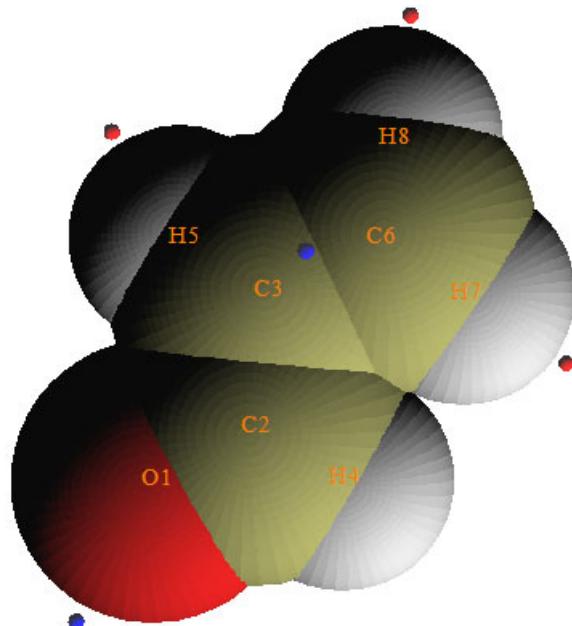
Boot up Multiwfn and input:

```
examples\acrolein.wfn // Optimized and produced at B3LYP/6-31G** level
```

```
12 // Quantitative analysis of molecular surface
```

```
0 // Start the analysis for ESP
```

After the calculation is finished, choose 0 to visualize surface extrema:



As you can see, there is a surface minimum of ESP at the boundary of  $\alpha$  carbon and it is very close to  $\beta$  carbon. This observation indirectly reveals that nuclear charge of  $\alpha$  carbon is more heavily screened by electron cloud, and hence is less probable to be the site of nucleophilic attack.

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However, quantitative analysis of ESP on the whole acrolein surface does not provide a direct and definitive interpretation on the preference of reactive sites, because no surface maxima are found on carbonyl and  $\beta$  carbons, hence we are unable to directly investigate the characteristic of carbonyl and  $\beta$  carbon.

In Multiwfn, the quantitative analysis can not only be applied to the whole molecular surface, but is also applicable to local molecular surface to reveal characteristic of atom or fragment. Here we select option 11 in post-process interface to calculate and output properties of the local surfaces corresponding to each atom. Some of the results are shown below

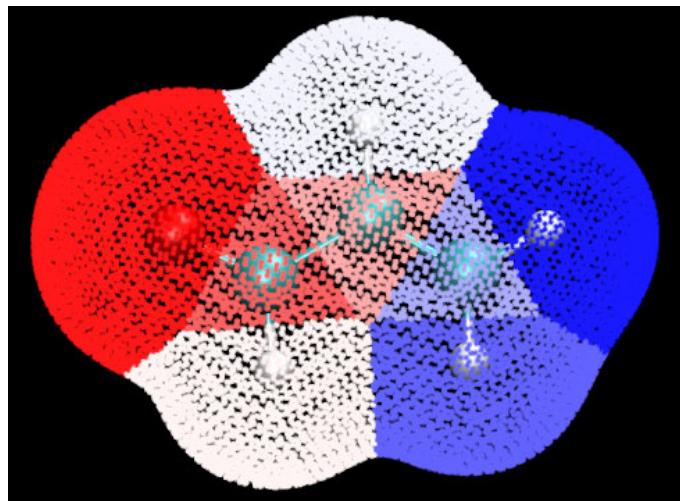
Note: Average and variance below are in kcal/mol and (kcal/mol)<sup>2</sup> respectively

Atom#	All Positive/Negative average		All Positive/Negative variance	
1	-24.35251	NaN	-24.35251	NaN
2	4.65672	5.74594	-1.45401	9.79575
3	1.30965	2.36405	-0.88391	2.70896
4	8.37174	10.35813	-6.00120	36.74187
5	7.07040	8.67973	-6.35468	49.99108
6	2.21578	3.02322	-0.73880	5.15593
7	15.34251	15.34251	NaN	22.85377
8	14.68486	14.68486	NaN	25.92230

As you can see, the average ESP values on the local surface of carbonyl carbon (atom 2),  $\alpha$  carbon and  $\beta$  carbon are 4.657, 1.310 and 2.216 kcal/mol, respectively. This result clearly explained the site-selectivity; the carbonyl carbon is the most favorable site because the average ESP on its local surface is the most positive, and hence nucleophilic reagents (especially the hard ones) tend to be attracted to this site. In contrast, on the local surface of  $\alpha$  carbon the average of ESP is the smallest compared to the other two carbons, and thus  $\alpha$  carbon has less capacity to attract nucleophilic reagents.

Note that some of the outputted data are NaN (Not a Number), these are not bug but understandable. For example, the average of positive part of ESP of atom 1 is NaN, this is because oxygen has large electronegativity, and thus on the local surface of atom 1 the ESP is completely negative, so the average of positive ESP is unable to be computed.

If you are confused about what is "local surface of atoms" or you want to visualize them, after you choose option 11 you can select "y" to output the surface facets to locsurf.pdb file in current folder. Each atom in this file corresponds to a surface facet, the B-factor value corresponds to its attribution. By this file you can visualize how the whole molecular is partitioned, the method is: boot up VMD program and drag the pdb file into the VMD main window, in "Graphics"- "Representation" set the "Drawing method" as "Points", set the point size to 4, and set "Coloring Method" as "Beta". In VMD main window select "Display"- "Orthographic" and deselect "Display"- "Depth Cueing". Then load the molecular structure file of acrolein into VMD and render it as CPK mode, you will see below graph

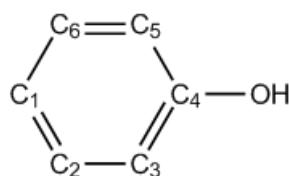


In the graph, each point represents a surface facet; different colors represent different local surface regions, and each one corresponds to an atom.

Beware that the "imolsurparmode" parameter in settings.ini directly affect the result of local surface analysis, currently we are using imolsurparmode=1.

#### 4.12.4 Fukui function distribution on local molecular surface of phenol

I have exemplified how to study Fukui function by visualizing its isosurface (Section 4.5.4) and by condensing it to atomic value via population analysis (Section 4.7.3). In this section, I will introduce another way to study this function, namely examine its average value on the local molecular surface corresponding to each atom. The advantage of this scheme over visualizing isosurface is that the relative magnitude of Fukui function can be obtained clearly and quantitatively. Meanwhile, unlike condensed Fukui function, this scheme is free of ambiguity of selection of population methods. I will still use phenol as example.



Boot up Multiwfn (referred to as Multiwfn A) and input following commands

*examples\phenol.wfn*

12

2 // Select the mapped real space function on the molecular surface

0 // The function value will be loaded from an external file

1 // Set the way to define the surface

1 // Use electron density isosurface as molecular surface

0.01 // Because Fukui function on default isosurface  $\rho=0.001$  is often too small, enlarging the isovalue to 0.01 makes the discussion easier

0 // Start the surface analysis

Multiwfn will generate grid data of electron density and then generate the surface vertices.

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After the coordinate of these vertices are automatically outputted to surfptpos.txt in current folder, Multiwfn A pauses. Do not terminate Multiwfn A, we boot up another Multiwfn now (referred to as Multiwfn B), and then input below commands in Multiwfn B

```
examples\phenol.wfn
5 // We use this module to generate Fukui function on the points recorded in surfptpos.txt
0 // Set custom operation
1
-,examples\phenol+1.wfn // Subtract the properties from phenol+1.wfn from phenol.wfn
1 // Electron density
100 // Load the coordinate of the points to be calculated from an external file
surfptpos.txt
.t.txt // Output the coordinate and calculated function values (Fukui function) of the points
(surface vertices) to this file
```

Now we terminate Multiwfn B, and return to Multiwfn A, then input  
.txt // Load the Fukui function values at the surface vertices from this file  
11 // Output the quantitative data of Fukui function distributed on the local vdW surface corresponding to each atom

You can find below content from the output

Atom#	All /Positive/Negative	Average
1	9.3967E-03	1. 93967E-03
2	8. 13794E-04	8. 13794E-04
3	1. 41595E-03	1. 41595E-03
4	2. 01898E-03	2. 01898E-03
5	1. 25625E-03	1. 25625E-03
6	9. 39694E-04	9. 39694E-04
...	[ignored]	

NaN means there is not negative value of Fukui function on the local molecular surfaces. From the result it is clear that the averages of the Fukui function on the local molecular surface corresponding to *ortho* and *para* carbons are larger value than that of *meta* carbons, thus correctly reflecting the fact that hydroxyl is an ortho-*para*- director.

### 4.12.5 Becke surface analysis on guanine-cytosine base pair

The concept of Hirshfeld and Becke surface analysis have been detailedly introduced in Section 3.15.5, please read them first. In this section I will exemplify how to perform Becke surface analysis on guanine-cytosine (GC) base pair to analyze the weak interaction between the two monomers.

Boot up Multiwfn and input

```
examples\GC.wfn // Generated at M06-2X/6-31+G** level, optimized at PM7 level
12
1 // Change the definition of surface
6 // Use Becke surface. You can also select 5 to use Hirshfeld surface
1-13 // The index range of the atoms you are interested in (cytosine in present case)
2 // Change mapped function
```

*11 // Electron density*

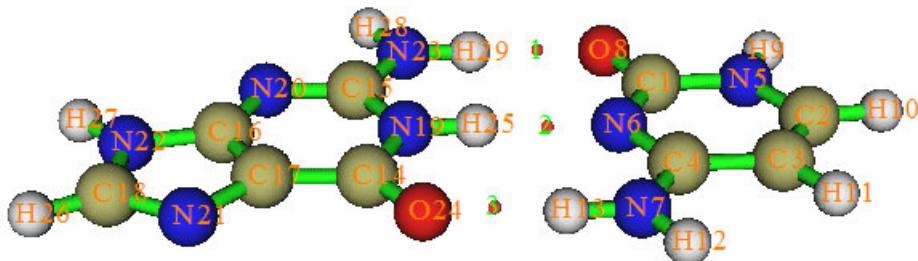
*0 // Start calculation*

Multiwfn found numerous surface minima, which are meaningless in this case, and at the same time three surface maxima are found

Number of surface maxima: 3

#	Value	X/Y/Z coordinate(Angstrom)		
1	0. 042331	-0. 721650	2. 605906	0. 043754
2	0. 049281	0. 767524	0. 959671	-0. 013820
*	3	0. 053205	1. 628343	-1. 269364
				0. 030387

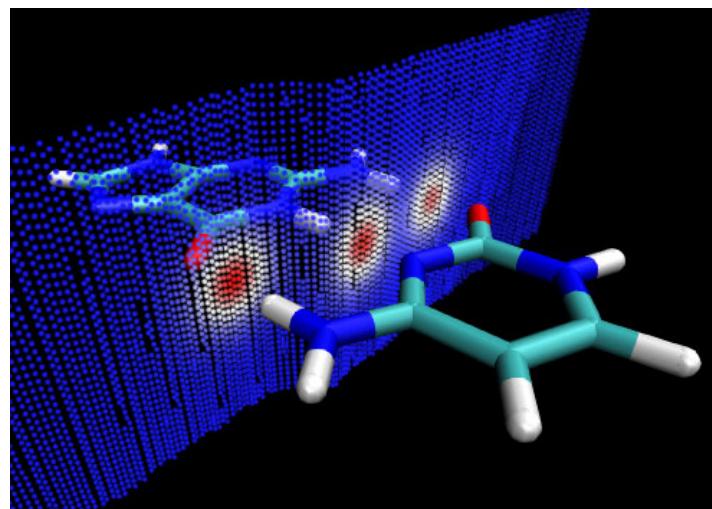
You can choose 0 to visualize them, see below



Since the sequence of electron density at these maxima is  $3 \geq 2 > 1$ , one can expect that the sequence of H-bond strength is  $O24-H13 \geq H25-N6 \geq H29-O8$ . This conclusion is identical to the analysis of AIM bond critical point analysis.

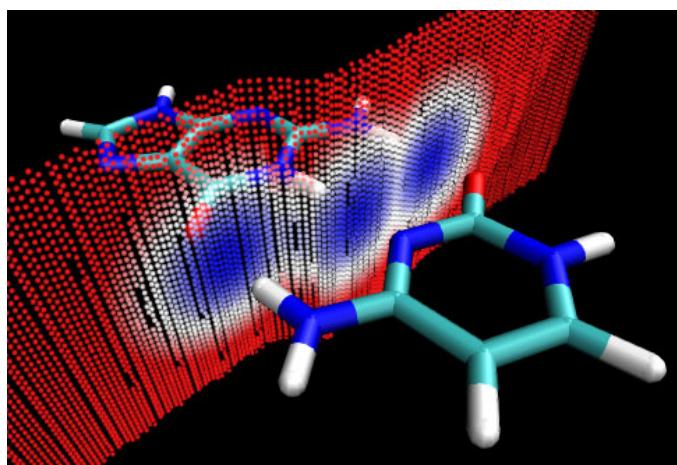
If you want to visualize the shape of Becke surface, simply choose option -3. If you want to plot the Becke surface colored by mapped function value, you need to make use of VMD, as described below. Select option 6 and input 100 to export all surface vertices to vtx.pdb in current folder and in the meantime multiply the data by 100 (since electron density in the Becke surface is small, while the B-factor in pdb format only has two decimal places). Each atom in vtx.pdb now corresponds to a surface vertex, and its B-factor stands for electron density at corresponding position.

Drag "examples\GC.pdb" into main window of VMD program, this file contains geometry of present system. Select "Graphics"- "Representation", change the drawing method to "Licorice" and decrease bond radius to 0.2. Then drag the vtx.pdb into VMD, select "Graphics" - "Representation", change the drawing method from "Lines" to "Points", set coloring method to "Beta", enlarge the size to 6. Run the command *color scale method BWR* in VMD console window. Then you will see



Becke surface is represented by points, and the three red zones correspond to high electron density region, which stem from H-bonds. This example demonstrated that Becke surface analysis is useful to reveal the region where intermolecular interaction is evident.

Repeat above analysis but with  $d_{\text{norm}}$  as mapped function, and replot the Becke surface with the same procedure. Then in the graphical representation window, select "Trajectory" tab, input - 0.5 and 2.0 in the "Color scale data range", you will see below graph

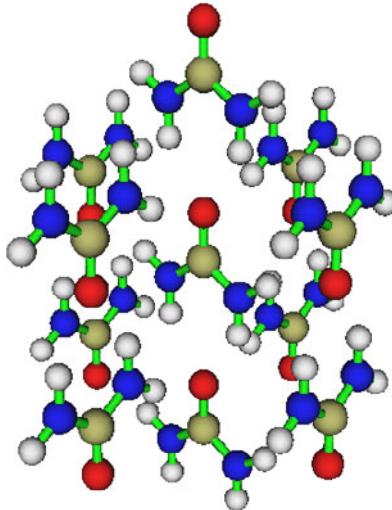


As you can see, using  $d_{\text{norm}}$  as mapped function is also capable of revealing weak interactions; the blue regions corresponds to close contact between the fragment you are interested in (cytosine) and other fragments (guanine only). The advantage of using  $d_{\text{norm}}$  over electron density is that the former does not rely on wavefunction information, so the input file you used can only contain geometry information, such as .pdb and .xyz are completely acceptable in this case. However the physical meaning and robustness of  $d_{\text{norm}}$  is not as good as electron density.

#### **4.12.6 Hirshfeld surface analysis and fingerprint plot analysis on urea crystal**

This time we perform Hirshfeld surface analysis for urea crystal. .cif is the most popular crystal structure format, however currently Multiwfn does not support it. So I dug out a cluster of

ureas from its crystal structure; the file "examples\Urea\_crystal.pdb" contains 11 ureas, the central one will be defined as the fragment in our Hirshfeld surface analysis.



Notice that Hirshfeld surface analysis requires electron density of atoms in their free-states, in Multiwfn there are two ways to generate them: 1. Using built-in atomic densities, this is very convenient, see Appendix 3 for detail; 2. Evaluating atomic densities based on atomic .wfn files, see Section 3.7.3 for detail. In this example we will use way 2 (way 1 works equally well). What we need to do is simply moving the "atomwfn" folder in "examples" folder to current folder. Then during generating Hirshfeld surface, Multiwfn will automatically use the atomic wavefunction files in this folder.

Boot up Multiwfn and input

*examples\Urea\_crystal.pdb*

12

1 // Change surface type

5 // Use Hirshfeld surface

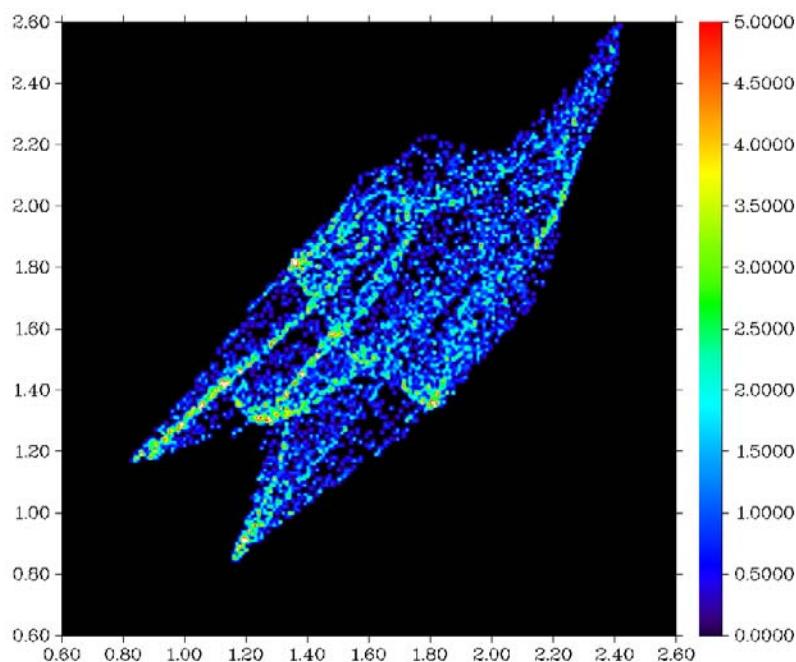
16,36,58,2,77,55,34,13 // The index of the atoms in the central urea

0 // Start calculation. Note that the default mapped function  $d_{\text{norm}}$  is used here

2 // Evaluating atomic densities based on atomic .wfn files

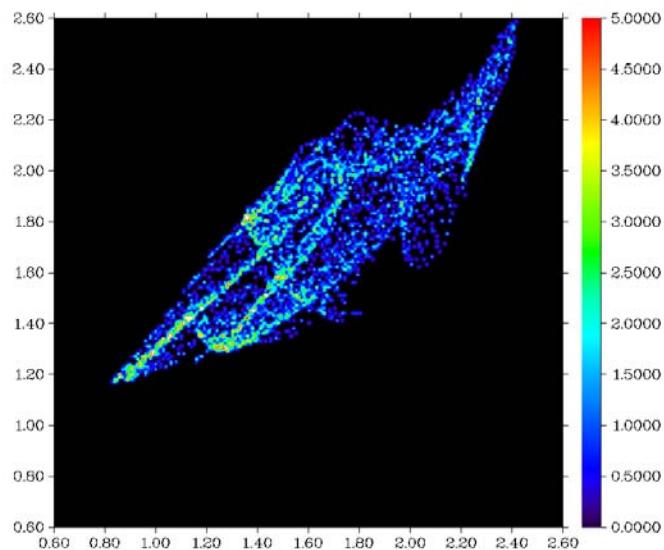
After the calculation is finished, select option 6 to export the surface vertices with  $d_{\text{norm}}$  value to vtx.pdb, and then plot them in VMD by using the method shown in the last section, you will see a graph very similar to the second figure in Section 3.15.5.

Next, we draw fingerprint plot. In the post-process menu select 20 and choose option 0, then choose option 0 again, you will see below graph



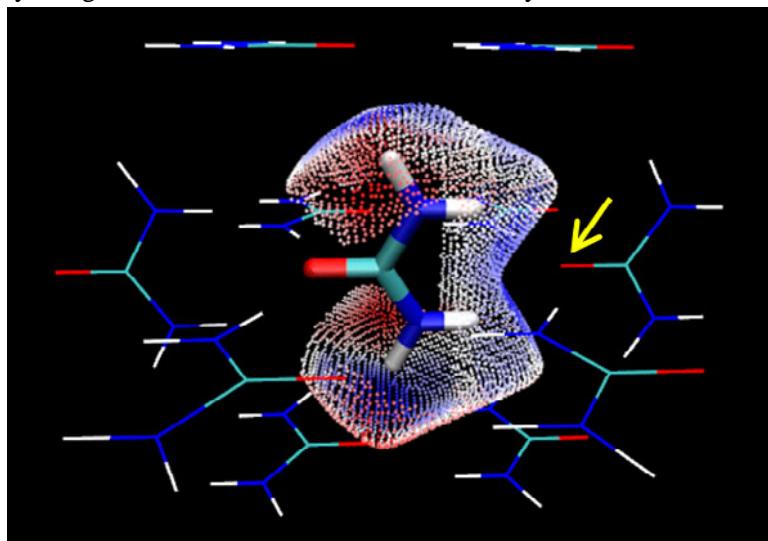
In this figure, X and Y axes correspond to  $d_i$  and  $d_e$ , respectively. It can be seen that there is a pair of spikes at the bottom left of the plot (i.e. short  $d_i$  and  $d_e$ ), this observation suggests that urea behaves as both H-bond acceptor (the lower spike,  $d_i > d_e$ ) and H-bond donor (the upper spike,  $d_i < d_e$ ).

In Multiwfn, the fingerprint plot can be drawn not only for overall Hirshfeld surface, but also for local contact surface (see section 3.15.5 for detail). Let's check the fingerprint plot of the local contact surface between the four hydrogens in central urea and all of the atoms in peripheral ureas. After closing the window showing fingerprint plot, select -1 to return, then input 20 to enter the interface of fingerprint plot analysis again. We need to first define "inside atoms" set and "outside atoms" set, because only the points on the contact surface between the two sets will be taken into account in the fingerprint plot analysis. Choose option 1 to define "inside atoms" set, then press ENTER button directly to use default atom range (i.e. all atoms in the central urea) and then input *H*. Now all hydrogens in the central urea are defined as the "inside atoms" set. Since the default "outside atoms" set is just all of the atoms in peripheral ureas, we do not need to modify it. Select option 0 to start the fingerprint plot analysis, then choose 0, you will see



As you can see, since this time we only considered the hydrogens in the central urea, the urea purely behaves as hydrogen donor, so only one spike at bottom left of the plot is observed

It is interesting to check the shape of the local contact surface, so after closing the window we choose option 5 to export all of the points on the surface to finger.pdb in current folder. Plot them in VMD by using the method shown in the last section, you will see



Clearly, the surface very well portrays the contact between the hydrogens in central urea and the atoms in peripheral ureas. The color corresponds to  $d_{\text{norm}}$  value, more blue implies more close contact.

Next, we check the fingerprint plot between the hydrogens in central urea and the oxygen marked by yellow arrow in above figure. Input below commands

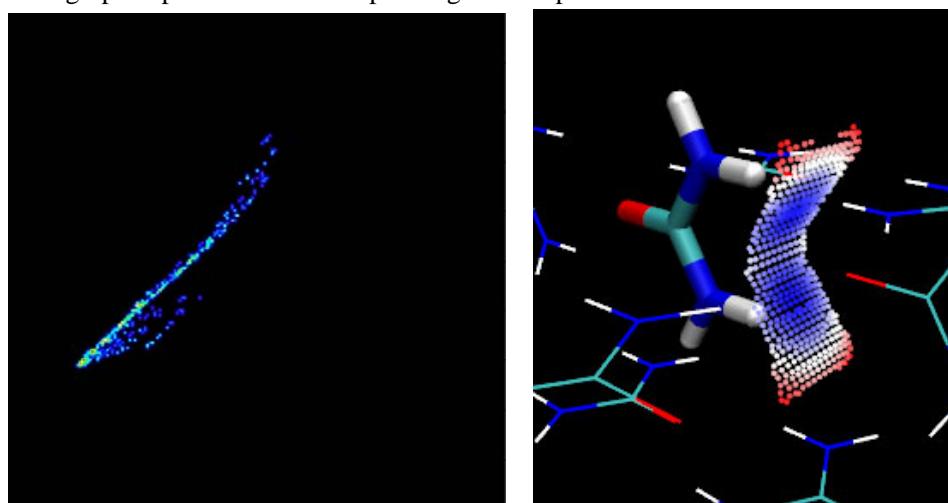
```
-I // Return
20 // Fingerplot analysis
1 // Set inside atoms set
[Press ENTER directly]
H
2 // Set outside atoms set
```

```

76 // The index of the oxygen marked by yellow arrow
[Press ENTER directly] // Namely do not use element type as filter condition
0 // Start fingerprint analysis
3 // Set color scale. Because the default color scale in this case is different to above
fingerprints, the plots are not directly comparable
0,5
0 // Show fingerprint graph on screen

```

The fingerprint plot and the corresponding surface points are shown below



In the fingerprint plot you can see that the distribution scope of surface points is narrow, and the spike is quite evident, showing strong H-bond character due to the contact of H and O.

Fingerprint is especially useful for comparison of the intermolecular interactions in different crystals, see *CrystEngComm*, **11**, 19 (2009) for discussions.

#### 4.12.7 Two tricks to reduce computational time in ESP analysis on vdW surface

Evaluation of ESP on vdW surface is time-consuming, especially for large system with high-quality basis-set. Here I introduce two tricks to reduce computational time in ESP analysis on vdW surface.

##### **Part 1 Reuse ESP data from previous calculations**

If you have performed ESP analysis on a system, and which will be analyzed again later, you can export the ESP data to a plain text file, so that next time when you analyze the same system you can directly make use of the data.

Let's see an example. We first perform ESP analysis on vdW surface as usual

*examples\N-phenylpyrrole.fch*

12

0

Once the calculation is finished, select option 7 to export the surface vertices with ESP values to a plain text file named *vtx.txt* in current folder. After that select -1 to return to last menu.

Assume that we want to perform the analysis again. This time we will directly use the ESP data recorded in the plain text file rather than let Multiwfn calculate them. Input below commands

```

5 // Load mapped function values from external file
1 // Load mapped function at all surface vertices from plain text file
0 // Start the analysis. After the molecular surface is constructed, Multiwfn will prompt you
to input the path of the plain text file recording mapped function values at the surface vertices.

```

*vtx.txt*

Since the ESP values are not calculated this time but readed from *vtx.txt* directly, the analysis results immediately show up on the screen, and they are exactly identical to the ones we obtained at the first time.

### Part2 Using *cubegen* to significantly reduce calculation cost of ESP

Frankly speaking, the calculation speed of ESP in Multiwfn is not as fast as the *cubegen* utility of Gaussian. For very large system, such as carbon nanotube, if you directly use Multiwfn to calculate the ESP value at all surface points, you will find the computational cost is prohibitively high. In this circumstance, one can make use of *cubegen* to calculate the ESP values to significantly reduce the overall time-consuming of quantitative molecular surface analysis. This section will illustrate how to do this. Note that even if you are not a Gaussian user, as long as the program you used can produce .molden file (e.g. ORCA), or are using GAMESS-US, you can also benefits from *cubegen*, because by using subfunction 2 of mainfunction 100 Multiwfn can convert loaded .molden/.gms file to .fch file.

We take N-phenylpyrrole as example. *cubegen* can be found in the Gaussian installation directory.

Boot up Multiwfn and input following commands

*examples\N-phenylpyrrole.fch*

12

5 // Load data of mapped function (viz. ESP in this example) from external file rather than directly calculate them via Multiwfn during the surface analysis

2 // This option is specific for *cubegen*

0 // Start analysis

Multiwfn will calculate electron density and generate surface vertices as usual, then the coordinate (in Angstrom) of all surface vertices will be outputted to *cubegenpt.txt* in current folder.

Now we invoke *cubegen* to calculate ESP at these points. Run the command like below in MS-DOS/Linux/Mac OS command-line window. (Beware that the *N-phenylpyrrole.fch* provided herein may or may not be incompatible with your *cubegen* version)

*cubegen 4 potential N-phenylpyrrole.fch result.cub -5 h < cubegenpt.txt*

where the argument 4 means using 4 threads for parallel calculation; *potential* means calculating ESP; -5 means the points to be calculated are inputted by users manually or redirected in from an external file (*cubegenpt.txt* in this case); *h* means the output file, namely *result.cub*, will be a formatted plain text file. For more detail about *cubegen* utility please consult Gaussian manual.

Return to the Multiwfn window and input the path of the *cubegen* output file *result.cub*, Multiwfn will load the calculated ESP data from it and performs subsequent analysis as usual. You will find that the result is almost exactly identical to that based on the ESP directly evaluated by Multiwfn.

As mentioned in Section 4.4.4, by making use of the *cubegen*, the total time cost of plotting

plane map for ESP can also be significantly reduced. We still take N-phenylpyrrole as example, we will plot ESP for its YZ plane of X=0.

First set parameter "iplaneextdata" in settings.ini to 1, then boot up Multiwfn and input examples\N-phenylpyrrole.fch

```
4 // Plot plane map
12 // ESP
2 // Contour map
[Press ENTER to use default grid setting]
0 // Adjust extension distance
10 // 10 Bohr
2 // XZ plane
0 // Y=0
```

Now *cubegenpt.txt* has been generated in current folder, which contains coordinate of all points in the plotting plane. Run below command to invoke *cubegen* to generate their ESP values

```
cubegen 4 potential N-phenylpyrrole.fch result.cub -5 h < cubegenpt.txt
```

In the Multiwfn window, input the path of the *result.cub*, Multiwfn will load the ESP data from this file and then immediately presents the ESP contour map on screen.

## 4.13 Process grid data

Main function 13 includes a bunch of subfunctions, by using them you can process the grid data loaded from Gaussian-type cube file (.cub) or DMol3 grid file (.grd) or the grid data directly generated by such as main function 5 of Multiwfn. In this section I present several simple applications, please play with other subfunctions by yourself.

### 4.13.1 Extract data points in a plane

In this example we extract average XY-plane data between Z=28 and Z=32 angstrom to a plain text file.

*dens.cub* // A cube file generated by Multiwfn or by some external programs, since cube file is generally large, it is not provided in "example" folder. You can also use the grid data generated internally by Multiwfn instead, that is use main function 5 to calculate grid data first and then choose 0 to return to main menu (the just generated grid data is present in memory)

```
13 // Process grid data
5 // Extract average plane data
28,32 // Range of Z (in Angstrom)
```

Now the data points are exported to output.txt in current folder, including X,Y coordinates and value. You can import this file to plotting software such as sigmaplot to draw plane graph.

Another example, we extract data point on the plane defined by atom 4,6,2.

```
dens.cub
13 // Process grid data
8 // Output data in a plane by specifying three atom indices. This function is commonly used
```

to extract tilted plane, if the plane is parallel to XY, YZ or XZ, you should use function 1,2 or 3 instead respectively

*0* // Use automatically determined tolerance distance. If vertical distance between any point and the plane you defined is smaller than tolerance distance, then the point will be outputted.

*1* // Project the data points in the plane you defined to XY plane, so that you can directly import the outputted file to plotting software to draw plane graphs

Now the data value along with coordinates is exported to output.txt in current folder.

Notice that Multiwfn does not do interpolation during plane data extraction, hence if the quality of grid data is not fine enough (namely spacing between points is large), then the extracted plane data will be sparse (especially severe for the plane not parallel to XY, YZ or XZ plane).

### 4.13.2 Perform mathematical operation on grid data

#### Example 1

Assume that we have two cube files A.cub and B.cub, in this example we obtain their difference cube file (viz. A.cub minus B.cub).

Boot up Multiwfn and input following commands

*A.cub* // Load the first cube file into memory

*13* // Process grid data

*11* // Grid data calculation

*4* // Subtract the grid data in memory by another grid data

*B.cub* // The cube file containing another grid data. Notice that this cube file must have identical grid setting as the first cube file

Now the grid data in the memory has been updated, choose 0 to export it as a new cube file, which is what we need.

#### Example 2

Assume that we have two cube files MO1.cub and MO2.cub, each of them records wavefunction value of an orbital. In this example we will generate a cube file containing total electron density deriving from these two orbitals. According to Born's probability interpretation, square of an orbital wavefunction value is simply its density probability, therefore what we need is the sum of square of the two grid data.

Boot up Multiwfn and input following commands

*MO1.cub*

*13* // Process grid data

*11* // Grid data calculation

*10* // Perform  $A^2+B^2=C$  operation, where A is present grid data (MO1.cub), B is another cube file (MO2.cub), C is the new grid data

*MO2.cub* // Load another cube file

After calculation, the grid data in memory has been updated to C.

*0* // Output the updated grid data

*totdes.cub* // Filename of the new cube file, which contains total electron density of the two orbitals

### 4.13.3 Scaling numerical range of grid data

The numerical range of ELF function is [0,1], in this example, we scale its numerical range to [0,65535] (which is value range of unsigned 16bit integer). We first compute ELF grid data in Multiwfns as described in Section 4.5.1, and then input

```
0 // Return to main menu from post-process interface of grid data calculation
13 // Process grid data
16 // Scale data range
0,1 // Original data range
0,65535 // The range after scaling. Please read Section 3.16.12 for the detail of scaling
algorithm.
```

Now the grid data has been scaled. You can choose function 0 to export the updated grid data to Gaussian cube file, or extract plane data to plain text file by corresponding functions.

### 4.13.4 Screen isosurfaces in local regions

Sometimes we do not want all isosurfaces in the whole space are shown, because too many isosurfaces will confuse our eyes. This section I will show how to screen the isosurfaces of not interest

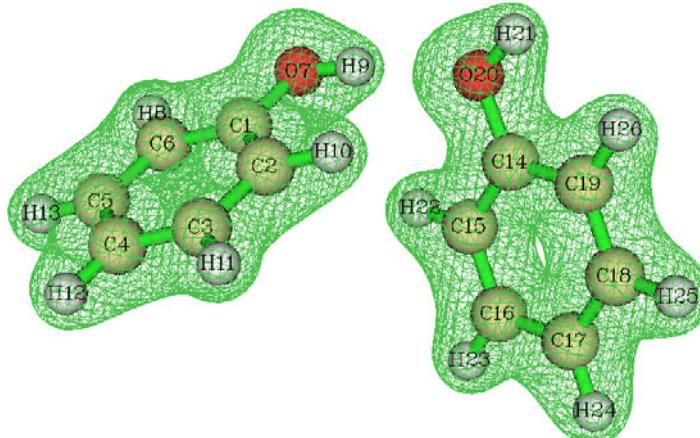
#### 4.13.4.1 Screen isosurfaces inside or outside a region

This section I take electron density of phenol dimer as example. First we generate the grid data as follows (you can also directly load a .cub/.grd file and then enter main function 13)

*examples\phenoldimer.wfn*

```
5
1
2
-1 // Visualize isosurface
```

As you can see, the isosurfaces appear on both phenol molecules.



Assume that we only want the isosurface around the right phenol will be shown, we need to

set the value of the grid points that close to the left phenol to a very small value, for example, zero.

Now prepare an atom list files, e.g. *C:\ltwd\atmlist.txt*, the content should be

```
13
1 2 3 4 5 6 7 8 9 10 11 12 13
```

The first line is the number of atoms in the left phenol, the second line is their indices.

Close the Multiwfn GUI window and input

```
0 // Return to main menu
13 // Process grid data
13 // Set value of the grid points that far away from / close to some atoms
```

-0.7 // That means we will set the value of the grid points inside 0.7 times of vdW radius of the atoms. If input 0.7, then the value of the grid points outside 0.7 times of the vdW radius will be set

```
0 // Set the value to 0
C:\ltwd\atmlist.txt // The file containing the index of the atoms
```

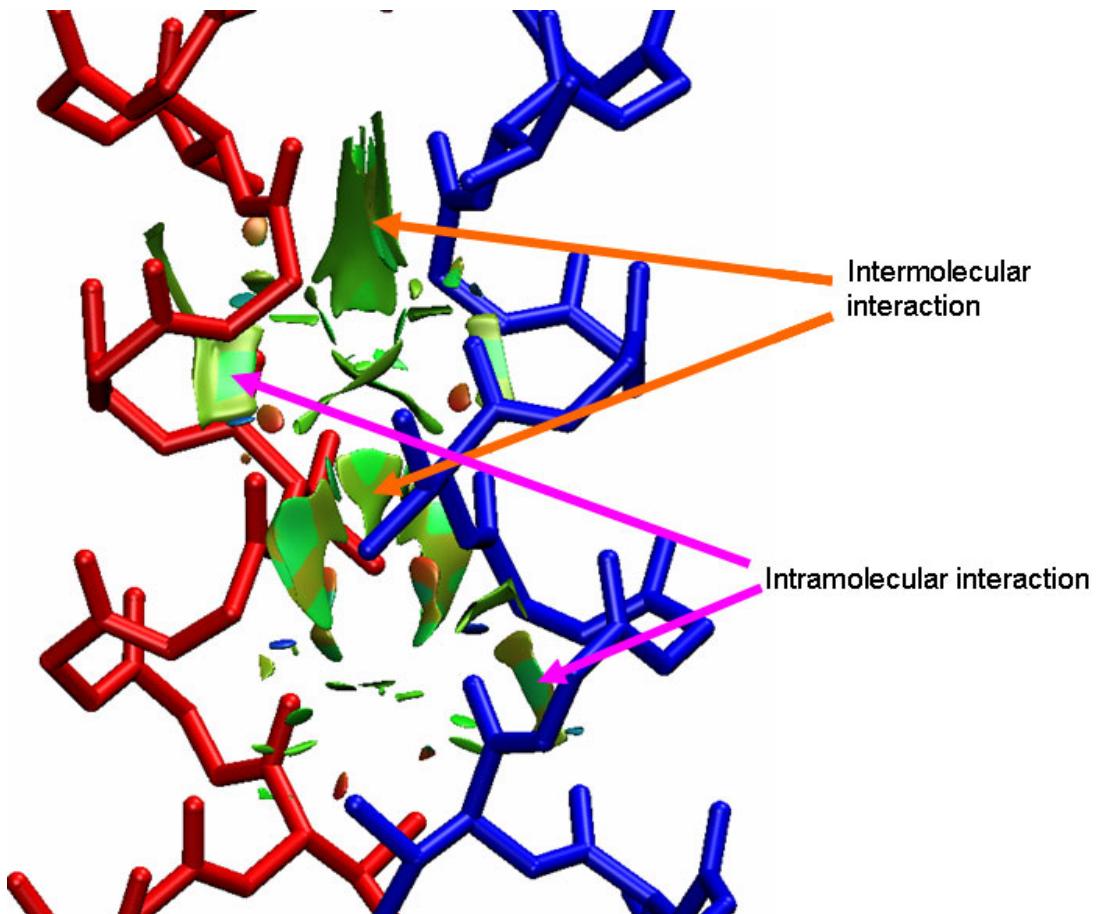
Now the grid data has been updated, let's choose option -2 to visualize the isosurface of current grid data. As you can see, the isosurface of the left phenol has disappeared.

#### **4.13.4.2 Screen isosurfaces outside overlap region of two fragments**

During analysis of inter-molecular interaction by reduced density gradient method (Section 4.100.1), what we want to study is only the isosurfaces in inter-molecular regions. In order to screen isosurfaces in other regions, we can set the value of grid points outside superposition region of scaled vdW regions of two molecules to a very large value (at least larger than maximum value in current grid data). In this section I give you a practical example.

The so-called "scaled vdW regions" is the superposition region of scaled vdW spheres of all atoms in the fragment. While the "scaled vdW sphere" denotes the sphere corresponding to the scaled vdW radii.

Below is a segment of dimeric protein plotted by VMD program (you will know how to draw a similar picture after reading Section 4.100.1), red and blue representing backbone structure of the two chains respectively. Isosurfaces of reduced density gradient exhibit weak interaction region. However, these isosurfaces includes both intermolecular and intramolecular parts, they are interwinded and result in difficulty in visual study of weak interaction between the two chains.



In order to screen those intramolecular isosurfaces, we will use subfunction 14 in main function 13 of Multiwfn. First, we need to prepare two atom list files for the two chains (each chain corresponds to a fragment). *atmlist1.txt* includes atom indices of chain 1, the head and tail of the file are:

```

159 <--- Total number of atoms in chain 1
1 <--- Atom index of the first atom in chain 1
2 <--- Atom index of the second atom in chain 1
3
...
159 <--- Atom index of the last atom in chain 1

```

Similarly, *atmlist2.txt* defines atom list for chain 2, its head and tail parts are:

```

159 <--- Chain 2 has 159 atoms too
160 <--- Atom index of the first atom in chain 2
161 <--- Atom index of the second atom in chain 2
162
...
318 <--- Atom index of the last atom in chain 2

```

Then boot up Multiwfn and input:

*RDG.cub* // The cube file of reduced density gradient corresponding to above graph

*13* // Process grid data

*14* // Set value of the grid points outside overlap region of the scaled vdW regions of the two fragments

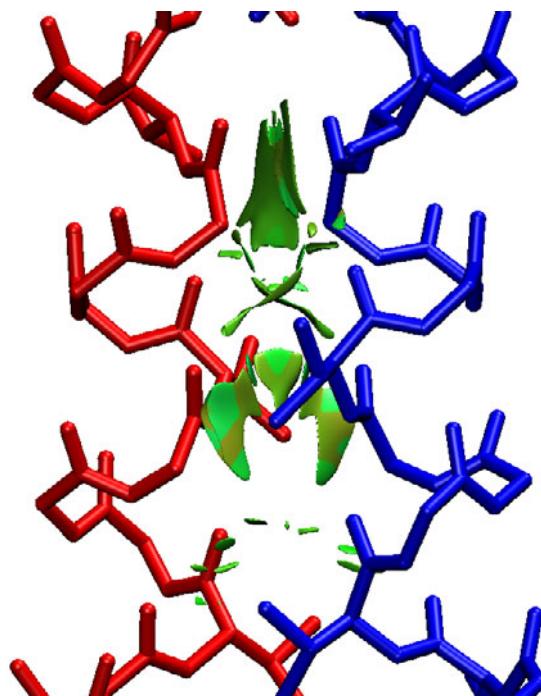
1.8 // The value for scaling vdW radius. In your practical studies, you may need to try this value many times

1000 // Set value of those grid points to 1000, this value is large enough

atmlist1.txt // The name of the atom list file for chain 1

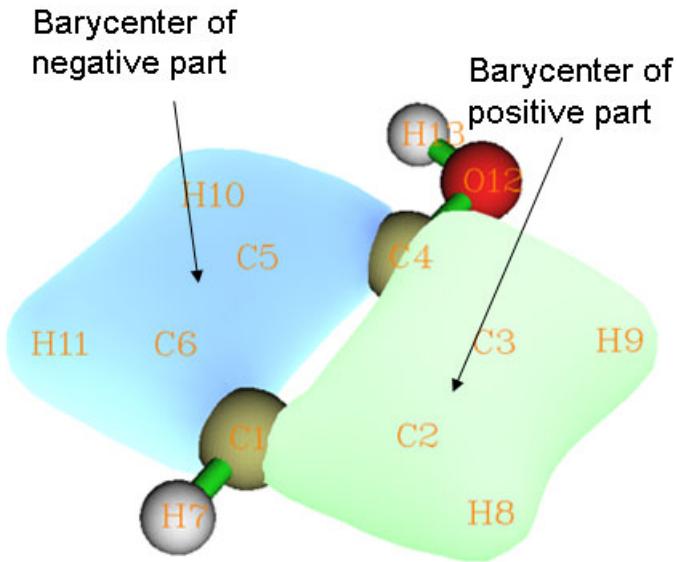
atmlist2.txt // The name of the atom list file for chain 2

Wait for a while, the grid data will be updated. Then choose function 0 to export it as cube file. Using this new cube file to redraw above picture, we find all of intramolecular isosurfaces have disappeared, the graph becomes very clear.



#### 4.13.5 Acquire barycenter of a molecular orbital

In this example, we will calculate barycenter of a molecular orbital. You can also obtain barycenter of other real space functions by similar manner. The definition of barycenter is given in Section 3.16.13. Below is the isosurface of the 10th MO of phenol.



Before calculate the barycenter of the MO, we need to obtain the grid data of the MO. We can do this in Multiwfn, namely boot up Multiwfn and input following commands:

*examples/phenol.wfn*

5 // Calculate grid data

4 // Choose orbital wavefunction

10 // The 10th orbital

2 // Medium quality grid. Finer quality of grid will give rise to more accurate barycenter position

0 // Return back to main menu

Now the grid data has been stored in memory, we will analyze it now

13 // Process grid data

17 // Show statistic data

1 // Select all points

From the output, we can find that the X, Y, Z components of barycenter of the positive part of the MO are (in Bohr) 2.612, -0.524, 0.000 respectively, while that of the negative part are -2.586, -0.710, 0.000. The total barycenter is meaningless currently, since total integral value is zero for this MO. However, total barycenter of absolute value of the MO is useful, especially for macromolecules, from this we can understand where the MO is mainly located. In order to do this, we input:

11 // Grid data calculation

13 // Get absolute value

17 // Show statistic data

1 // Select all points

We find X, Y, Z of total barycenter of the MO are -0.015, -0.618, 0.000. Since there is no negative region now, barycenter of negative part is shown as NaN (Not a Number).

#### 4.13.6 Plot charge displacement curve

Multiwfn is able to calculate and plot integral curve for grid data, see the introduction in

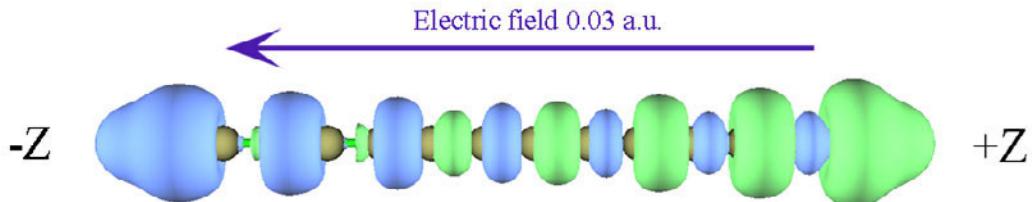
Section 3.16.14. If the grid data is selected as electron density difference, then the integral curve is commonly known as charge displacement curve (CDC), by which the charge transfer can be studied visually and quantitatively, extremely suitable for linear systems. In this example, by means of CDC, we will investigate the intermolecular charge transfer in polyyne ( $n=7$ ) due to the externally applied electric field of 0.03 a.u. along the molecular axis.

The polyyne.wfn and polyyne\_field.wfn files in "example" folder correspond to the polyyne in its isolated state and in the case that external electric field of 0.03 a.u. is applied, respectively. B3LYP/6-31G\* is used in the calculations, and the geometry optimized in isolated state is used for both cases. In Gaussian program, the field can be activated via keyword "field=z+300".

Before plotting the CDC, we must calculate the grid data of electron density difference between these two files first. Boot up Multiwfn and input following commands:

```
examples\polyyne_field.wfn
5 // Calculate grid data
0 // Custom operation
1
-,examples\polyyne.wfn //Subtract the property of polyyne.wfn from polyyne_field.wfn
1 // Electron density
2 // Medium quality grid
```

We first visualize the isosurface of the electron density difference. After select -1 and set the isovalue to 0.004, we will see the graph like below

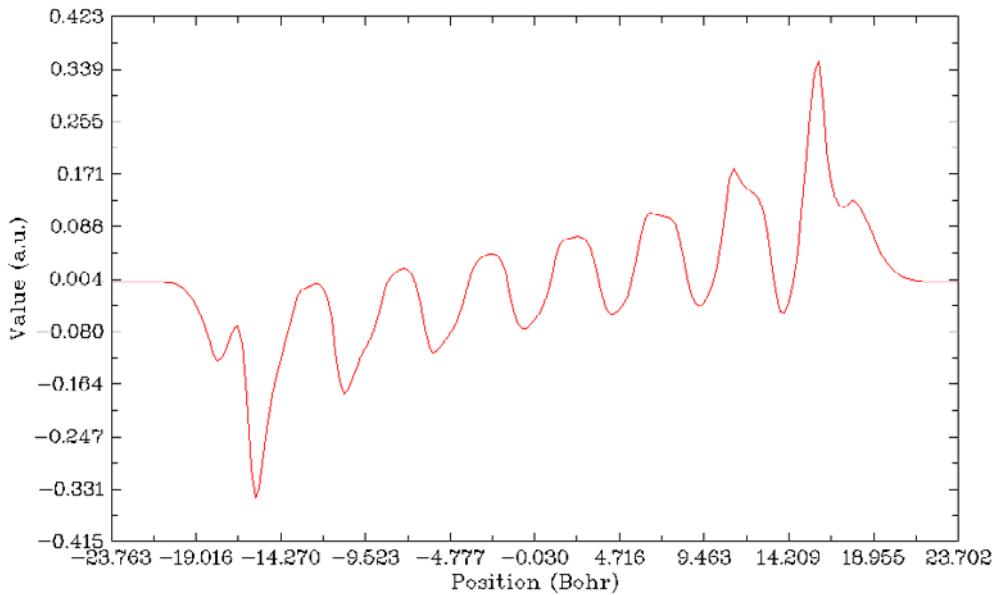


The green and blue parts represent the regions where electron density is increased and decreased after the external electric field is applied, respectively. It can be seen that although green and blue parts interlace with each other, the total trend is that electron transferred to positive side of Z-axis (namely toward the source of the electric field). Next we will plot CDC, which is able to characterize the electron transfer in different regions quantitatively.

Click "Return" button in the GUI and then input

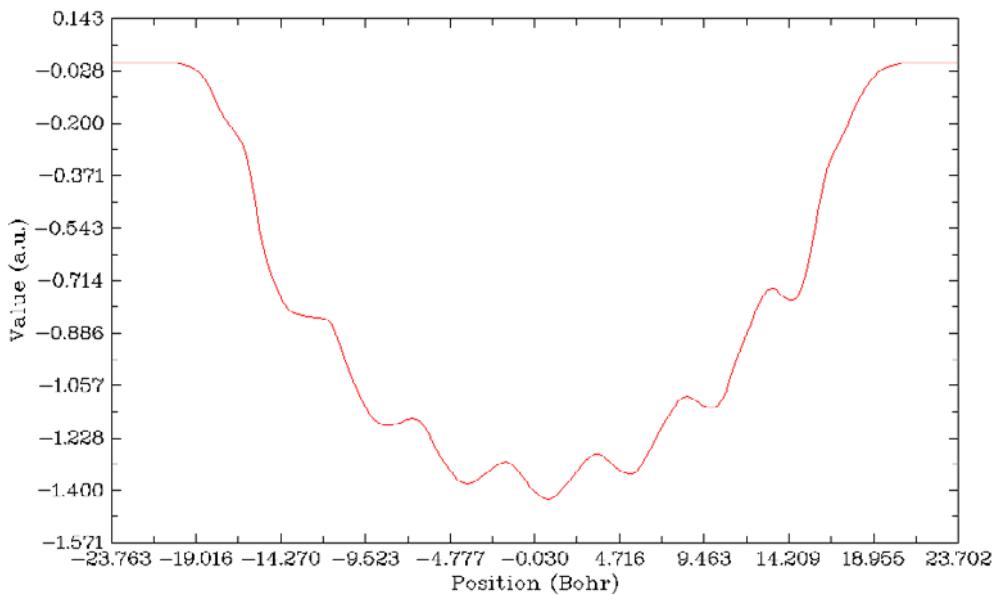
```
0 // Return to main menu
13 // Process grid data
18 // Calculate and plot integral curve
Z // The curve will be plotted in Z direction
a // Select the entire range
```

In the menu, we first choose 2 to plot local integral curve of the grid data of the electron density difference. You will see



From the graph we can examine the integral of electron density difference in the XY planes corresponding to different Z coordinates. The Z coordinate and the value correspond to X and Y axes of the graph. You can directly compare this curve with the isosurface graph shown above, the peaks lower and higher than zero (dashed line) correspond to the blue and green isosurfaces.

Clicking right mouse button on the graph to close it, and then select option 1, the CDC will be shown immediately

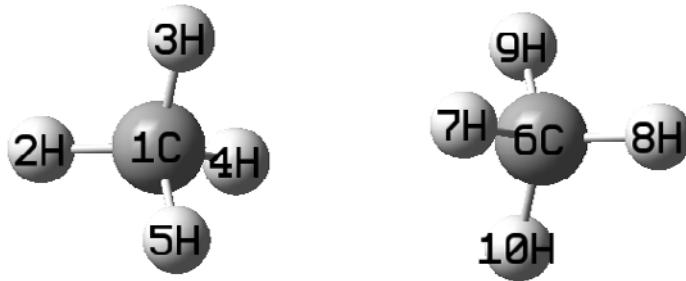


This graph is yielded by integrating the curve shown in the last graph along the molecular axis. In its left part, although there are some fluctuations, the CDC gradually becomes more and more negative and reaches minimum value of 1.4 in the midpoint of the X-axis (corresponding to the center of the polyyne), that means due to the external electric field, the number of lost electrons in the left part of polyyne is 1.4. In the right part of the graph, the CDC increases gradually from -1.4 and finally reaches zero, suggesting that 1.4 electrons are transferred to right part of the polyyne,

and due to the amount of increase and decrease of electron are cancelled with each other exactly in the whole molecular space, there is no variation of the total number of electrons (in other words, integral of the electron density difference in the whole molecular space is exactly zero).

#### 4.13.7 Evaluation of electron density overlap

In this example we take methane dimer as example to evaluate where electron density of the two monomers overlap with each other evidently. The structure of the methane dimer is



We first obtain grid data for an arbitrary real space function for the dimer. Boot up Multiwfn and input:

```
examples\rho_overlap\dimer.pdb
5
100 // User define function, by default this function doesn't take any computational time
-10 // Set grid extension distance
2 // Decrease the distance to 2 Bohr to avoid waste of grid at system boundary
2 // Medium quality grid
2 // Export grid data as userfunc.cub
```

Now we calculate wavefunction file by Gaussian for the two monomers, the input files are *monomer1.gjf* and *monomer2.gjf* in *examples\rho\_overlap* folder. Finally we obtained *monomer1.wfn* and *monomer2.wfn*. Beware that the *nosymm* keyword must be used in Gaussian calculation to avoid the automatic reorientation and translation.

Now we calculate electron density grid for monomer 1 over the whole space

```
monomer1.wfn
5
1 //Electron density
8
userfunc.cub // Use this cube file to define the grid, which corresponds to the whole space
2 // Export grid data
```

Then rename the resulting *density.cub* to *density1.cub*. Repeat above steps for monomer2 to obtain *density2.cub*.

Now we calculate grid data of  $\min(\rho(1), \rho(2))$ , namely take the minimal value of the two sets of electron density everywhere. Boot up Multiwfn and input:

```
density1.cub
13
11
```

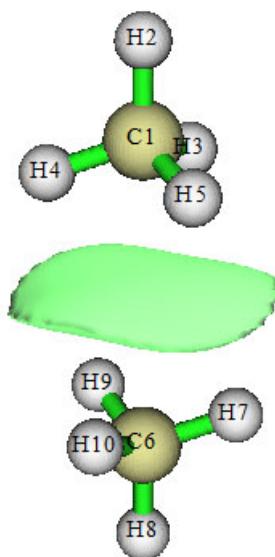
```
21 // Take min(rho(1),rho(2))
density2.cub
0 //Export resulting grid data
overlap.cub
```

we open the overlap.cub and density2.cub by text editor, copy atomic coordinates from the latter to the former, and meantime change the number of atoms. Then the head of the overlap.cub should look like below (the highlighted texts are modified parts)

Generated by Multiwfn

Total 531846 grid points				
10	-3. 693194	-3. 955866	-7. 444301	
63	0. 119334	0. 000000	0. 000000	
67	0. 000000	0. 119334	0. 000000	
126	0. 000000	0. 000000	0. 119334	
6	6. 000000	0. 000000	0. 000000	3. 371271
1	1. 000000	0. 000000	0. 000000	5. 444301
1	1. 000000	0. 000000	1. 955867	2. 677742
1	1. 000000	-1. 693195	-0. 976988	2. 677742
1	1. 000000	1. 693195	-0. 976988	2. 677742
6	6. 000000	0. 000000	0. 000000	-3. 371271
1	1. 000000	1. 693195	0. 976988	-2. 677742
1	1. 000000	0. 000000	0. 000000	-5. 444301
1	1. 000000	-1. 693195	0. 976988	-2. 677742
1	1. 000000	0. 000000	-1. 955867	-2. 677742

Boot up Multiwfn and load the overlap.cub, enter main function 0, change the isovalue to a small one such as 0.0005, you will clearly see the density overlap region:



## 4.14 Adaptive natural density partitioning (AdNDP) analysis

Theory basis of AdNDP analysis has been introduced in Section 3.17.1, please read it first. Below I will show you how to use AdNDP approach to study multi-centers orbitals of several practical molecules.

NOTICE: Using diffuse functions in AdNDP analysis is strongly deprecated, because they often cause numerical problems (which sometimes leads to crash when Multiwfn loading input file) and never improve AdNDP results at all!

### 4.14.1 Analyze $\text{Li}_5^+$ cluster

In *Chem. Eur. J.*, **6**, 2982, the authors showed that  $\text{Li}_5^+$  cluster has two 4-centers 2-electrons (4c-2e) bonds by examining ELF isosurfaces. In present example, we will use AdNDP approach to study this cluster to verify their statement. We first optimize  $\text{Li}_5^+$  cluster under B3LYP/6-311G\* level and then compile an input file of single point task for Gaussian. *pop=nboread* keyword must be specified in route section, and *\$NBO AONAO DMNAO \$END* must be added to the end of the input file. Run this file by Gaussian, and then convert check point file to .fch format. The input file, output file and .fch file have been given in "examples\AdNDP" folder.

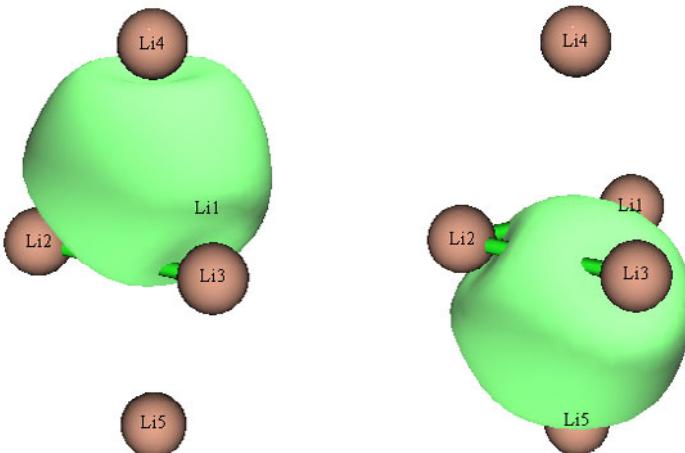
Boot up Multiwfn and input *examples\AdNDP\Li5+.out*, and then choose main function 14. After Multiwfn loaded some necessary information, a menu appears. Since this cluster is small, we can directly use exhaustive manner to search all possible 1c-2e, 2c-2e, 3c-2e, 4c-2e and 5c-2e orbitals in turn. We first choose option 2 to search 1c-2e orbitals (namely lone pairs), however, because occupation numbers of all tried 1c orbitals are lower than default threshold (which is a value close to 2.0 and can be adjusted by option 4), the candidate orbitals list shown in front of the menu is still empty. We then choose option 2 twice to search 2c-2e and 3c-2e orbitals in turn, we still can't find any orbital with high occupation numbers. Next we select option 2 again to search 4c-2e orbitals, this time the candidate orbital list is no longer empty, there are two orbitals in it:

```
# 2 Occ: 1. 9966 Atom: 1Li 2Li 3Li 4Li
# 1 Occ: 1. 9966 Atom: 1Li 2Li 3Li 5Li
```

Due to their high occupation number, it clear that they are ideal 4c-2e orbitals, therefore we decide to choose option 0 and input 2 to pick them out from candidate list and save as AdNDP orbitals. Whereafter the list of AdNDP orbitals can be printed by option 5.

You may have noticed that the number of residual valence electrons (shown at the top of the menu) has been updated to 0.020027, which is already very close to zero, it is suggested it is meaningless to continue to search 5c-2e orbitals because they would be impossible to be found.

Now you can choose option 7 to visualize the two 4c-2e AdNDP orbitals. In order to calculate orbital wavefunction, Multiwfn needs to load basis-set information from corresponding .fch file first. Since Li5+.fch is in the same folder and has identical name as Li5+.out, the .fch file will be directly loaded. When loading is finished, a GUI pops up, which is completely identical to the one of main function 0. AdNDP orbitals can be plotted by selecting corresponding numbers in the right-bottom list. The 0.05 isosurfaces of the two orbitals are shown below.



Grid data of AdNDP orbitals can be exported as Gaussian cube files by option 9, so that you can draw them by some third-part visualization programs such as VMD. You need to input orbital index range, assume that we want to output the two 4c-2e AdNDP orbitals we just found, we should input 1,2, then they will be exported as AdNDPorb0001.cub and AdNDPorb0002.cub in current folder.

By option 3, you can set the number of centers of multi-centers orbitals in the next exhaustive search. So, assume that you have already known that there are two 4c-2e orbitals in present system, you can directly choose option 3, input 4 and then select option 2 to start the exhaustive search of 4c-2e orbitals, the exhaustive searchs of 1c-2e, 2c-2e and 3c-2e orbitals will be skipped.

It is also possible to obtain energies of the AdNDP orbitals that have been picked out. To realize this, you need to provide additional plain text file containing Fock matrix of present system in lower-triangular sequence, so that orbital energies can be yielded after some transformations of this matrix. The most straightforward procedure is as follows: Copy *examples\Li5+.gif* as *examples\Li5+\_47.gif*, change content between \$NBO ... \$END to *archive file=C:\Li5+*. Then after running this file, *C:\Li5+.47* will be yielded, which is input file of GENNBO program and contains the Fock matrix that we need. Open this file by text editor, search \$FOCK, and then copy all data between \$FOCK ... \$END to a plain text file named *Li5+\_FOCK.txt*. Then choose " 16 Output energy of picked AdNDP orbital" in the AdNDP analysis interface, input the path of *Li5+\_FOCK.txt*, Multiwfn will load it and immediately print out AdNDP orbital energies, as shown below:

Energy of picked AdNDP orbitals:

Orbital :	1	Energy (a.u./eV) :	-0.325776	-8.8648
Orbital :	2	Energy (a.u./eV) :	-0.325776	-8.8648

As expected, the two orbitals are degenerate in energy, since they have exactly equivalent shape.

#### 4.14.2 Analyze $B_{11}^-$ cluster

This time, we will try to reproduce the AdNDP analysis result of  $B_{11}^-$  cluster that given in AdNDP original paper (*Phys. Chem. Chem. Phys.*, 10, 5207).

The files needed by this instance, namely *B11-.out* and *B11-.fch* can be found in "examples\AdNDP" folder. The geometry was optimized under B3LYP/6-311+G\*, while the wavefunction was generated under HF/STO-3G level. You may wonder whether the result is meaningful under such low level of basis-set, actually, AdNDP analysis is rather insensitive to

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basis-set quality, even STO-3G is able to produce at least qualitative resonable result. In addition, using larger basis set will bring additional cost at AdNDP analysis stage.

Boot up Multiwfn and input *examples\AdNDP\B11-.out*, then choose 14 to enter AdNDP module. As usual, we select 2 to search 1c-2e orbitals first, but we find nothing (this is common case). Then select 2 again to exhaustively search 2c-2e orbitals from the 11 atoms, Multiwfn will totally try  $11!/(11-2)!/2!=55$  combinations, finally there are nine 2c orbitals present in candidate list (sorted according to occupation number from large to small):

```
# 9 Occ: 1. 9727 Atom: 6B 10B
# 8 Occ: 1. 9727 Atom: 5B 11B
# 7 Occ: 1. 9742 Atom: 7B 9B
# 6 Occ: 1. 9742 Atom: 7B 8B
# 5 Occ: 1. 9869 Atom: 2B 6B
# 4 Occ: 1. 9869 Atom: 3B 5B
# 3 Occ: 1. 9871 Atom: 9B 11B
# 2 Occ: 1. 9871 Atom: 8B 10B
# 1 Occ: 1. 9942 Atom: 2B 3B
```

All of them have occupation number close to 2.0, ostensibly one can directly pick all of them out as AdNDP orbitals, however, it is not recommended to do so, because neighboring orbitals may share the same densities. For example, the 1th and the 4th candidate orbitals share the same densities, since both of them related to atom 3. In order to avoid overcount of electrons, firstly you should pick out the first three orbitals by choosing option 0 and input 3, then the density of the first three orbitals will be depleted from density matrix, after that wavefunction and occupation number of remained candidate orbitals will be updated automatically. After that the candidate list becomes

```
# 6 Occ: 1. 9538 Atom: 6B 10B
# 5 Occ: 1. 9538 Atom: 5B 11B
# 4 Occ: 1. 9556 Atom: 7B 8B
# 3 Occ: 1. 9556 Atom: 7B 9B
# 2 Occ: 1. 9750 Atom: 2B 6B
# 1 Occ: 1. 9750 Atom: 3B 5B
```

Since some densities have been depleted, occupation number of remained six candidate orbitals slightly decreased. Now, we pick out the first four candidate orbitals by choosing option 0 and input 4. Although both of 3th and 4th orbitals related to atom 7, here we have to ignore the slight overcount of electrons, otherwise their degeneration will be broken and thus the final AdNDP pattern will not be consistent with molecular symmetry anymore (you can choose option 8 to carefully inspect candidate orbitals before you decide to pick them out). Finally, we pick out the last two orbitals (6-10 and 5-11). Currently the number of residual valence electrons is 16.307, it reveals that it is probable to find several higher number of centers orbitals with nearly two electrons occupied.

Now we select option 2 to start the search of 3c-2e orbitals, the resulting candidate orbital list is

```
# 9 Occ: 1. 7399 Atom: 1B 6B 10B
# 8 Occ: 1. 7399 Atom: 4B 5B 11B
# 7 Occ: 1. 7502 Atom: 1B 3B 4B
```

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```
# 6 Occ: 1. 7502 Atom: 1B 2B 4B
# 5 Occ: 1. 8504 Atom: 1B 2B 6B
# 4 Occ: 1. 8504 Atom: 3B 4B 5B
# 3 Occ: 1. 8603 Atom: 1B 4B 7B
# 2 Occ: 1. 8673 Atom: 4B 9B 11B
# 1 Occ: 1. 8673 Atom: 1B 8B 10B
```

After we pick out two orbitals (1-8-10 and 4-9-11), one orbital (1-4-7) and two orbitals (3-4-5 and 1-2-6) as AdNDP orbitals in turn, the highest occupation number of remained candidate orbitals is 1.41, which is obviously too low to be recognized as 3c-2e orbital, so they will not be concerned. Currently the number of residual valence electrons is 7.03.

Then you can start to search higher number of centers orbitals, however this is never a trivial task, and there is no absolute rule on how to pick out candidate orbitals, different picking manners result in diverse AdNDP patterns. You may have to try many times before obtaining an optimal AdNDP pattern. It is recommended to use option 11 to save present density matrix and AdNDP orbital list into memory, so that you needn't to worry about improperly picking out candidate orbitals, since present state can be recovered anytime by choosing option 12.

Assumed that you didn't pick out any 4c orbital and have performed exhaustive search of 5c-2e orbitals, you will find many 5c candidate orbitals whose occupation numbers are about 1.9. Indeed they have qualifications to be picked out as AdNDP orbitals since their occupation number is high, however it does not mean that picking them out is the best choice, since it is possible that one can find higher number of centers orbitals with occupation numbers more closed to 2.0.

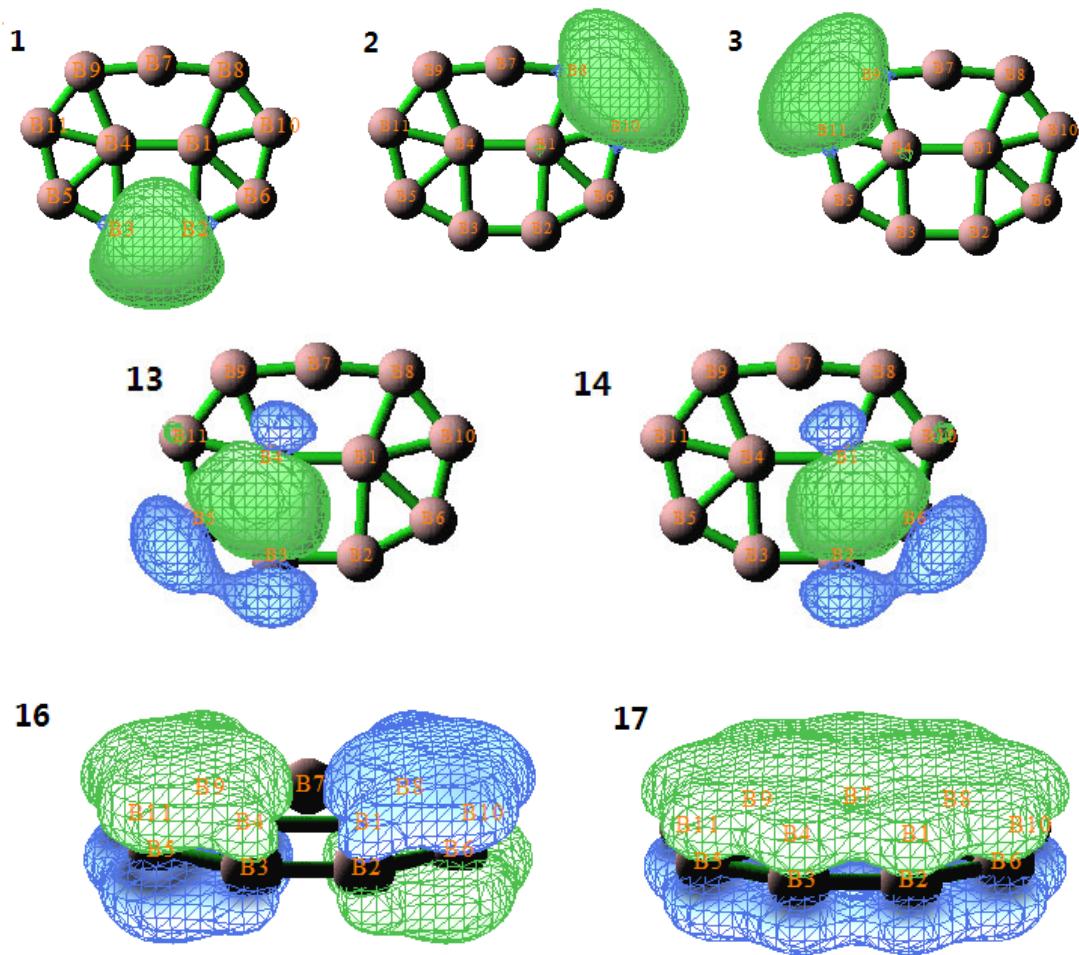
Canonical molecular orbitals (CMOs) sometimes are useful guidances on the search of multi-centers orbitals. From CMO graph of  $\text{B}_{11}^-$  (see Fig. 6 in AdNDP original paper) we find there are three globally delocalized  $\pi$ -orbitals, they may mixed with each other in some way to form 11c-2e AdNDP orbitals. Therefore we choose option 3, input 11 and then choose option 2 to directly search 11c orbitals. As expected, three orbitals present in candidate orbitals list with ideal double occupation. After picking them out as AdNDP orbitals, the entire analysis process is finished. The number of residual valence electrons is 1.03 currently, this value reflects the electrons that cannot be fully represented by present AdNDP pattern (analogous to non-Lewis composition in NBO language). By choosing option 5, information of all AdNDP orbitals can be printed out:

```
# 1 Occ: 1. 9942 Atom: 2B 3B
# 2 Occ: 1. 9871 Atom: 8B 10B
# 3 Occ: 1. 9871 Atom: 9B 11B
# 4 Occ: 1. 9750 Atom: 2B 6B
# 5 Occ: 1. 9750 Atom: 3B 5B
# 6 Occ: 1. 9556 Atom: 7B 9B
# 7 Occ: 1. 9556 Atom: 7B 8B
# 8 Occ: 1. 9337 Atom: 5B 11B
# 9 Occ: 1. 9337 Atom: 6B 10B
# 10 Occ: 1. 8673 Atom: 1B 8B 10B
# 11 Occ: 1. 8673 Atom: 4B 9B 11B
# 12 Occ: 1. 8533 Atom: 1B 4B 7B
# 13 Occ: 1. 8451 Atom: 3B 4B 5B
# 14 Occ: 1. 8451 Atom: 1B 2B 6B
```

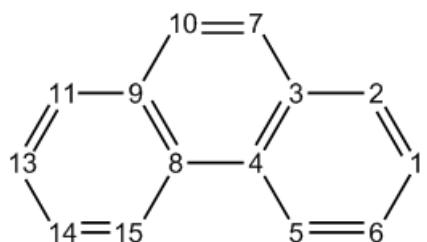
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```
#   15 Occ: 2.0001 Atom: 1B 2B 3B 4B 5B 6B 7B 8B 9B
    10B 11B
#   16 Occ: 2.0000 Atom: 1B 2B 3B 4B 5B 6B 7B 8B 9B
    10B 11B
#   17 Occ: 1.9999 Atom: 1B 2B 3B 4B 5B 6B 7B 8B 9B
    10B 11B
Total occupation number in above orbitals 32.9754
```

Isosurface of several selected 2c-2e, 3c-2e and 11c-2e AdNDP orbitals are shown below (plotted by option 7), isovalue is set to 0.03.



#### 4.14.3 Analyze phenanthrene



AdNDP analysis of phenanthrene ( $C_{14}H_{10}$ , see above) has been given in *J. Org. Chem.*, **73**,

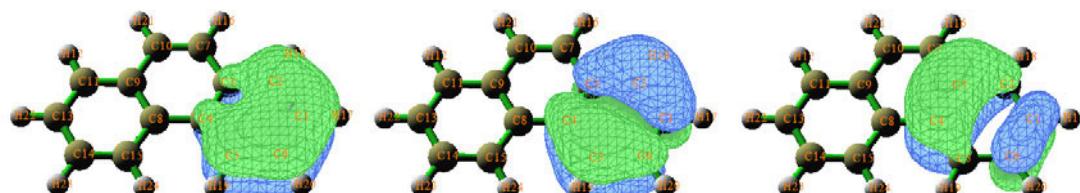
9251, in this section we will repeat their result, you will learn how to use user-directed search. Files used in this example can be found in *examples\AdNDP* folder with phenanthrene prefix.

First we load *examples\AdNDP\phenanthrene.out* and enter main function 14. Consistent with the previous examples, we select option 2 twice to search 1c orbitals and then search 2c orbitals. No 1c-2e orbitals can be found, while there are 31 candidate 2c orbitals present in the list. Ten of them correspond to C-H  $\sigma$ -bonds and have no overlapping with each other, so we can pick them out first, namely choosing option 0, input 8,15, then choose option 0 again and input 9,10. Next, we successively pick out sixteen 2c candidate orbitals that corresponding to C-C  $\sigma$ -bonds (the most careful input is 0 2 0 1 0 2 0 1 0 2 0 2 0 2 0 2 0 2, where space denotes pressing ENTER key). Then there are only five orbitals remain, the first orbital with occupation number of 1.80 corresponds to the  $\pi$ -bond between C7 and C10, it seems worth to be picked out. The occupation numbers of the four remained orbitals are about 1.72, thus they are not ideal 2c-2e bonds, we do not concern these five orbitals at the moment.

Although we can use option 2 to exhaustively search 3c, 4c, 5c ... orbitals as usual, however this may be not a good idea for present system, user-directed search is often more effective. We first choose option 13 to check population of residual electrons on each atom, see below, this information is usually helpful for guiding users to properly set up exhaustive search list. (Note: The exhaustive search triggered by option 2 is only applied to the atoms in exhaustive search list, which contains all atoms in present system by default)

1C : 1. 0250	2C : 1. 0370	3C : 1. 0280	4C : 1. 0414
5C : 1. 0339	6C : 1. 0262	7C : 0. 1322	8C : 1. 0414
9C : 1. 0280	10C : 0. 1322	11C : 1. 0370	12H : 0. 0117
13C : 1. 0250	14C : 1. 0262	15C : 1. 0339	16H : 0. 0121
17H : 0. 0113	18H : 0. 0117	19H : 0. 0126	20H : 0. 0111
21H : 0. 0121	22H : 0. 0113	23H : 0. 0111	24H : 0. 0126

From above data it is clear that hydrogens have almost zero population numbers, hence they could be safely removed from the exhaustive search list. Due to the same reason C7 and C10 can be removed too. The other atoms, whose occupation numbers are about 1.03, are the carbons composing the two 6-member rings in both sides of the molecule. It can be expected that the two rings may be analogous to benzene ring and hence representing local aromaticity in phenanthrene. Based on this consideration, we choose option -1 to enter the interface for defining exhaustive search list, input *clean* to clean up the default content first, then input *a 1-6* to add atom 1,2,3,4,5,6 into the list, and then input *x* to save and exit. Now the search list only contains carbon atoms in a single ring. Select option 3 and input 6, then choose option 2 to search 6-centers orbitals in the ring, three candidate orbitals will be found, whose occupation numbers are 2.000, 1.985 and 1.821 respectively, they are appropriate to be picked out as 6c-2e AdNDP orbitals, so we pick them out now. Their 0.03 isosurfaces are shown below, which look like  $\pi$  molecular orbitals of benzene.



Next, with the same method, we define exhaustive search list as atoms 8,9,11,13,14,15 and

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then search out the corresponding three 6c-2e orbitals, then finally pick them out. Now all AdNDP orbitals (26\*2c-2e, 6\*6c-2e) have been found, the AdNDP analysis is finished.

With similar procedure, we evaluate AdNDP orbital energies like Section 4.14.1. The plain text file containing Fock matrix of current molecule is directly provided as *examples\phenanthrene\_FOCK.txt*, which was yielded by *examples\phenanthrene\_47.gjf*. We choose option 16 and input the path of this file, Multiwfn immediately outputs the orbital energies:

... (ignored)

Orbital :	23	Energy (a. u. /eV):	-0. 697578	-18. 9821
Orbital :	24	Energy (a. u. /eV):	-0. 697578	-18. 9821
Orbital :	25	Energy (a. u. /eV):	-0. 685803	-18. 6616
Orbital :	26	Energy (a. u. /eV):	-0. 685803	-18. 6616
Orbital :	27	Energy (a. u. /eV):	-0. 348201	-9. 4750
Orbital :	28	Energy (a. u. /eV):	-0. 255535	-6. 9535
Orbital :	29	Energy (a. u. /eV):	-0. 264372	-7. 1939
Orbital :	30	Energy (a. u. /eV):	-0. 348201	-9. 4750
Orbital :	31	Energy (a. u. /eV):	-0. 255535	-6. 9535
Orbital :	32	Energy (a. u. /eV):	-0. 264372	-7. 1939

As you can see, the last six, which correspond to  $\pi$  orbitals, have energy much higher than  $\sigma$  orbitals. The three  $\pi$  orbitals in left six-membered ring is symmetric to the counterpart three  $\pi$  orbitals in right six-membered ring. In each set, the highest two are nearly degenerate and evidently higher than the lowest one, this situation is very similar to occupied  $\pi$  orbitals of isolated benzene.

Sometimes composition of AdNDP orbitals are interesting. In order to perform the analysis, we select option 14 to output all of the 26+6=32 AdNDP orbitals as *AdNDP.molden* in current folder, note that this step requests .fch file of present system. Our system has 146 basis functions, so there are 146 orbitals in the .molden file, but only the first 32 orbitals correspond to the AdNDP orbitals that we have found, the other orbitals are meaningless and should be simply ignored.

By using the *AdNDP.molden* as input file, you can use main function 8 to analyze the composition of AdNDP orbitals. Some examples of orbital composition analysis can be found in Section 4.8, related theoretical introductions can be found in Section 3.10. All orbital composition analysis methods except for NAO method can be applied to AdNDP orbitals. For example, here we analyze the composition of the 27th AdNDP orbital, namely the orbital at left side of above graph. Boot up a new Multiwfn and input below command:

```
AdNDP.molden
8
1 // Mulliken analysis
27
```

Contribution of the six carbons in the ring are shown below, please compare the data with the corresponding AdNDP orbital isosurface.

Atom	1(C ) :	33. 144079%
Atom	2(C ) :	13. 320911%
Atom	3(C ) :	1. 585369%

```

Atom    4(C ) :   1. 925742%
Atom    5(C ) :  15. 297803%
Atom    6(C ) :  34. 805871%

```

## 4.15 Fuzzy atomic space analysis

Delocalization index, PDI, FLU and FLU- $\pi$  were originally proposed for AIM atomic space, it has been shown that, if they are calculated in fuzzy atomic space, the computational cost would be significantly reduced, while the results are still reasonable. The introduction of basic concepts of fuzzy atomic space has been given in Section 3.18.0. In this section, we will calculate these quantities in the fuzzy atomic space defined by Becke. Multiwfn also supports Hirshfeld and Hirshfeld-I methods to defined atomic space, however, the Becke's definition has the advantage that the calculation is independent on reference atomic densities, so we do not need to concern the preparation of .wfn files for atoms in their free-states, and therefore the calculation procedure is somewhat simpler.

### 4.15.1 Study delocalization index of benzene

The definition of delocalization index (DI) has been detailedly introduced in Section 3.18.5. In present instance we will calculate DI in Becke's fuzzy atomic space to study the extent of electron delocalization between different atom pairs in benzene. Notice that the original DI is defined in Bader's AIM atomic space, so the DIs calculated in this example may somewhat differ to the ones in some literatures.

Boot up Multiwfn, and input following commands

```
examples\benzene.wfn // Generated under B3LYP/6-311G*
```

```
15 // Fuzzy atomic space analysis
```

`4` // Calculate localization index (LI) and DI. Multiwfn first makes use of DFT numerical quadrature scheme to calculate atomic overlap matrix (AOM) in each fuzzy atom space, and then convert AOM to DI and LI.

```
n // Do not output LI and DI to plain text file
```

Multiwfn automatically checks and output the error of AOM, for present calculation the error is less than 0.001, which is completely negligible. If the error is too larger to be accepted, you can set "iautointgrid" in settings.ini to 0, and set "radpot" and "sphpot" to a large value. When "iautointgrid" is equal to 1, Multiwfn uses (40,230) grid points to calculate AOM, accuracy of which directly affect the accuracy of LI, DI, as well as of PDI and FLU.

From the DI matrix outputted on the screen, we can see that DI between adjacent two carbon atoms and adjacent C-H atoms are large (1.467 and 0.877, respectively), that means electron delocalization between bonded atoms is strong, this is mainly due to the shared electron of  $\sigma$  bond. In contrast, the DI between non-bonded carbon atoms is very small, about 0.1, nevertheless evidently not zero, reflecting the high-degree delocalization nature of  $\pi$  electrons.

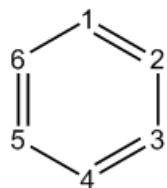
The DI calculated in fuzzy atomic space is essentially the fuzzy bond order proposed by Mayer. According the DI data, we can say that the bond order between C-C bond and C-H bond in benzene is 1.467 and 0.877 respectively, the former corresponds to single  $\sigma$  bond + "semi"  $\pi$  bond,

while the latter corresponds to typical single  $\sigma$  bond.

Since benzene is an exactly planar molecule, we can decompose DI to DI- $\sigma$  and DI- $\pi$ . Here we calculate the latter. Input 0 to return to main menu, and then following commands

```
6 //Modify wavefunction
26 //Modify occupation number
0 // Select all orbitals
0 // Make occupation number of all orbitals to zero
17,20,21 // MO 17,20,21 correspond to  $\pi$  orbitals.
2 // Set their occupation numbers to 2 (close-shell orbitals)
q // Return to upper level of menu
-I //Return to main menu
```

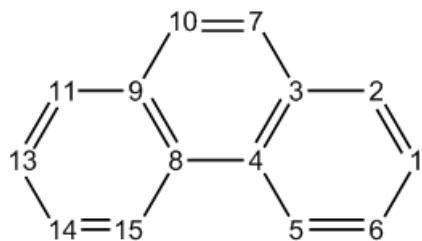
Now recalculate DI as before, since the occupation numbers of all orbitals except  $\pi$  orbitals have been set to zero, the result will be DI- $\pi$ .



The DI- $\pi$  between C1-C6, C1-C5 and C1-C4 are 0.438, 0.055 and 0.093 respectively, it is obvious that  $\pi$  electron delocalization is larger for para-related than for meta-related carbon atoms.

#### 4.15.2 Study aromaticity of phenanthrene by PDI, FLU, FLU- $\pi$ and PLR

PDI, FLU, FLU- $\pi$  and PLR are very useful aromaticity indices, their definitions have been introduced in Section 3.18.6, 3.18.7 and 3.18.9. In present instance, we will calculate them in Becke's fuzzy atom space to study aromaticity of different rings of phenanthrene.



We first calculate PDI. Boot up Multiwfn, and input following commands:

```
examples\phenanthrene.wfn // Optimized at B3LYP/6-31G* level
```

```
15 // Fuzzy atomic space analysis
5 // Calculate PDI
```

Then Multiwfn starts to calculate atomic overlap matrix (AOM), this is a computationally intensive work. After that AOM will be converted to delocalization index (DI), then DI matrix will be outputted on screen. Finally, you will be prompted to input atom indices of the ring you are interested in, the input order should be in consistency with atomic connectivity. We first calculate PDI of the central ring, namely input 4,8,9,10,7,3, the result is

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```
Delocalization index of    4(C ) -- 10(C ): 0.053069
Delocalization index of    8(C ) -- 7(C ): 0.053069
Delocalization index of    9(C ) -- 3(C ): 0.036350
PDI value is 0.047496
```

PDI value is just the average of the DIs between C4-C10, C8-C7 and C9-C3. Now we input 8,9,11,13,14,15 to calculate PDI of the boundary ring, the result is 0.0817. From this result it is evident that the electron delocalization in the boundary rings is stronger than in the central ring, so boundary rings possess larger aromaticity. Next, we use FLU and FLU- $\pi$  to study the aromaticity, and check if we can draw the same conclusion.

Input *q* to return to upper level of menu, and input *6* to calculate FLU, then input *4,8,9,10,7,3* and *8,9,11,13,14,15* in turn. The FLU of central ring and of boundary rings are 0.025311 and 0.007537 respectively, this result suggests that the boundary rings is more like to typical aromatic system (benzene), and hence possesses larger aromaticity than the central ring. Note that since the AOM has already been calculated during calculating PDI, so this time the calculation process of AOM is automatically skipped.

Next, input *q* to return to upper level of menu, and input *7* to calculate FLU- $\pi$ . First you need to input the indices of  $\pi$  orbitals. By visually checking isosurface of all orbitals (or utilizing option 22 in main function 100), we know that 36, 40, 43, 44, 45, 46, and 47 are  $\pi$  orbitals, so here we input 36,40,43,44,45,46,47, then DI of  $\pi$  electrons will be outputted. After that you will be prompted to input the atom indices in the ring, we input 4,8,9,10,7,3 and 8,9,11,13,14,15 in turn. The FLU- $\pi$  of central ring and boundary rings are 0.149288 and 0.035037, respectively. Obviously, FLU- $\pi$  analysis also confirms that boundary ring is more aromatic.

Finally, let's calculate para linear response index (PLR). PLR is based on linear response kernel, which relies on virtual MOs information; however .wfn file only contains occupied MOs, therefore we must use .fch/.molden/.gms file as input. Reboot Multiwfn and input following commands

```
examples\phenanthrene.fch // Obtained at the same level as phenanthrene.wfn
15
10 // Calculate PLR
```

Multiwfn will calculate condensed linear response kernel (CLRK) matrix, after that input 4,8,9,10,7,3 and 8,9,11,13,14,15 in turn, the result is 0.247848 and 0.489434, respectively. Since the former is much smaller than the latter, PLR also validates the conclusion that boundary rings have larger aromaticity than central ring.

Note that both PDI and PLR can be separated as  $\alpha$  and  $\pi$  parts to respectively investigate  $\alpha$  and  $\pi$  aromaticity, see Section 3.18.6 and 3.18.9 for detail.

## 4.16 Charge decomposition analysis and plotting orbital interaction diagram

The theoretical background of charge decomposition analysis (CDA, *J. Phys. Chem.*, **99**, 9352), extended CDA (*J. Am. Chem. Soc.*, **128**, 278), orbital interaction diagram and the usage of CDA module of Multiwfn have been detailedly introduced in Section 3.19. In this section I present three practical examples.

The CDA module of Multiwfn supports Gaussian output file, .fch file, Molden input file (.molden) and GAMESS-US output file (.gms) as input. If the calculation conditions are identical, they will give rise to the same CDA result. In next severals sections only Gaussian output files will be used to exemplify the usage of the CDA module.

### 4.16.1 Close-shell interaction case: COBH<sub>3</sub>

In COBH<sub>3</sub>, CO makes use of its lone pair to form coordinate bond with BH<sub>3</sub>, which is an electron-deficient system (Lewis acid). Therefore, electrons will transfer from CO to BH<sub>3</sub> during the formation of the complex. In this example we will employ CDA scheme to provide a deeper insight on the electron transfer.

First we generate Gaussian output file for CO (fragment 1), BH<sub>3</sub> (fragment 2) and COBH<sub>3</sub> (complex). The output files and corresponding input files have been provided in "examples\CDA\COBH3" folder. The calculations were performed at HF/6-31G\* level. On how to prepare the input files for CDA, see Section 3.19.2 for detail

Now boot up Multiwfn, and input following contents:

```
examples\CDA\COBH3\COBH3.out // Gaussian output file of the complex
```

```
16 // Enter CDA module
```

```
2 // We define two fragments
```

```
examples\CDA\COBH3\CO.out // Gaussian output file of fragment 1
```

```
examples\CDA\COBH3\BH3.out // Gaussian output file of fragment 2
```

Immediately, below CDA result will be outputted on screen

Orb.	Occ.	d	b	d - b	r
1	2.000000	-0.000004	0.000000	-0.000004	-0.000001
2	2.000000	0.001119	-0.000023	0.001141	0.000326
3	2.000000	-0.000002	-0.000472	0.000470	0.000313
4	2.000000	-0.013250	-0.000704	-0.012546	-0.005674
5	2.000000	0.041709	-0.003304	0.045013	0.232249
6	2.000000	0.037395	-0.020097	0.057492	0.212242
7	2.000000	-0.000545	0.000645	-0.001190	0.022180
8	2.000000	-0.000545	0.000645	-0.001190	0.022180
9	2.000000	0.171282	0.026887	0.144395	-0.741025
10	2.000000	-0.000565	0.043762	-0.044327	-0.038933
11	2.000000	-0.000565	0.043762	-0.044327	-0.038933
12	0.000000	0.000000	0.000000	0.000000	0.000000
13	0.000000	0.000000	0.000000	0.000000	0.000000
14	0.000000	0.000000	0.000000	0.000000	0.000000
15	0.000000	0.000000	0.000000	0.000000	0.000000
.....					
51	0.000000	0.000000	0.000000	0.000000	0.000000
<hr/>					
Sum:	22.000000	0.236029	0.091101	0.144928	-0.335075

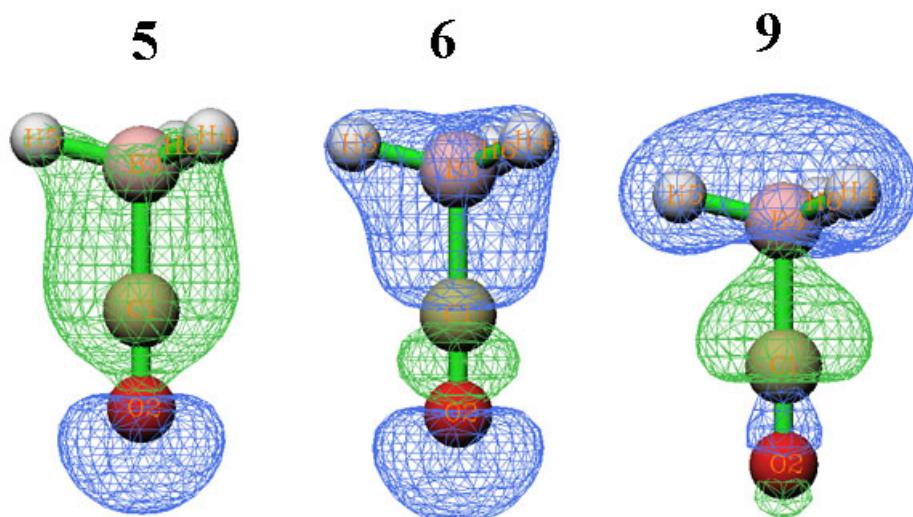
"Orb." denotes the indices of the orbitals of the complex; "occ." is corresponding occupation number. "d(i)" stands for the amount of donated electrons from fragment 1 to 2 via corresponding

complex orbital, "b(i)" stands for the amount of electrons back donated from fragment 2 to 1 via corresponding complex orbital. "r(i)" corresponds to the overlap population between the occupied fragment orbitals (FOs) of the two fragments in corresponding complex orbital; its positive and negative signs imply that in this complex orbital, the electrons of occupied FOs are accumulated to and depleted (mainly due to Pauli repulsion) from the overlap region between the two fragments, respectively. The sum of r(i), namely -0.335, reveals that repulsive effect dominates the overall interaction between occupied FOs, which results in corresponding electrons moved away towards nonoverlapping regions from overlap regions.

The difference between d(i) and b(i), to some extent can be viewed as the number of net transferred electrons from fragment 1 to 2 due to formation of corresponding complex orbital. But bear in mind, electron polarization effect is also included into this value.

From the data, it can be seen that the first three complex orbitals have almost zero b, d and r values, this is because they are core orbitals of O, C and B, respectively, and hence it can be expected that they are not involved in bond formation. The virtual complex orbitals have exactly zero b, d and r terms, since their occupation numbers are exactly zero. Orbital 9 leads 0.171 electrons donate from CO to  $\text{BH}_3$ , which is the primary source of the donor-acceptor bonding, and causes as high as 0.741 electrons removed from overlap region between CO and  $\text{BH}_3$ , which stabilized the complex by diminishing electron repulsion. Orbital 5 and 6 have small contributions to electron donation, meanwhile lead evident accumulation of electrons from respective occupied FOs to the overlap region, which must be beneficial to the bonding between the two fragments. Orbital 10 and 11 are  $\pi$  orbitals and degenerate in energy, they exhibit  $\pi$ -back donation characteristics.

Isosurfaces of orbital 9, 5 and 6 are shown below. As you can see, a node occurs in the overlap region between CO and  $\text{BH}_3$  in orbital 9, while the isosurfaces of orbital 5 and 6 uniformly cover the overlap region. These observations largely explained why r(9) is a large negative value, and r(5) and r(6) are obvious positive values.



Notice that the definition of CDA used in Multiwfn is a generalized version proposed by me, so that CDA is also applicable to post-HF and open-shell circumstances, see corresponding part of Section 3.19.1 for detail. For the cases when original CDA is applicable (namely MO for FO, MO

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or natural orbital for complex orbital), the d and b terms produced by generalized CDA are exactly identical to the ones produced by original definition, while the r term is exactly twice of the one produced by original definiton.

Note: The COBH3 example was also given in original paper of CDA, in which, although the formulae of d, b and r are correct, the data in their examples are incorrectly: all of the data should be divided by two. I also found that all of the results of the CDA program written by Dapprich and Frenking (<http://www.uni-marburg.de/fb15/ag-frenking/cda>), and the results of AOMix program (<http://www.sg-chem.net>) should be divided by two. So, if you want to compare the CDA results calculated by Multiwfn with theirs, the d and b terms should be multiplied by two first. But do not do this for r term, since the r term computed by Multiwfn has already been doubled with respect to its original definition.

The amount of net electron transfer between the two fragments can be characterized by b-d term, however it was argued that ECDA is a more reasonable method to calculate the amount of net electron transfer, since the contribution of electron polarization effect (PL) is completely excluded. ECDA result is outputted after CDA result:

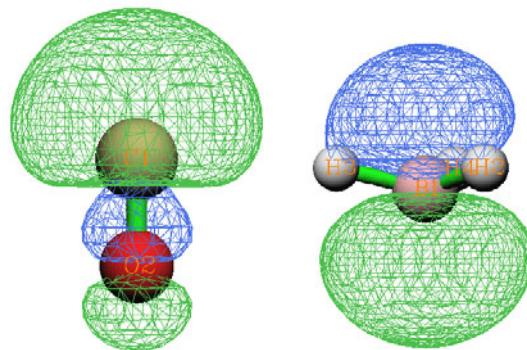
```
===== Extended Charge decomposition analysis (ECDA) =====  
Contribution to all occupied complex orbital:  
Occupied, virtual orbitals of fragment 1: 680.4180% 8.0677%  
Occupied, virtual orbitals of fragment 2: 390.4001% 21.1224%  
Contribution to all virtual complex orbital:  
Occupied, virtual orbitals of fragment 1: 19.6029% 2291.9374%  
Occupied, virtual orbitals of fragment 2: 9.6388% 1678.8554%  
PL(1) + CT(1->2) = 0.3921 PL(1) + CT(2->1) = 0.1614  
PL(2) + CT(1->2) = 0.4224 PL(2) + CT(2->1) = 0.1928  
The net electrons obtained by frag. 2 = CT(1->2) - CT(2->1) = 0.2307
```

Commonly, you only need to pay attention to the last line. The data shows that the net number of electrons transferred from fragment 1 to 2 is 0.2307.

In the menu that appears on screen, by using option 2, composition of FOs in a specific complex orbital can be outputted. Here we select this option and input 9, the composition of complex orbital 9 are shown below

```
Occupation number of orbital 9 of the complex: 2.00000000  
Orbital 7 of fragment 1, Occ: 2.00000 Contribution: 25.8447%  
Orbital 13 of fragment 1, Occ: 0.00000 Contribution: 1.0800%  
Orbital 2 of fragment 2, Occ: 2.00000 Contribution: 57.3119%  
Orbital 5 of fragment 2, Occ: 0.00000 Contribution: 14.5589%
```

Only the FOs with contribution  $\geq 1\%$  to the complex orbital are shown (the threshold can be altered by "comphresCDA" in settings.ini). As already mentioned, the electron transfer from CO to  $\text{BH}_3$  is mainly due to the complex orbital 9, therefore from above data we can infer that the nature of the  $\text{CO} \rightarrow \text{BH}_3$  electron transfer can be largely interpreted as the mix between FO 7 of CO (an occupied orbital) and FO 5 of  $\text{BH}_3$  (a virtual orbital). This viewpoint can also be manifested by comparing the shape of the two FOs (see below) with the shape of complex orbital 9 given above.



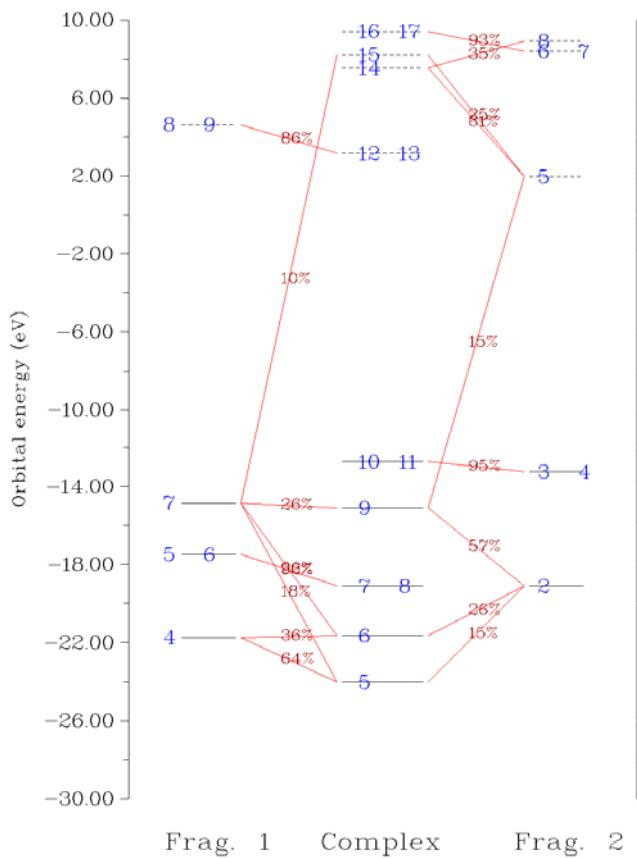
Note: Sometimes a few contributions of FOs may be negative, this is a well-known drawback of Mulliken analysis, which is the method employed in CDA module to calculate the complex orbital composition. Since the magnitudes of the negative values are often small, you can simply ignore them.

We can also directly decompose d, b, r terms of a complex orbital to FO pair contributions, let's do this for complex orbital 9. Now input 0 to return to the last menu, select option 6 and input 9, then input a threshold e.g. 0.005, then all FO pairs whose contribution to any of d, b, r term larger than 0.005 are printed:

FragA Orb(0cc.)	FragB Orb(0cc.)	d	b	d - b	r
4( 2.0000)	2( 2.0000)	0. 000000	0. 000000	0. 000000	-0. 009919
7( 2.0000)	1( 2.0000)	0. 000000	0. 000000	0. 000000	-0. 005757
7( 2.0000)	2( 2.0000)	0. 000000	0. 000000	0. 000000	-0. 723543
7( 2.0000)	5( 0.0000)	0. 176462	0. 000000	0. 176462	0. 000000
7( 2.0000)	8( 0.0000)	0. 006213	0. 000000	0. 006213	0. 000000
7( 2.0000)	11( 0.0000)	0. 005799	0. 000000	0. 005799	0. 000000
7( 2.0000)	12( 0.0000)	-0. 023898	0. 000000	-0. 023898	0. 000000
13( 0.0000)	2( 2.0000)	0. 000000	0. 021962	-0. 021962	0. 000000

From the output it is clear that the mix between FO 7 of CO and FO 5 of BH<sub>3</sub> contributes most of the d term of complex orbital 9.

Finally, we plot orbital interaction diagram. Input 0 to return to the last menu, and then select 5 to enter the menu for plotting orbital interaction diagram. Choose option 3 and input -30,10 to set lower and upper energy limits of the plot to -30eV and 10eV, respectively. Then select option 1 to plot the diagram under default settings, a graph will pop up on screen:



In above graph, occupied and virtual orbitals are represented as solid and dashed bars, respectively. Orbital indices are labelled by blue texts. If two or more labels occur in the same bar, e.g. 7 and 8, that means these orbitals are degenerate in energy. If composition of a FO in a complex orbital is larger than 10%, then the corresponding two bars will be linked by red line, and the composition will be labelled on the lines. By simply viewing the diagram we can directly understand how the MOs of  $\text{COBH}_3$  are constructed by FOs of CO and  $\text{BH}_3$ . For example, complex orbital 7 and 8 only link to FO 5 and 6 of CO in this diagram, hence we immediately know that these two orbitals basically remain unperturbed during formation of the complex. In fact they are  $\pi$  orbitals of CO, certainly they cannot participate to the  $\sigma$  type donor-acceptor interaction between CO and  $\text{BH}_3$ .

There are many options used to adjust plotting parameters (such as label size, the rule for drawing and linking bars, position of composition labels, energy range), please play with them, and replot the graph to check their effects.

#### 4.16.2 Open-shell interaction case: $\text{CH}_3\text{NH}_2$

In this example, I use CH<sub>3</sub>NH<sub>2</sub> to illustrate how to perform CDA for the complex in which the two fragments interact with each other covalently (open-shell interaction).

First we need to generate Gaussian output file for CH<sub>3</sub> (fragment 1), NH<sub>2</sub> (fragment 2) and CH<sub>3</sub>NH<sub>2</sub> (complex). For fragment 1 and 2, in present example we use unrestricted B3LYP method; for the complex, since this is a close-shell system, we use restricted B3LYP method (unrestricted B3LYP can also be used, the CDA result will be the same). The output files and corresponding input files can be found in "examples\CDA\CH3NH2" folder, the geometry was pre-optimized

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under B3LYP/6-31G\*\* level.

Note that both CH<sub>3</sub> and NH<sub>2</sub> have 5 alpha and 4 beta electrons, while CH<sub>3</sub>NH<sub>2</sub> has 9 alpha and 9 beta electrons. Evidently, the total numbers of alpha and beta electrons in the two fragments, namely 5+5 and 4+4, does not match the ones of the complex. So, we must flip electron spin of one fragment (either CH<sub>3</sub> or NH<sub>2</sub>). In this example, we will flip electron spin of NH<sub>2</sub>, i.e. exchanging all information of its alpha and beta electrons.

Boot up Multiwfn and input following contents:

```
examples\CD\CH3NH2\CH3NH2.out // Gaussian output file of the complex
```

```
16 // Enter CDA module
```

```
2 // We define two fragments
```

```
examples\CD\CH3NH2\CH3.out // Gaussian output file of fragment 1
```

```
examples\CD\CH3NH2\NH2.out // Gaussian output file of fragment 2
```

```
n // Do not flip electron spin of fragment 1
```

```
y // Flip electron spin of fragment 2, then NH2 will have 4 alpha and 5 beta electrons.
```

CDA and ECDA results will be calculated and printed on screen for alpha electrons and beta electrons separately. As you can see, for alpha (beta) part, both d - b and CT(1->2) - CT(2->1) terms are positive (negative), showing that alpha (beta) electrons are transferred from CH<sub>3</sub> to NH<sub>2</sub> (from NH<sub>2</sub> to CH<sub>3</sub>). This is mainly because CH<sub>3</sub> has more alpha electrons (5) than beta electrons (4), while after flipping electron spin, NH<sub>2</sub> has more beta electrons (5) than alpha electrons (4), hence when they combine together to form CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub> prefer to donate alpha electrons to NH<sub>2</sub> and accept beta electrons from NH<sub>2</sub>.

Result for total electrons, namely the sum of alpha and beta results are also outputted. Below is total result of CDA and ECDA, respectively

```
d= 0.044311 b= 0.145182 d - b = -0.100871 r= -0.172320
```

```
CT(1->2) - CT(2->1) for all electrons: 0.1249
```

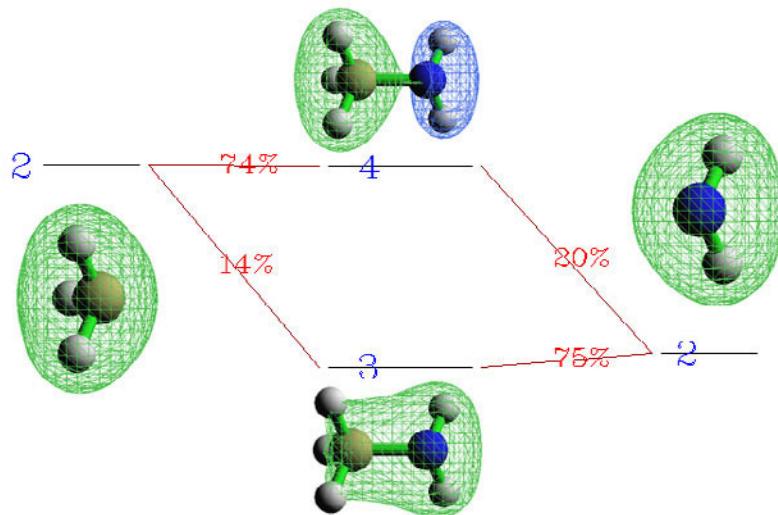
It is obvious that electron should transfer from CH<sub>3</sub> to NH<sub>2</sub>, because nitrogen has evidently larger electronegativity. The total ECDA result is in line with our expectation, it shows that the amount of transferred electrons from CH<sub>3</sub> to NH<sub>2</sub> is 0.1249. However, the d - b term conflicts with our expectation, the transfer direction is totally inverted. This example illustrates that d - b term is not as reliable as ECDA to reveal total amount of net electron transfer for open-shell interaction, although d and b terms are still quite useful for decomposing electron transfer into orbital contributions.

If you select to flip electron spin for CH<sub>3</sub> rather than for NH<sub>2</sub> when loading their Gaussian output files, you will see the alpha and beta results of CDA and ECDA are exchanged, but the result for total electrons remains unchanged.

Now select 2 and input 6, you will see both the composition of the 6<sup>th</sup> alpha orbital and the 6<sup>th</sup> beta orbital of the complex are printed on screen. Though the complex is a close-shell system and thus the two orbitals are essentially the same, owing to the alpha and beta FOs in the two fragments are not equivalent, the printed compositions have slight difference. Then input 0 to return.

Select option 5 to enter the menu for plotting orbital interaction diagram. By option 5 in the menu, you can control for which set of spin-space orbitals the diagram will be plotted. We select it once to switch the status to "Beta". Then select option 1 to plot the orbital interaction diagram.

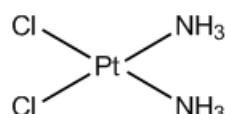
From the graph it is very clear that, beta orbital 3 and 4 of  $\text{CH}_3\text{NH}_2$  are formed by mixing beta FO 2 in  $\text{CH}_3$  and beta FO 2 in  $\text{NH}_2$ . To illustrate this point more intuitively, corresponding part is extracted from the whole diagram, and the orbital isosurfaces are attached on it, see below



It can be seen that, beta complex orbital 3 shows bonding character (this is why  $r(3)$  is a positive value, namely 0.103), which is constructed by slightly mixing beta FO 2 of  $\text{CH}_3$  into beta FO 2 of  $\text{NH}_2$  with the same wavefunction phase. Beta complex orbital 4 is an anti-bonding orbital (this explained why  $r(4)$  is a negative value, namely -0.056), formation of which is due to the mixture of beta FO 2 of  $\text{NH}_2$  into beta FO 2 of  $\text{CH}_3$  in terms of different phase.

#### 4.16.3 More than two-fragments case: $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

In this section I use cisplatin (see below) as instance to show how to perform CDA analysis on the system consisting of more than two fragments.



We will define  $\text{Pt}^{2+}$  cation,  $(\text{Cl}_2)^2-$  anion and  $(\text{NH}_3)_2$  as fragment 1, 2 and 3 respectively. This definition of fragments is the best choice for present system. Note that the  $\text{Pt}^{2+}$  cation is in  $3d^8$  low-spin configuration.

The related Gaussian input files and output files have been provided in *examples\CDA\Pt(NH3)2Cl2* folder. Lanl2DZ pseudo-potential was used for Pt, cc-pVDZ was used for other atoms. B3LYP functional was chosen as the theoretical method. The geometry of the complex has already been optimized. In the input file of  $\text{Pt}^{2+}$ , "scf=xqc" keyword was used to solve the convergence problem, but this is not needed in general.

Note 1: For certain types of basis-sets, such as Pople series of basis-sets (e.g. 6-31G\*), by default Gaussian employs Cartesian type basis functions rather than spherical-harmonic basis functions, which may results in inconsistency problem of basis-set between complex and fragment calculations. If you are not very familiar with Gaussian, I highly recommend you to always add "5d 7f" keyword in all Gaussian input files when mixed basis-set is used in the calculation of the complex.

Note 2: The sequence of the fragments is crucial. Because in the input file of complex, the atomic sequence is  $\text{Pt}-\text{Cl}_2-(\text{NH}_3)_2$ , we should not for example define  $\text{Pt}^{2+}$ ,  $(\text{NH}_3)_2$  and  $(\text{Cl}_2)^2-$  as fragment 1, 2 and 3, respectively.

Now boot up Multiwfn and input:

```
examples\cda\Pt(NH3)2Cl2\Pt(NH3)2Cl2.out // Gaussian output file of the complex
```

```
16 // Enter CDA module
```

```
3 // We define three fragments
```

```
examples\cda\Pt(NH3)2Cl2\Pt.out // Gaussian output file of fragment 1
```

```
examples\cda\Pt(NH3)2Cl2\Cl2.out // Gaussian output file of fragment 2
```

```
examples\cda\Pt(NH3)2Cl2\Cl2(NH3)2.out // Gaussian output file of fragment 3
```

Then choose option 0 and input 1,2 to output CDA analysis result for fragment pair 1-2. Similarly, we get the CDA result for fragment pair 1-3 and 2-3. We cannot obtain ECDA result for present system because ECDA is only applicable to two-fragment cases. The total CDA results are summarized below.

	1-2	1-3	2-3
d	0.0083	0.0068	0.0647
b	0.5061	0.1493	0.0024
d-b	-0.4977	-0.1425	0.0623
r	0.0529	-0.0149	-0.1442

The table shows that there are 0.4977 and 0.1425 net electrons transferred from  $(\text{Cl}_2)^{2-}$  and  $(\text{NH}_3)_2$  to  $\text{Pt}^{2+}$ , respectively. Basically no electrons are donated from  $\text{Pt}^{2+}$  to its ligands. This result is in line with our chemical intuition because according to classical theory, the electrons of coordinate bonds are purely contributed from ligands. The charge transferation between  $(\text{Cl}_2)^{2-}$  and  $(\text{NH}_3)_2$  is trivial, mainly due to there is no direct chemical interaction between them. Note that the r term between fragment 2 and 3 is a small but non-negligible negative value, exhibiting that there is detectable electron repulsion effect between the ligands.

Deeper analyses on this system are left for you. You can discuss orbital contribution to charge transferation based on the detail output of CDA analysis, use option 2 to study the composition of complex orbital in fragment orbital basis, and use option 5 to plot orbital interaction diagram.

## 4.17 Basin analysis

Below I will show how to use basin analysis module of Multiwfn to perform basin analysis for several molecules and for various real space functions. Related theory, numerical algorithms and the usage of this module have been detailedly introduced in Section 3.20. If you are not familiar with the concept of basin, please consult Section 3.20.1 first. While if you want to know more detail about basin analysis, please consult Sections 3.20.2 and 3.20.3.

You should know that Multiwfn uses a grid-based method (in particular, near-grid method) to locate attractors, generate and integrate basins; in other words, most tasks realized in the basin analysis module rely on grid data. This is why in below sections "grid data" is frequently mentioned.

### 4.17.1 AIM basin analysis for HCN

In this example we will analyze the basins of total electron density (also known as AIM basins) for HCN molecule. After you finished it you will understand most of the basic operations of the basin analysis module in Multiwfn.

### Generate basins and locate attractors

Boot up Multiwfn and input following commands

*examples\HCN.wfn*

17 // Basin analysis

1 // Generate basins and locate attractors

1 // The grid data to be calculated and thus analyzed is for electron density

2 // Medium quality grid. This is enough for most cases, if you want to obtain a better result, you can choose "High quality grid", but much more computational time will be spent

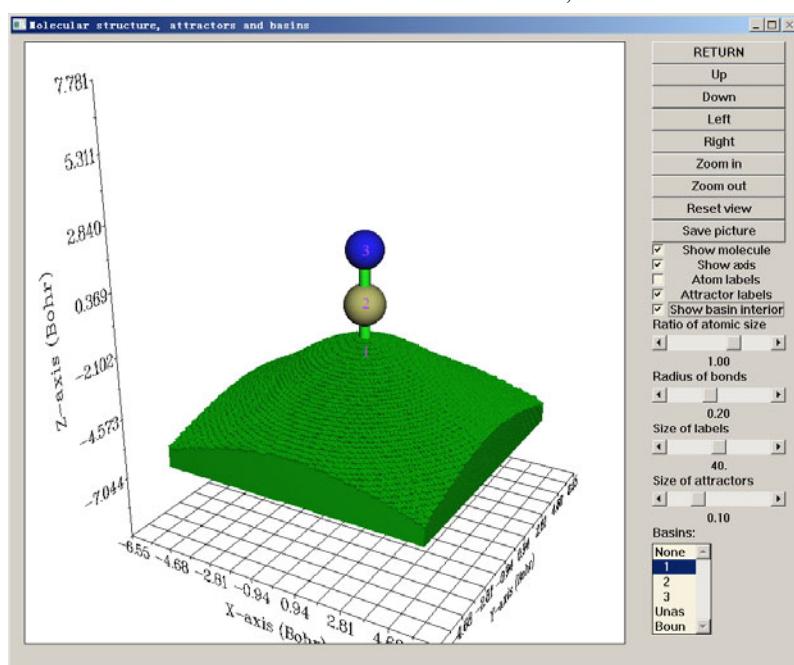
Multiwfn now starts to calculate grid data for electron density, and then generates basins and locates attractors based on the grid data; soon you will see attractor information, as shown below (notice that the attractor sequence may be different to your actual case if parallel mode is enabled, similarly hereinafter):

Attractor	X, Y, Z coordinate (Angstrom)	Value
1	-0.02645886 -0.02645886 -1.52058663	0.33959944
2	0.02645886 0.02645886 -0.51514986	49.48609717
3	-0.02645886 -0.02645886 0.64904009	76.55832377

From now on you can check the information of the located attractors anytime by option -3.

### Visualization of basins and attractors

Now choose 0 to visualize the basins and attractors. The purple labels indicate the index of the located attractors. Since attractors of electron density are very close to nuclei, if you want to see them, you should deselect "Show molecule" check box first. Here we select 1 from the basin list at the right-bottom corner, the basin corresponding to attractor 1 will be immediately shown. By default only interbasin part of the basin is shown, if you want to inspect the whole basin you should select "Show basin interior" checkbox. After we select it, the GUI will look like below:



Now click "RETURN" button to close the GUI.

Hint: If you are not satisfied with the graph shown in the Multiwfn GUI, you can choose function -4 to export the attractors as .pdb file, and choose option -5 to export the basins as cube file, then you can easily plot them in

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your favourite visualization software such as VMD. The isosurface representing the basin can be visualized by plotting an isosurface with isovalue of 0.5. Note that When Multiwfn asking you "If output internal region of the basin?", if you input "n" rather than "y", only interbasin surface will be shown when you plotting the isosurface.

You may have noticed below statements in command-line window

```
The number of unassigned grids:          0
The number of grids travelled to box boundary:      0
```

Commonly the number of these two types of grid should be zero, only in rare cases they are not zero; in such cases, you can visualize them by respectively selecting "Unas" and "Boun" in the basin list of the GUI. These grids do not belong to any basin, and generally they lack of physical meaning; to understand when and why they occur please consult Section 3.20.2.

### Integrating basins

Next, we calculate the integral of electron density (electron population number) in these basins. Select function 2, then you will see many options. Each option with the serial  $\geq 1$  corresponds to a real space function; if you select one of them, corresponding real space function will be integrated in the generated basins. In present example we can select option 1, which corresponds to electron density. However, since we have already calculated grid data for electron density, and the grid data of electron density thus have been stored in memory, we can directly use it rather than recompute it again to reduce computational time, so here we select option 0 to use "The values of the grid data stored in memory".

Since electron density at the grids is not needed to be re-evaluated, the integrals are outputted immediately:

#Basin	Integral (a. u.)	Volume(a. u. ^3)
1	0. 7356142812	441. 70000000
2	5. 3511723358	566. 84900000
3	7. 9020047534	829. 72600000

Sum of above values: 13. 98879137

There should be totally  $1+6+7=14$  electrons in present system; unfortunately the sum of the integrals of electron density is 13.98879, which evidently deviates from the ideal value!

Because the basin we are studying is AIM basin, the best choice to obtain the basin integral is using function 7 rather than function 2. In function 7, mixed atomic-center and uniform grid is used, while function 2 only employs uniform grid to integrate. We input:

```
7 // Integrate real space functions in AIM basins with mixed type of grids
1 // Integrate a specific function with atomic-center + uniform grids
1 // Select electron density as the integrand
```

The result is

#Basin	Integral (a. u.)	Vol (Bohr^3)	Vol (rho>0. 001)
1	0. 7356461193	441. 700	34. 884
2	5. 3552283604	566. 849	102. 832
3	7. 9086490986	829. 726	134. 228

Sum of above integrals: 13. 99952358

Sum of basin volumes (rho>0. 001): 271. 944 Bohr^3

As you can see, the sum of the integrals of electron density (13.9995) is almost exactly identical to the expected value 14.0, obviously the result is much better than using function 2. The

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basin volumes are also outputted. The terms "vol(Bohr^2)" do not have clear physical meaning, since they are directly affected by the spatial range of grid setting. However, the terms "vol(rho>0.001)" are useful, they exhibit the volume of the basin enclosed by the isosurface of electron density > 0.001 (Bader's vdW surface) and thus can be regarded as atomic sizes.

The atomic charge (AIM charge) of these atoms and their volumes are also outputted

```
1 (C ) Charge: 0.644589 Vol ume: 102.832 Bohr^3
2 (N ) Charge: -0.908918 Vol ume: 134.228 Bohr^3
3 (H ) Charge: 0.264329 Vol ume: 34.884 Bohr^3
```

Note that above AIM charges are inaccurate! To obtain more accurate integrals in AIM basins, you should select 2 or 3 in function 7, compared to 1, they will refine the assignment of basin boundary to improve the integration result, but additional computational cost must be afforded. Here we try it, select option 2 in function 7, then input *I*, the result is

```
1 (C ) Charge: 0.748979 Vol ume: 100.160 Bohr^3
2 (N ) Charge: -1.003917 Vol ume: 136.304 Bohr^3
3 (H ) Charge: 0.254938 Vol ume: 35.480 Bohr^3
```

Although the sum of the integral of electron density is still 13.9995, the charge of the atoms are somewhat varied (more accurate than before).

To further improve the integration accuracy, when generating basins one should select a grid setting better than "medium quality grid", e.g. "High quality grid" or even "Lunatic quality grid". But bear in mind that for large systems, "high quality grid" (or a better one) may consumes very large amount of computational time and memory.

Although as we have seen the integration accuracy of function 7 is much better than function 2, the former is only applicable to AIM basins, while the latter can be used for any type of basin (e.g. ELF basin).

Note: If you used option 2 or 3 in function 7, during the boundary grid refinement process, the assignment of basin boundary will be updated permanently, that means the result of later analysis (e.g. calculating LI/DI, electric multipole moment) will become more accurate.

**Hint:** In summary, the general steps for obtaining reliable AIM charges after you entered basin analysis module is

```
I // Generate basin
I // Electron density
2 // Medium quality grid. Select high quality grid if you wish to get more accurate result
7 // Integrate real space functions in AIM basins with mixed type of grids
2 // Integrate and meanwhile refine basin boundary
I // Electron density
```

### Calculate electric multipole moments in basins

Enter function 8 to calculate electric multipole moments in the AIM basins (you can also use 3 to do this, but the accuracy is much lower). Only the result for carbon is pasted below

```
Resul t of atom 1 (C )
Basin electric monopole moment: -5.250849
Basin electric dipole moment:
X= 0.000003 Y= 0.000003 Z= 1.095846 Magnitude= 1.095846
Basin electron contribution to molecular dipole moment:
X= 0.000003 Y= 0.000003 Z= 6.026238 Magnitude= 6.026238
```

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Basin electric quadrupole moment (Cartesian form):

```
QXX= -0.759571 QXY= 0.000000 QXZ= -0.000002
QYX= 0.000000 QYY= -0.759571 QYZ= -0.000002
QZX= -0.000002 QZY= -0.000002 QZZ= 1.519142
```

The magnitude of electric quadrupole moment (Cartesian form): 1.519142

Electric quadrupole moments (Spherical harmonic form):

```
Q_2, 0 = 1.519142 Q_2, -1= -0.000002 Q_2, 1= -0.000002
Q_2, -2= 0.000000 Q_2, 2 = 0.000000
```

Magnitude: |Q\_2|= 1.519142

The formulae used to evaluate these terms are basically identical to the ones given in Section 3.18.3, the only differences are that in that formulae the nuclear positions should be replaced by attractor positions, and the ranges of integration should be basins rather than fuzzy atomic spaces.

The electric monopole moment (-5.251) is just the negative value of electron population number in the basin. Z-component of electric dipole moment of the basin is a positive value (1.096), suggesting that in basin 2, most of electrons are distributed in the regions where Z-coordinate is more negative than attractor 2. The ZZ-component of basin electric quadrupole moment is positive (1.519), while the other diagonal components are negative, indicating that relative to attractor 2, electron cloud in this basin contracts in Z-direction but elongates in other directions.

### Calculate localization index and delocalization index in basins

Delocalization index (DI) is a quantitative measure of the number of electrons delocalized (or say shared) between two regions, while localization index (LI) quantitatively measures how many electron are localized in a region. For details about LI and DI please see Section 3.18.5. The only difference relative to the statements in that section is that here the LI and DI will be calculated based on basins rather than based on fuzzy atomic spaces.

Enter function 4, Multiwfn will start to calculate LI and DI, then you will see:

```
***** Total delocalization index matrix *****
```

	1	2	3
1	0.97290584	0.90037928	0.07252656
2	0.90037928	3.49303345	2.59265416
3	0.07252656	2.59265416	2.66518072

Total localization index:

```
1: 0.259 2: 3.496 3: 6.658
```

Since present molecule is a close shell system, only total LI and DI are outputted, the LI and DI for  $\alpha$  and  $\beta$  electrons are not outputted separately. As you can see, between basin 2 and 3, which correspond to AIM atomic space of C and N respectively, the DI is 2.593, exhibiting that in average there are 2.593 electrons shared by the two atoms. To some extent DI can be regarded as covalent bond order, the DI value 2.593 is indeed comparable with the formal bond order (3.0) between C and N in HCN. The diagonal terms are the sums of the elements in corresponding row/column, for close-shell cases they can be somewhat considered as atomic valency. So we can say in HCN the nitrogen atom has atomic valency of 2.665.

The LI of basin 1 is only 0.259 which conspicuously deviates from the basin electron

population number. This observation reflects that in HCN, the electron in the AIM atomic space of hydrogen can easily delocalize out.

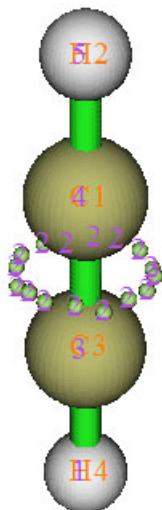
#### 4.17.2 ELF basin analysis for acetylene

This time we analyze ELF basin for acetylene. Boot up Multiwfn and input  
*examples\c2h2.wfn*

17

```
1 // Generate basins and locate attractors
9 // ELF
2 // Medium quality grid
0 // Visualize attractors and basins
```

In the GUI, as the graph shown below, you can see there are lots of closely placed attractors encircling the C-C bond. In fact, they have very similar ELF values, and collectively represent the ring-type ELF attractor. These attractors have been clustered together by Multiwfn automatically, therefore all of them have identical attractor index, namely 2; in another word, attractor 2 is a "degenerate" attractor, which has many member attractors. Correspondingly, basin 2 is composed by the member basins. The interested user is recommended to visualize basin 2 in the GUI.



The presence of attractor 2 signifies the  $\pi$  electrons shared by the two carbons. According to the well-known ELF symbolic method, basin 2 should be identified as  $V(C_1, C_3)$ , which means this basin is comprised by the valence electrons of  $C_1$  and  $C_3$ .

Attractor 3 and 4 correspond to core-type ELF attractors, their basins should be identified as  $C(C_3)$  and  $C(C_1)$ , respectively, where the letter C out of parentheses stands for "Core". If you deselect the "Show molecule" check box and select corresponding terms in the basin list then you can visualize the basins. The graph shown below portrays  $C(C_3)$ .



Although basin 1 and 5 cover the whole hydrogen spaces, they should be identified as  $V(C_3, H_4)$  and  $V(C_1, H_2)$ , rather than  $C(H_4)$  and  $C(H_2)$ , respectively. This is because hydrogen does not have core electrons.

Now close the GUI window by clicking "RETURN" button, and then input

```
2 // Integrate a real space functions in the basins
1 // Electron density
```

Soon, we get the integrals, namely the average electron population number in each basin:

#Basin	Integral (a. u.)	Volume(a. u. ^3)
1	2.2159821115	768.39800000
2	5.3670485473	972.79700000
3	2.0949016050	0.83200000
4	2.0949016050	0.83200000
5	2.2159824751	768.55500000

Sum of above values: 13.98881634

Both  $C(C_1)$  and  $C(C_3)$  in average contain 2.095 electrons, which is in line with the fact that carbon has two electrons in its core. Also, the average population number in  $V(C_3, H_4)$  and  $V(C_1, H_2)$  are close to two, approximately reflecting that in average there is a pair of electron shared between C and H.

According to classical chemical bond theory there are three electron pairs and hence six electrons are shared by the two carbons, however in the  $V(C_1, C_3)$  basin the integral is only 5.37. Although the deviation is relatively large, this is a normal situation. It is senseless to require that the result of ELF basin analysis must be able to reproduce classical Lewis picture, and actually, ELF analysis is more advanced and more close to real physical picture.

Next, enter function 3 to calculate electric multipole moments. We want the result for all basins to be outputted, so we input -1. The result of  $C(C_1)$  is pasted below

```
Basin      4
Basin electric monopole moment: -2.094902
Basin electric dipole moment:
X= -0.104745 Y= -0.104745 Z= 0.020728 Magnitude= 0.149575
```

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Basin electron contribution to molecular dipole moment:

X= 0.000000 Y= 0.000000 Z= -2.388409 Magnitude= 2.388409

Basin electric quadrupole moment (Cartesian form):

QXX= -0.003034 QXY= -0.007856 QXZ= 0.001555

QYX= -0.007856 QYY= -0.003034 QYZ= 0.001555

QZX= 0.001555 QZY= 0.001555 QZZ= 0.006067

The magnitude of electric quadrupole moment (Cartesian form): 0.006067

Electric quadrupole moments (Spherical harmonic form):

Q\_2,0 = 0.006067 Q\_2,-1= 0.001795 Q\_2,1= 0.001795

Q\_2,-2= -0.009071 Q\_2,2 = 0.000000

Magnitude: |Q\_2|= 0.011205

First you should note that although in present case, due to the symmetry, the X and Y components of the basin electric dipole moment should vanish, the actual values are not so close to zero, rendering that the integration accuracy is not very high. This is why "high quality grid" is often necessary when electric multipole moment analysis is involved. However, present result is still useful on the qualitative level. The magnitude of electric quadrupole moment in the basin measures how evidently does the electron distribution in the basin deviate from spherical symmetry. This value for C(C<sub>1</sub>) is very small (0.0061), showing that the distribution of core electron of the carbon basically remains unperturbed during the formation of the molecule.

Note: If the basins you are interested in are only valence basins, "medium quality grid" is enough for electric multipole moment analysis, since valency density is not as high as core density, and hence does not need high accuracy of integration.

Input 0 to return. Finally, let's choose option 4 to study LI and DI. The result is shown below

\*\*\*\*\* Total delocalization index matrix \*\*\*\*\*

	1	2	3	4	5
1	1.31231709	1.03496561	0.16085935	0.02291204	0.09358009
2	1.03496561	2.71090548	0.32048710	0.32048709	1.03496568
3	0.16085935	0.32048710	0.51131492	0.00705643	0.02291205
4	0.02291204	0.32048709	0.00705643	0.51131492	0.16085937
5	0.09358009	1.03496568	0.02291205	0.16085937	1.31231719

Total delocalization index:

1: 1.560 2: 4.011 3: 1.834 4: 1.834 5: 1.560

Between C(C<sub>1</sub>) and C(C<sub>3</sub>), namely DI(3,4), the value is trivial, reflecting the general rule that the electron delocalization between atomic cores is rather difficult. DI(1,3) and DI(2,3) are very small values but not close to zero, representing that the electrons in C(C<sub>3</sub>) have a few probability to exchange with the ones in V(C<sub>3</sub>,H<sub>4</sub>) and V(C<sub>1</sub>,C<sub>3</sub>), which are the only two basins adjacent to C(C<sub>3</sub>).

DI(2,1) and DI(2,5) are about 1.0, such a large value indicates that the electron delocalization between C-C bonding region and C-H bonding region is easy. Though the average electron population number in C(C<sub>1</sub>) and C(C<sub>3</sub>) are 2.095, their LI values are as high as 1.834, implying that the core electrons of carbon highly prefer to stay in the core region rather than delocalize out. In contrast, for V(C,H) and V(C,H), their LI values are less than their average electron population numbers distinctly, revealing that the electrons in these basins do not express very strong

localization character.

In the ELF basin analyses, some researchers prefer to use the concept of variance ( $\sigma^2$ ) and covariance (Cov) rather than LI and DI to discuss problems. Covariance of electron pair fluctuation is simply the half of the negative value of DI, for example,  $\text{Cov}(2,5) = -\text{DI}(2,5)/2 = -1.035/2 = -0.518$ . The variance of electronic fluctuation can be calculated as the half of the corresponding diagonal term of the DI matrix outputted by Multiwfn, for instance,  $\sigma^2(2) = \text{DI}(2,2)/2 = 2.710/2 = 1.355$  (note that as mentioned earlier, the diagonal terms of the DI matrix outputted by Multiwfn are the sums of the elements in corresponding row/column).

### 4.17.3 Electrostatic potential basin analysis for H<sub>2</sub>O

In literatures, basin analysis technique is rarely applied on electrostatic potential (ESP). To illustrate the universality of basin analysis module of Multiwfn, in this example we will generate ESP basins for H<sub>2</sub>O, and then evaluate electron population numbers in them. In the first part of this section, we will let Multiwfn directly calculate ESP and electron density, while in the second part we will make use of the cube files produced by third-part program to do the same things.

It is noteworthy that unlike electron density and ELF, which we have analyzed earlier, ESP has positive part and negative part simultaneously. For such real space functions, Multiwfn will automatically locate attractors (maxima) for positive part and locate "repulsors" (minima) for negative part, but in Multiwfn all of them are collectively recorded as "attractors". You can easily discriminate them by inspecting their colors in the GUI, as illustrated below.

#### Part 1

Boot up Multiwfn and input following commands:

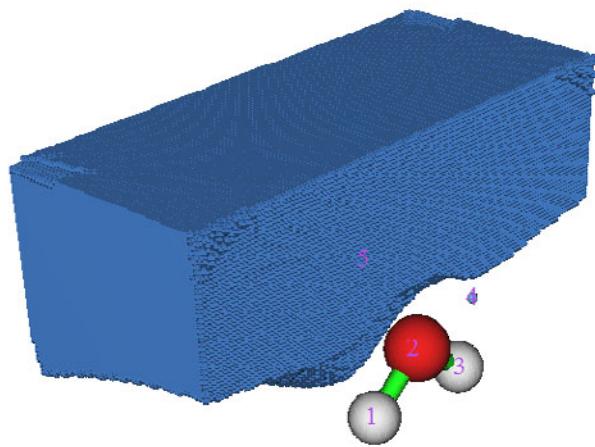
*examples\H2O.fch* // Optimized and produced at HF/6-31G\* level. Of course you can also use .wfn/.wfx file

```
17
1
12 // ESP
```

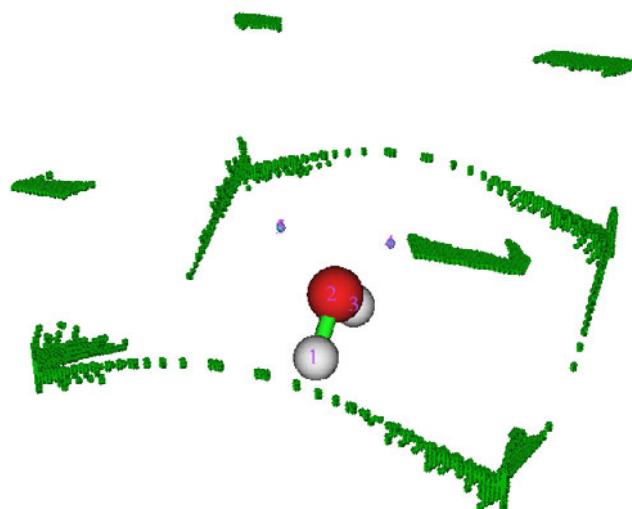
2 // Medium quality grid. Note that calculation of ESP is rather time-consuming, so do not use too high quality of grid, especially for large systems

After the calculation of ESP grid data and the basin generation are finished, five attractors are founded. Notice that this time the number of grids travelled to box boundary is not zero again (about 1627 grids).

Choose option 0 to open GUI, you can see that attractor 1, 2 and 3 correspond to ESP maxima due to nuclear charges. It is well known that the lone pairs of oxygen make the ESP at corresponding region negative, clearly attractor 4 and 5 reflected this effect. Attractor 4 and 5 are colored by light blue because they are lying in negative region, in fact they are not attractors but "repulsors" (minima) of ESP. By clicking term 5 in the basin list and checking "show basin interior" box, you will see below graph, which exhibits the basin corresponding to attractor 5.



If you want to visualize which grids have travelled to box boundary during basin generation, you can select "Boun" in the basin list, see below graph. Evidently, these grids lack of physical meaning and hence can be simply ignored. They only present at the regions far from atoms.



Now click "RETURN" button to close the GUI.

Sometimes one needs to obtain geometry information between attractors and nuclei. As an instance, we enter function -2, and input  $a1\ c4$ , the distance between nucleus of atom 1 (namely oxygen) and attractor 4 will be shown on the screen, the value is 2.237 Bohr. Next, input  $c4\ a1\ c5$ , then the angle of "attractor 2 -- atom 1 -- attractor 3" will be outputted, the value is 80.84 degree, which in some sense can be regarded as the angle between the two lone pairs.

Input  $q$  to exit the geometry measurement interface.

Assume that we want to cluster attractor 4 and 5 together as a degenerate attractor, we can input

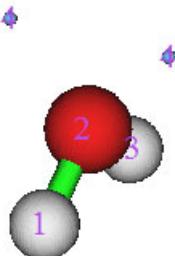
```
-6 // Set parameter for attractor clustering or manually perform clustering
```

3 // Cluster specified attractors

4,5 // attractor 2 and 3 will be clustered as a single one

0 // Return

Select option 0 to open GUI, as shown below, you can find that the index of all attractors have changed, and the two attractors corresponding to the oxygen lone pairs now sharing the same index, namely 4.



Close the GUI by clicking "RETURN" button, choose option 2 and then select 1 to integrate electron density in the ESP basins, the result is

#Basin	Integral (a. u.)	Volume(a. u. ^3)
1	0. 8647179457	391. 74200000
2	7. 5147940814	25. 01400000
3	0. 8647179450	391. 65000000
4	0. 7405385242	703. 11200000
Sum of above values:		9. 98476850
Integral of the grids travelled to box boundary:		0. 00000002

Since currently basin 4 is just the whole negative ESP region, the result shows that in average there are 0.740 electrons in the negative ESP region. Indeed this value is not large (one may expects that there should be about four electrons due to the two lone pairs), this is because most parts of the molecular space are dominated by nuclear charges and hence having positive ESP.

## Part 2

Now we redo some analyses in part 1 but using the grid data comes from external file. Since external grid data is supported, one can use third-part programs to generate the grid data, and then use basins analysis module of Multiwfn to study the basins of the real space functions recorded in the grid data. The real space function to be analyzed may be the one cannot be directly calculated by Multiwfn, or the one requires large amount of computational time, e.g. ESP (compared to some *ab initio* programs, using current Multiwfn to calculate ESP grid data is a bit slow).

Here we use *cubegen* utility in Gaussian package to yield grid data of ESP and electron density for the H2O.fch file. Run below commands in MS-DOS/Linux/Mac OS console to produce density.cub and ESP.cub. *cubegen* utility is assumed to be placed in current path

*cubegen 0 fdensity H2O.fch density.cub 0 h*

*cubegen 0 potential H2O.fch ESP.cub 0 h*

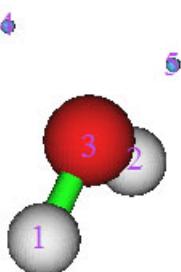
Then boot up Multiwfn and input

*ESP.cub* // This file contains ESP grid data. After loading it, the grid data will be stored in memory

```

1
2 // Generate the basins by using the grid data stored in memory
Now visualize the attractors in function 0

```



Exit GUI, after that input following commands

```

2 // Integrate real space functions in the basins
-1 // Use the grid data stored in external file as integrand
density.cub // This file contains electron density grid data

```

The result is very close to the one we obtained in Part 1 of present section. For example, the electron population number in negative ESP region we get here is  $0.367*2=0.734$ , while the counterpart one we obtained in Part 1 is 0.740.

At last, we select function 3 to calculate electric multipole moments for the basins. Because cube file does not contain GTF (Gauss type function) information, you will be prompted to input the path of a file containing GTF information of present system, so that electric multipole moments can be calculated. We input the path of the H2O.fch file, and then input -1, the electric multipole moments of all basins will be immediately outputted on screen.

#### 4.17.4 Basin analysis of electron density difference for H<sub>2</sub>O

In this example we analyze basins of electron density difference for H<sub>2</sub>O to quantitatively study the electron density deformation during formation of the molecule.

Before doing the basin analysis, we need to generate grid data of electron density difference first by main function 5, wavefunction file of all related elements must be available. Here we directly use the set of atomic wavefunction files provided in Multiwfn package, namely copying "atomwfn" subfolder in "example" folder to current folder, then during generating grid data of electron density difference Multiwfn will automatically use them. There are several different ways to prepare atomic wavefunction files, please recall Section 4.4.7 and consult Section 3.7.3.

After that, boot up Multiwfn and input:

```

examples\H2O.fch
5 // Calculate grid data
-2 // Obtain deformation property
1 // Electron density

```

3 // High quality grid. Because the variation of electron density difference is complicated, using relatively high quality of grid is compulsory. Note that the "high quality grid" we selected here only defines the total number of grids, and hence has different meaning to the one involved in function 1 of basin analysis module

```

0 // After the calculation is finished, return to main menu

```

```

17 // Basin analysis module
1 // Generate basins and locate attractors
2 // Generate the basins by using the grid data stored in memory (namely the grid data we
just calculated by main function 5)

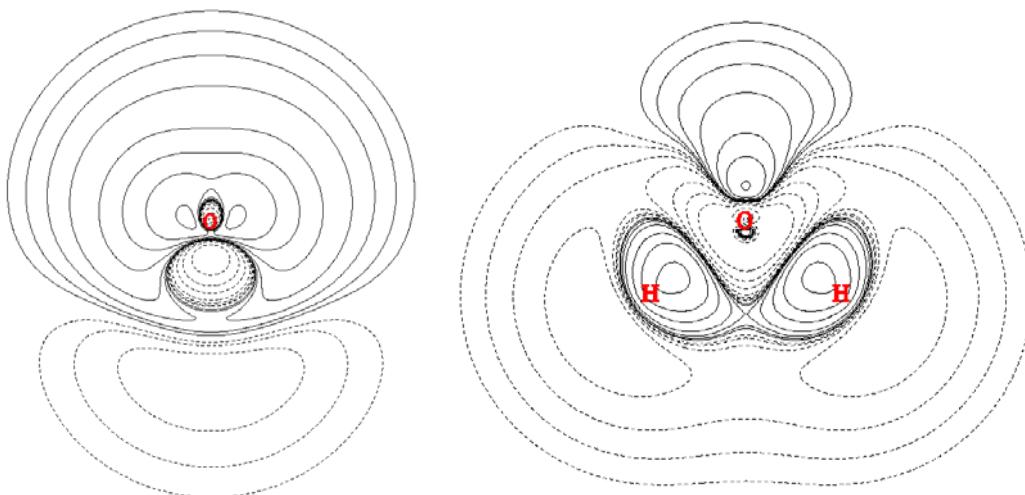
```

Enter function 0 to visualize the result, you will see the left graph shown below. After deselect "Show molecule", the graph will look like the right one



Positive (negative) part of electron density difference corresponds to the region where electron density is increased (decreased) after formation of the molecule. Light green spheres denote the maxima of the positive part, while light blue ones denote the minima of the negative part.

If you feel difficult to imagine why the maxima and minima distribute like this, I suggest you to plot plane maps for electron density difference. The left graph shown below is the electron density difference map vertical to the molecular plane, while the right graph is the map in the molecular plane.

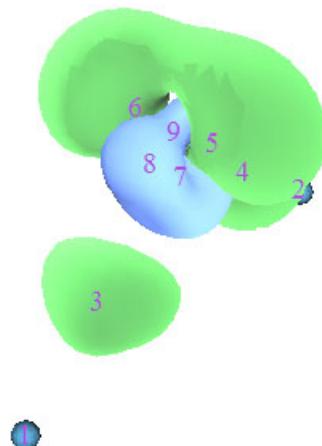


By comparing the attractors with plane maps, it is evident that attractor 3 and 4 are the maxima of the region where electron density is enhanced due to the formation of the O-H bonds. While the presence of attractor 5 and 6 mainly arise from the electron aggregation due to the formation of the lone pairs.

Note: In this example there are missing and misplaced attractors in negative regions (in fact they are repulsors). As you can see, attractor 8 does not have its counterpart in another side of molecular symmetry plane. Besides, attractor 7 deviates from its ideal position. The reason of these problems is that the grid quality is still not high enough relative to the complicated characteristic of electron density difference. However, since these attractors are not of chemical interested, these problems can be simply ignored.

It is interesting to examine how many electrons are aggregated between C and H due to the bond formation. There can be many ways to measure this quantity; the most reasonable one for present case is to integrate the electron density difference in basin 3 or in basin 4. Let's do this now. Choose function 2, and then select option 0 to take the grid data of electron density difference as integrand. From the output we can find that the integral is about 0.09e.

If you would like to compare the attractors with the isosurface of electron density difference, you can simply choose -10 to return to main menu of Multiwfn, and then choose suboption -2 in main function 13 to plot the isosurface of the grid data stored in memory, the attractors we located will be shown together, as shown below (isovalue=0.05), where green and blue parts correspond to positive and negative regions, respectively.

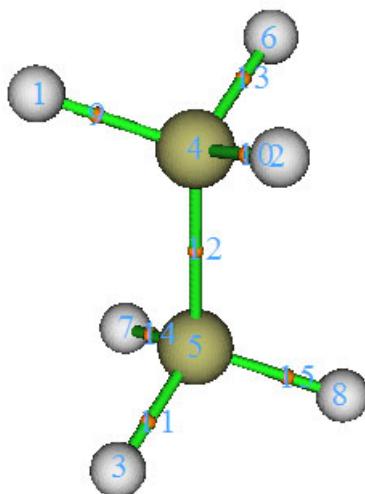


#### 4.17.5 Calculate source function in AIM basins

Source function has been briefed in part 19 of Section 2.6. Commonly, bond critical point (BCP) is taken as the reference point of source function when bonding problem is discussed. In this example we calculate source function in AIM basins for ethane; in particular, based on source function we will get the contribution from methyl group to the electron density at the BCP of its C-H bond. Before calculating source function we should perform topology analysis first to find out the position of the BCP.

Boot up Multiwfn and input:

```
examples\ethane.wfn // Optimized and produced at B3LYP/6-31G*
2 // Topology analysis
2 // Search nuclear critical points
3 // Search BCPs
0 // Visualize result, see below
```



Critical point 11 will be selected as the reference point of the source function. Of course, selecting which BCP is completely arbitrary. Now close the GUI of topology analysis module

You'd better choose option 7 and then input 11 to check the electron density at this CP, because theoretically the integral of source function in the whole space should equal to the electron density at its reference point, therefore this value is important to examine if the integration of source function is accurate enough. The electron density at CP11 is 0.276277.

From the information shown in the command-line window you can find the coordinate of CP11 is (0.0,-1.199262548,-1.909104063), copy it from the window to clipboard (if you do not know how to do this please consult Section 5.4). Next, we will set CP11 as the reference point of the source function. Although you can define reference point by "refxyz" parameters in settings.ini, there is a trick can do the same thing, by which you needn't to close Multiwfn and then reboot it to make the parameters take effect!

Input below commands

-10 // Return to main menu from topology analysis module

1000 // Secret menu

1 // Set reference point

Paste the coordinate of CP11 to the window and then press ENTER button.

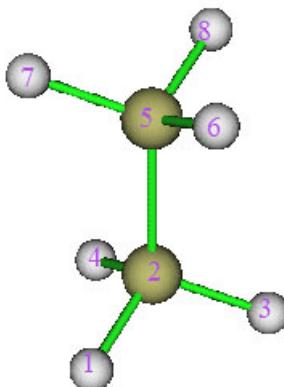
17 // Basin analysis

1 // Generate basins and locate attractors

1 // Electron density

2 // Medium quality grid

Enter GUI by choosing function 0, you will see



Now we integrate source function in the AIM basins. Input following commands

`7 // Integrate real space functions in AIM basins with mixed type of grids`

`1 // Integrate a specific function with atomic-center + uniform grids`

`19 // Source function`

The result is

Atom	Basin	Integral (a. u.)	Vol (Bohr^3)	Vol (rho>0.001)
1 (C)	5	0.00361772	149.307	70.392
2 (H)	8	0.00289355	468.732	50.058
3 (H)	6	0.00280041	443.982	50.097
4 (H)	7	0.00280276	418.343	50.095
5 (C)	2	0.12224052	150.514	70.396
6 (H)	1	0.12040142	475.383	50.054
7 (H)	4	0.01051821	424.105	50.095
8 (H)	3	0.01051742	450.072	50.097

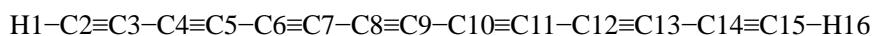
Sum of above integrals: 0.27579202

Sum of basin volumes (rho>0.001): 441.284 Bohr^3

The sum of the integrals is very close to the electron density at CP13 (0.276277). The sum of the integral in basin of 1, 2, 3 and 4 is 0.1204+0.1222+0.0105\*2=0.2636, which represents the integral in the space of methyl group and accounts for 0.2636/0.2758\*100%=95.6% of the total integral value, exhibiting that methyl group is the main source of the electron density of the BCP of its C-H bonds.

#### 4.17.6 Local region basin analysis for polyyne

Sometimes, the geometry of the system we studied is rather extended, for instance, polyyne  $C_{14}H_2$ , which can be formally illustrated as



If we are only interested in the electronic structure characteristic of local region in this system, by properly setting up grid, basin analysis can be conducted only for the interesting region rather than for the whole system to save computational time. As an example, in this section we will try to acquire electron population number in the ELF basin of  $V(C_7, C_8)$  and  $V(C_8, C_9)$  with minimum computational cost.

Boot up Multiwfn and input following commands:

`examples\polyyne.wfn // Optimized and produced under B3LYP/6-31G*`

`17 // Basin analysis`

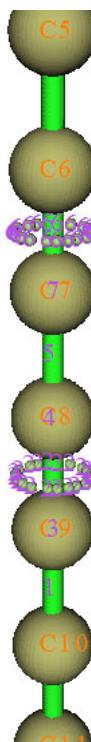
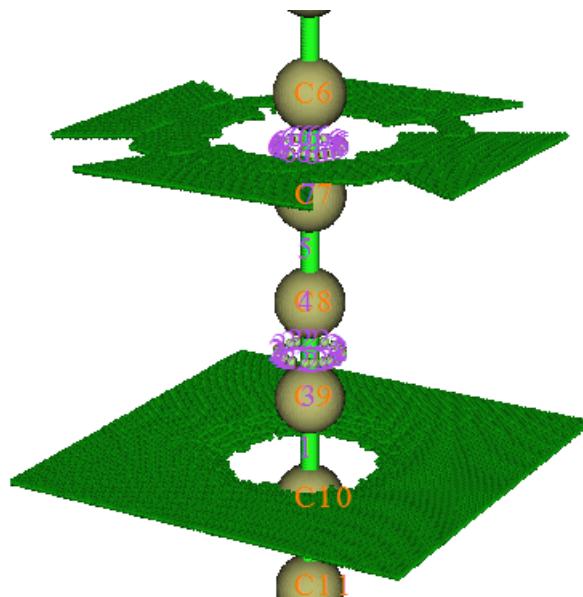
```

1 // Generate basins and locate attractors
9 // ELF
8 // Set the grid by inputting center coordinate, grid spacing and box length
a8 // Take the position of atom 8 as box center
0.08 // Grid spacing (Bohr)
10,10,8 // Box length in X, Y and Z directions (Bohr). Note that current
molecule is aligned in Z-axis. Obviously, the larger the box, the longer the
computational time must be spent. While the box should not be too small, otherwise the
basins of interest may be truncated. Choosing appropriate box size highly relies on
users' experience

```

After the calculation is finished, enter GUI by selecting option 0, you will see the graph shown at the right side. Clearly, only several attractors near C8 are located. Basin 5 and basin 21 correspond to  $V(C_7, C_8)$  and  $V(C_8, C_9)$ , respectively. Notice that although attractor 1 and 6 are also located, due to their corresponding basins are not only large but also close to box boundary, it can be expected basin 1 and 6 are severely truncated and hence studying them are meaningless.

When you use above manner to study local region, you will always find there are many grids travelled to box boundary. In present example, as shown in command-line window, the number of such type of grids is 60668. You can visualize them by choosing "Boun" in basin list of GUI, see the graph below



Now close GUI, select option 2 and then select 1, the result shows that the integral of electron density in  $V(C_7, C_8)$  and  $V(C_8, C_9)$  are 2.78 and 5.02, respectively. Evidently, the bonding between C8-C9 is much stronger than C7-C8, this is why the bond length of the former ( $1.236\text{\AA}$ ) is shorter than the latter ( $1.338\text{\AA}$ ). Note that the electron population number in  $V(C, C)$  of acetylene is 5.37 (see Section 4.17.2), therefore it can be expected that C8-C9 is weaker than typical C-C triple bond, mostly due to the electron global conjugation in polyyne.

The interested users can redo the basin analysis for the whole system with using the same grid spacing (0.08 Bohr), the computational amount will be much larger than current example. For  $V(C_7, C_8)$  and  $V(C_8, C_9)$ , you will find the result does not differ from the one we obtained above

detectably.

#### 4.17.7 Evaluate atomic contribution to population of ELF basins

In this section, I will use CH<sub>3</sub>NH<sub>2</sub> as example to show how to obtain contribution of C and N to population of V(C,N) ELF bond basin based on AIM partition of atomic space, this is useful to examine bond polarity. You can also use the similar way to obtain atomic contribution to population of any other kind of basins (e.g. LOL basin, ESP basin).

First, we need to generate a cube file named basin.cub, whose grid value corresponds to index of ELF basins. Boot up Multiwfn and input

*examples\CH3NH2.wfn*

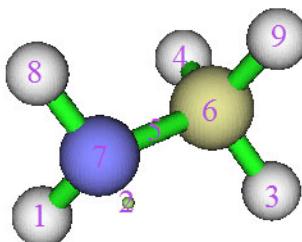
17

1

9 // ELF

2 // Medium quality grid

Now enter option 0 to examine the basin index



Evidently basin 5 corresponds to V(N,C), which is the one we will study. Then close the GUI and input

-5 // Export basin as cube file

0,0 // Export basin.cub in current folder, whose grid value directly defines ELF basin

Next, we generate AIM basins as usual, the grid setting must be exactly identical to basin.cub

1 // Regenerate basins

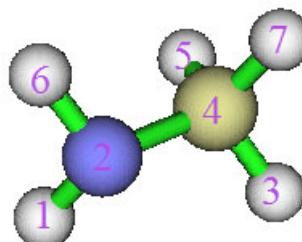
1 // Select real space function

1 // Electron density

9 // Use grid setting of another cube file, this is the safest way to ensure the grid data to be generated has the same grid setting as basin.cub

*basin.cub*

0 // Check attractors



It is clear that the attractor index corresponding to N and C are 2 and 4, respectively. Then we evaluate atomic contribution to population of the basins defined in basin.cub

9 // Then program loads basin.cub in current folder

2 // The index of the attractor corresponding to N

5 // The 5th ELF basin, i.e. V(N,C) basin

The result is 1.15866, namely N contributes 1.159 electrons to V(N,C) basin. Then input

4 // The index of the attractor corresponding to C

5

From the result we know C contributes 0.463 electrons to the V(N,C) basin.

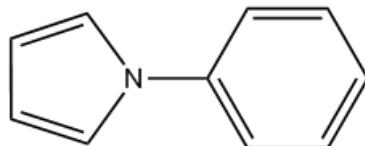
Since N contributes much more electrons than C to their ELF bond basin, it may thus be concluded that C-N is a bond with significant polarity.

## 4.18 Electron excitation analysis

Main function 18 of Multiwfn is very powerful, which is a collection of electron excitation analysis tools and able to provide very deep insight into electron transition problems.

### 4.18.1 Analyze hole-electron distribution, transition density, transition dipole moment and charge-transfer for N-phenylpyrrole

In this example we will study distribution of hole and electron, transition density, transition dipole moment, charge density difference, charge-transfer length and so on for different electron transition modes of N-phenylpyrrole (PP). All of the related theories in this example have been detailed in Section 3.21.1 and 3.21.4, please read them first. The structure of PP is shown below



All calculations were finished by Gaussian 09. Note that the geometry PP is not in this minimum geometry, but in planar transition state geometry, so that electronic excitation analyses could be illustrated easier. At this geometry, the excited state (TDDFT) calculation was performed at CAM-B3LYP/6-31+G\* level. The five lowest excited states were taken into account. Note that in the excited state calculation, *IOp(9/40=4)* is used so that all configuration coefficients >0.0001 could be printed out (otherwise only the ones >0.1 will be printed and will result in inaccurate analysis results). In summary, both the .fch file and .out file used below came from the calculation via *#p cam-b3lyp/6-31+g(d) td(nstates=5) IOp(9/40=4)*.

In single-electron excitation process, hole and electron distributions respectively denote the region where an electron leaves and goes to. According to the characteristic of hole and electron, there are three well-known types of excitations:

(1) Local excitation (LE): The hole and electron significantly share the same spatial range.

Note that even though the hole and electron distributions cover the whole system, the excitation is also identified as local excitation.

(2) Charge-transfer excitation (CT): The spatial separation of hole and electron is large, leading to evident movement of charge density from one place to another place.

(3) Rydberg excitation (R): Electron mainly consists of high-lying MOs, therefore the overlap between electron and hole is small. Note that Rydberg type of excitation in general does not lead

to prominent long-range movement of charge density; in other words, the interval between the centroid of hole and electron is small.

Present example consists of many parts, it is not necessary to read through all of them, some parts that you are not interested in may be skipped. However, you should read at least Part 2.

Worthnotingly, although in this section .fch file along with Gaussian excited state output file are used as input files, the functions involved in this section are not only limited to Gaussian users. For example, you can also use .molden file in combination with output file of CIS or TDA-DFT task produced by ORCA as input files, see Section 3.21.1.2 for detail.

### Part1: Calculating $\Delta r$ index

The  $\Delta r$  index proposed in *J. Chem. Theory Comput.*, **9**, 3118 is a quantitative indicator of electron excitation mode. The smaller the  $\Delta r$  index is, the more likely the excitation is a LE mode (the original paper also argued that  $\Delta r$  index is a measure of CT length, but this is often not true!).

First we examine  $\Delta r$  index of the five transition modes. Boot up Multiwfn and input  
`examples\N-phenylpyrrole.fch // The .fch file from excited state calculation (you can also use the .fch file from ground state calculation at exactly the same geometry and identical level)`

`18 // Electron excitation analysis`

`4 // Calculate  $\Delta r$  index`

`examples\N-phenylpyrrole_ext.out // The output file of excited state calculation`

`1 // Select the first transition mode`

You will see the  $\Delta r$  index is 0.793 Å. If you wish to examine the contribution of MO pair to this quantity, you can then input `y` and input a threshold for printing result. However, here we input `n` to skip this step.

Next, examine the  $\Delta r$  index for the second transition mode, namely select option 4 again and input 2 (the file `N-phenylpyrrole_ext.out` will be loaded automatically, its path is not needed to be input this time). The result is 1.846 Å. Repeat this operation to obtain  $\Delta r$  index for the other three transition modes. The results, as well as excitation energies ( $\Delta E$ ) and oscillator strengths ( $f$ ) are summarized below.

	Excited states				
	1	2	3	4	5
$\Delta E$ (eV)	5.0615	5.0739	5.2451	5.9365	5.9669
$f$	0.3935	0.0139	0.0214	0.0000	0.1674
$\Delta r$ (Å)	0.793	1.846	2.456	3.106	3.752

It is highly possible that modes 3, 4 and 5 possess strong CT character or Rydberg character since they have large  $\Delta r$ , while modes 1 and 2 may be regarded as LE mode due to their  $\Delta r$  indices are smaller than 2.0 (this threshold value was proposed in the original paper of  $\Delta r$ ). Bear in mind, the final conclusion can only be drawn after we have visualized the hole and electron distributions. In below text we will focus on analyzing transition modes 1 and 5.

### Part 2: Visualizing and analyzing hole, electron, their overlap and charge density difference

Now we perform another type of analysis. Boot up Multiwfn and input

`examples\N-phenylpyrrole.fch`

`18 // Electron excitation analysis`

`1 // Analyze and visualize hole-electron distribution, transition dipole moment and transition density`

#### 4 Tutorials and Examples

*examples\N-phenylpyrrole\_ext.out* // The output file of excited state calculation

1 // Select the first transition mode

1 // Visualize and analyze hole, electron and transition density and so on

2 // Medium quality grid

Multiwfn will calculate grid data for hole, electron, transition density and so on at medium quality grid. Once the calculation is finished, many statistic data are shown

Integral of hole: 0. 999384

Integral of electron: 0. 990516

Integral of transition density: -0. 000453

Transition dipole moment in X/Y/Z: -0. 000021 -0. 000045 1. 767332 a.u.

Integral of overlap of hole-electron distribution: 0. 5296733

Centroid of hole in X/Y/Z: 0. 000020 0. 000000 0. 294862 Angstrom

Centroid of electron in X/Y/Z: 0. 000277 0. 000110 -0. 152844 Angstrom

Distance between centroid of hole and electron in X/Y/Z:

0. 000257 0. 000110 0. 447706 Angstrom Norm: 0. 447706 Angstrom

Variation of dipole moment with respect to ground state in X/Y/Z:

-0. 000484 -0. 000207 0. 841769 a.u. Norm: 0. 841769 a.u.

RMSD of electron in x,y,z: 0. 992 1. 291 2. 263 Total: 2. 788 Angstrom

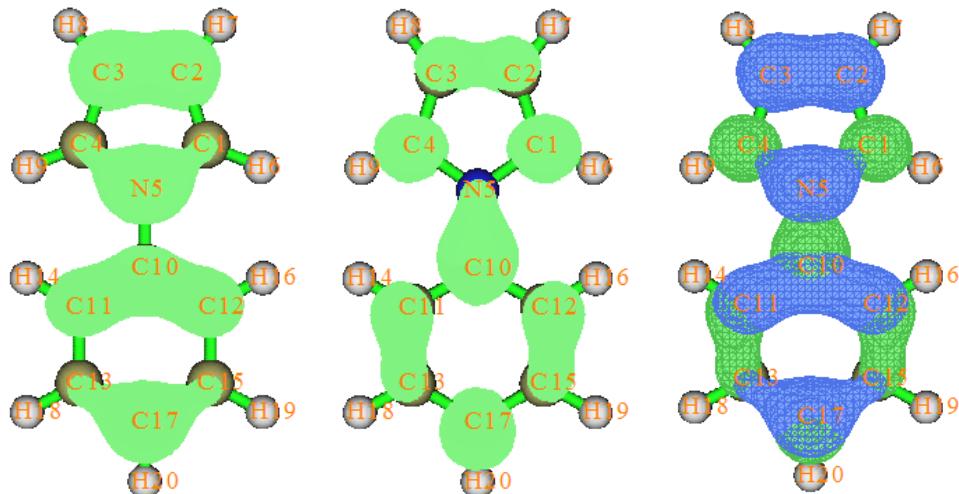
RMSD of hole in x,y,z: 0. 764 0. 817 2. 289 Total: 2. 547 Angstrom

H index in x,y,z: 0. 878 1. 054 2. 276 Norm: 2. 657 Angstrom

t index in x,y,z: -0. 878 -1. 054 -1. 828 Norm: 2. 286 Angstrom

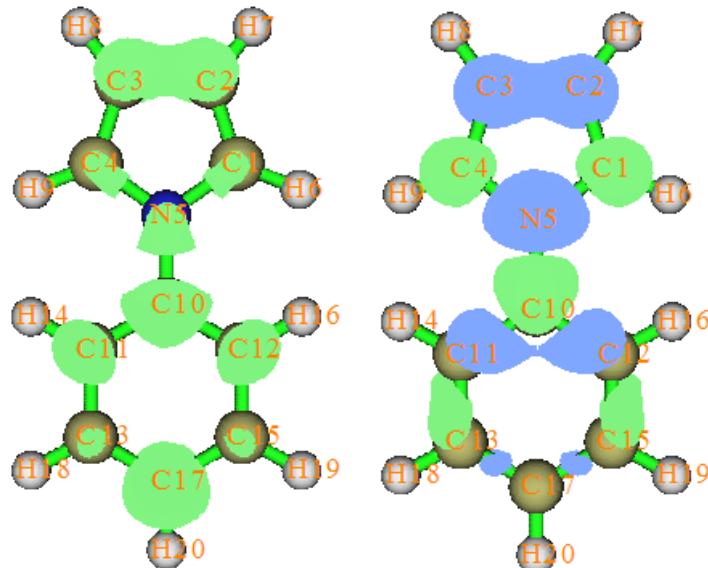
The ideal result of integral of hole and electron is 1.0, while for transition density the ideal value is 0. Our results are close to corresponding ideal values, reflecting that "medium-quality grid" is fine enough for present case. Transition dipole moment is calculated by integrating transition dipole moment density at uniform grids, the result is very close to the one outputted by Gaussian (namely 0.0, 0.0, 1.7813). The integral of overlap of hole-electron distribution is a measure of spatial separation of hole and electron. The distance between centroid of hole and electron is a measure of CT length; the larger the value, the longer length the charge transfers. As you can see, the variation of dipole moment with respect to ground state is also outputted, which is directly evaluated based on the position of centroid of hole and electron. RMSD of hole or electron quantitatively characterizes their distribution breadth, for example, the RMSD of electron in X and in Z is 0.992 and 2.263, respectively, indicating the electron distribution is much broader in Z than in X direction. t index is another measure of the separation of hole-electron.  $t > 0$  means the separation is clear. In present case  $t$  is evident negative in all directions, reflecting that hole and electron overlap with each other severely.

In the new menu choose 1 and then select 1 to visualize hole distribution, and then choose 2 and then select 1 to visualize electron distribution. You can also choose option 3 to visualize hole and electron simultaneously, the hole and electron distributions will be represented as blue and green isosurfaces, respectively. The three graphs are shown below at left, middle and right sides, respectively (at default isovalue 0.002).



As you can see, there is no evident spatial separation between hole and electron, exhibiting that this transition mode is not a CT or Rydberg excitation.

Overlap between hole and distributions is defined as  $\min(\text{hole}, \text{electron})$ , you can select option 4 to visualize it (see left graph below). The charge density difference is calculated by minusing hole from electron distribution, to visualize it you can choosing option 7 (see right graph below, green and blue parts correspond to the region where electron density is increased and decreased after electron excitation, respectively)



Clearly, the overlap between hole and electron is significant; the charge density difference map does not show overall charge transfer or spatial separation, again reflecting that this is a LE mode.

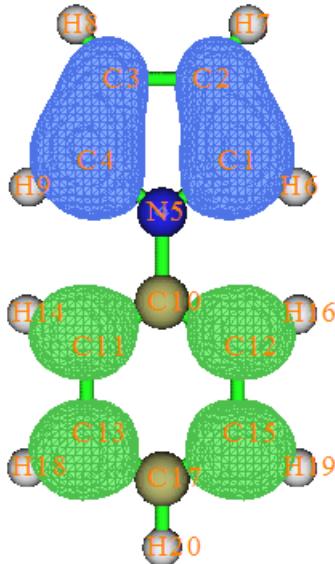
Now we study the 5th transition mode. Input below commands

```
0 // Return
0 // Return to the interface of main function 18
1 // Enter function 1 of main function 18 again
5 // Select the 5th transition mode
1 // Visualize and analyze hole, electron and transition density and so on
```

## 2 // Medium quality grid

From the output we can see that the integral of overlap of hole-electron distribution is 0.0883, which is much smaller than that of transition mode 1 (0.5297); while the distance between centroid of hole and electron now is 3.6433 Å, which is much larger than that of transition mode 1 (0.4477 Å). These quantitative data show that transition mode 5 has conspicuously stronger CT character than mode 1.

Then choose option 3 to visualize isosurface of hole and electron distribution simultaneously

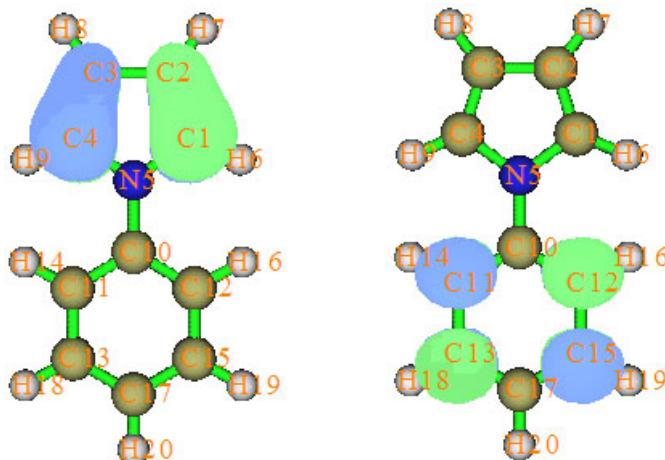


Undoubtedly this is a typical CT transition mode, corresponding to charge transfer from pyrrole to phenyl region. If you visualize the overlap between hole and electron, at default isosurface (0.002), nothing is shown, suggesting that the spatial overlap between hole and electron is trivial.

Choose 0 to return to upper level of menu, then select option 3 and input *0.001* to show MO contribution to hole and electron, you will see

MO	35, 0cc:	2. 00000	Hole:	0. 00132	Electron:	0. 00000
MO	37, 0cc:	2. 00000	Hole:	0. 95980	Electron:	0. 00000
MO	38, 0cc:	2. 00000	Hole:	0. 03589	Electron:	0. 00000
MO	39, 0cc:	0. 00000	Hole:	0. 00000	Electron:	0. 03551
MO	40, 0cc:	0. 00000	Hole:	0. 00000	Electron:	0. 95461
MO	52, 0cc:	0. 00000	Hole:	0. 00000	Electron:	0. 00522
Sum of hole:		1. 00000	Sum of electron:		1. 00000	

Since MO37 and MO 40 dominate hole and electron respectively, it is evident that the 5th transition mode can be approximately symbolized as MO37→MO40. The graph of MO 37 and 40 are shown at left and right side below, respectively.

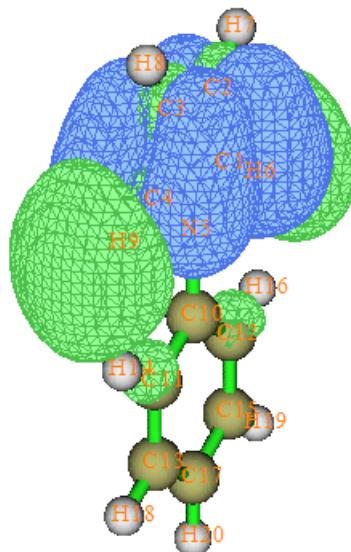


Repeat above steps to investigate hole, electron and related quantities for other transition modes. The integral of overlap of hole-electron ( $S$ ) and the distance between centroid of hole and electron ( $D$ ) are collected below

	Excited state				
	1	2	3	4	5
$S$	0.530	0.650	0.364	0.132	0.088
$D$ (Å)	0.448	0.705	1.946	0.308	3.643

According to  $D$  values, we can conclude that both mode 3 and 5 belong to CT type, since their  $D$  are large; while modes 1 and 2 should be attributed to LE type.

If you carefully study transition mode 4, although its  $S$  value is small, you will find this is not a CT mode, since both hole and electron are mainly localized in pyrrole region. The hole (blue) and electron (green) distributions are shown below (isovalue=0.001). The reason why  $S$  is small is mainly because the hole exhibits  $\pi$  character, while electron primarily shows  $\sigma$  character with some portion of Rydberg component, therefore their overlap is impossible to be very large.

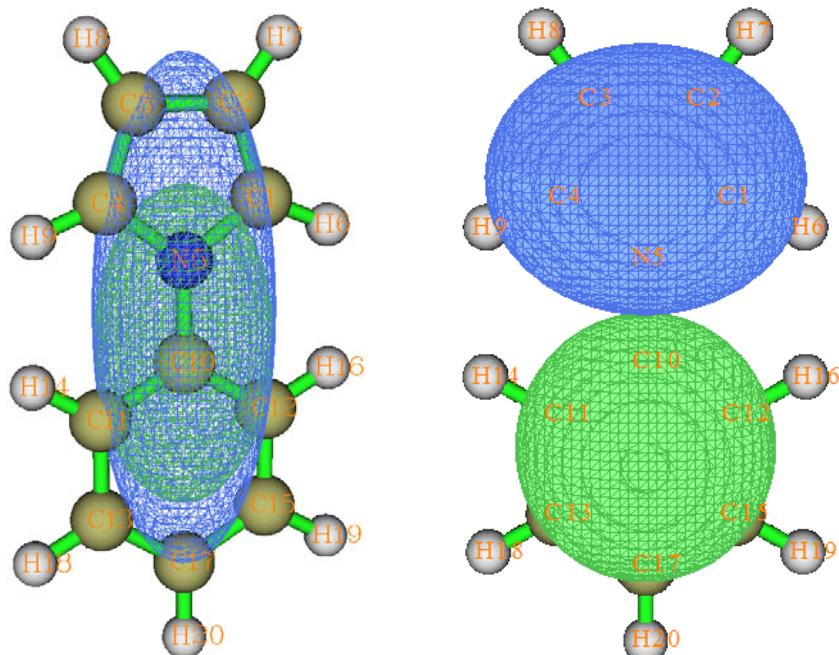


Personally, I recommend using below criterion to identify the type of electron excitation

	D	S
LE	Small	Large
CT	Large	Small
Rydberg	Small	Small

I found the definition  $\Delta r$  has a drawback and thus should be used with caution. LE mode should have small  $\Delta r$ , but in rare cases the value may be large!

Worthnoting, after the grid data was calculated, you can find an option "8 Show isosurface of Cele and Chole functions simultaneously". Cele (Chole) is a Gauss type function transformed from electron (hole) distribution. For excitation mode 1 and 5, if we select this option you will see left and right graph below, respectively (isoval=0.002)



Please compare the Cele and Chole functions with the electron and hole distributions shown earlier. Evidently, Cele (Chole) has the similar spatial scope and exactly the same centroid as electron (hole) distribution, but is free of node and fluctuation characters. Therefore Cele (Chole) can be regarded as an abstract and meantime much more clear representation of electron (hole) distribution.

### Part 3: Analyzing transition density and transition dipole moment

In order to gain a deeper insight into transition dipole moment, we can decompose it to MO pair contributions. Let's do this for transition mode 1.

Return to the interface of main function 18, then choose 1 and input 1 to select the first transition mode. Next, select option 2 and input 0.02, and then input 0, immediately the orbital pairs whose contribution to transition dipole moment larger than 0.02 are shown, see below (Note: For very large system, e.g. more than 100 atoms, if contribution of all orbital pairs are calculated, the cost will be forbiddingly high. In this case, the 0 you input above should be replaced with such as 0.002, so that only the orbital pair with absolute value of coefficient larger than 0.002 will be computed.)

## 4 Tutorials and Examples

```
#Pair          Coefficient   Transition dipole X/Y/Z (au)
1213    35 ->    46   0.040230   0.000000   0.000000   0.037709
1214    35 ->    50   -0.047670   0.000000   0.000000   0.040152
1239    36 ->    40   -0.101270   0.000000   0.000000  -0.280355
1259    37 ->    40   -0.127550   0.000000   0.000000  -0.148489
1260    37 ->    52   0.069960   0.000000   0.000000  -0.122222
1262    37 ->    58   -0.036060   0.000000   0.000000  -0.025065
1278    38 ->    39   0.672690   0.000000   0.000000   2.796678
1280    38 ->    50   0.052570   0.000000   0.000000   0.046724
2489    36 <-    40   -0.014330   0.000000   0.000000  -0.039671
2506    37 <-    52   0.015140   0.000000   0.000000  -0.026450
2522    38 <-    39   -0.027240   0.000000   0.000000  -0.113249

Sum (including the ones not shown):   0.000000   0.000000   1.781438
Norm of transition dipole moment:  1.7814377 a.u.
Oscillator strength:  0.3935307
```

From the output, we can figure out which MO pairs have primary contribution to transition dipole moment. As you can see, the configuration corresponding to MO38→MO39 is the main source (2.797 a.u.) of Z component of transition dipole moment (1.7814 a.u.). X and Y components of transition dipole moment are exactly zero, this is because no MO pair has contribution to them.

Oscillator strength directly relates to norm of transition dipole moment, therefore it can be expected that if the configuration coefficient corresponding to MO38→MO39 is set to zero, namely ignore its contribution, then oscillator strength will be lowered evidently. Let's check this point. Input following commands

```
n // Do not output all results to transdip.txt
10 // Modify or check excitation coefficients
1 // Set coefficient of an orbital pair
38,39 // The MO indices in the orbital pair
1 // Excitation, namely MO38→MO39 (if input 2, then what we selected is MO38←MO39)
0 // Set the configuration coefficient to zero
0 // Return
2
0.02
```

Now the oscillator strength is only 0.1278, which is less than 1/3 of its original value.

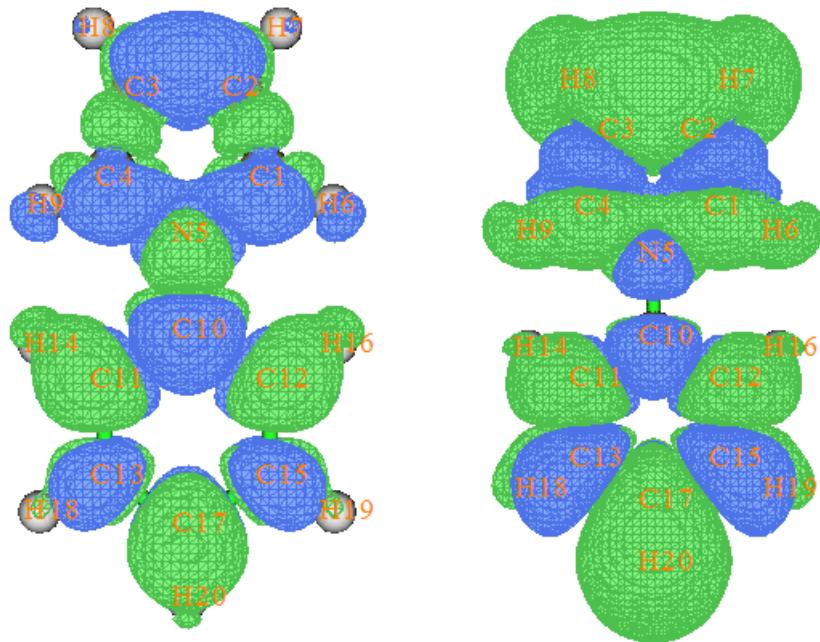
Note that since the coefficient of MO38→MO39 is as large as 0.6727, the sum of the square of remaining coefficients is less than 0.1, which is far from the ideal value 0.5 (not 1.0 since this is a close-shell calculation).

Next, we visualize transition density and transition dipole moment density. Before doing this we should retrieve the original configuration coefficients. Input below commands

```
n // Do not output all result to transdip.txt
10 // Modify or check excitation coefficients
-1 // Reset coefficient of all orbital pairs
0 // Return
1 // Visualize and analyze hole, electron and transition density and so on
2 // Medium quality grid
```

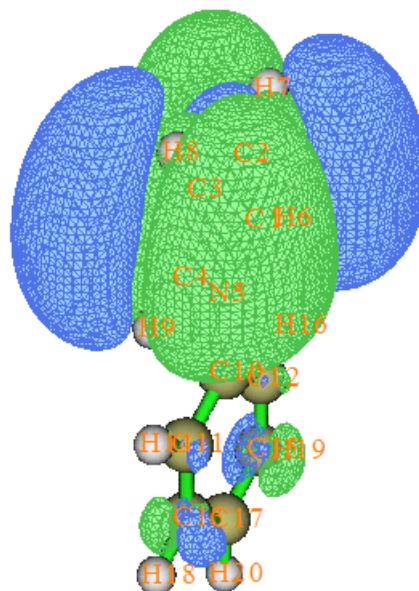
## 5 // Show isosurface of transition density

You will see left graph below, which exhibits the transition density in real space representation. If the transition density is multiplied by negative value of Z coordinate variable, then we obtain Z component of transition dipole moment density. To visualize it, choose "6 Show isosurface of transition dipole moment density" and then select "3: Z component", you will see right graph below



The integral of Z component of transition dipole moment density over the whole space is just Z component of transition dipole moment ( $D_z$ ). From right graph above one can see that the positive (green) part is obviously larger than negative (blue) part. Since the former (latter) contribute positive (negative) value to  $D_z$ ,  $D_z$  must be an evident positive value (1.7814 a.u.).

Now draw the isosurface of Z component of transition dipole moment density for transition mode 4 by yourself (see graph below)



The green and blue isosurfaces occupy the same amount of space, indicating that positive and negative contributions to  $D_z$  are exactly the same, this is why  $D_z$  of present transition mode is zero. Note that the transition dipole moment density almost only distributes in the pyrrole region, this is because this transition mode corresponds to the local excitation on pyrrole moiety (as we have shown earlier).

You may have felt that visual study of transition dipole moment density is interesting and useful, indeed, by which you can clearly identify the contribution of transition dipole moment from different molecular regions.

#### **Part 4: Visualizing transition magnetic dipole moment density**

The transition dipole moment we discussed above is transition **electric** dipole moment. There are also other kinds of transition dipole moments, such as transition **velocity** dipole moment and transition **magnetic** dipole moment. Multiwfn is also capable of calculating transition magnetic dipole moment and showing the corresponding density, the definitions can be found in "Theory 5" of Section 3.21.1. Since this quantity is less important than transition electric dipole moment, I will not discuss it deeply, but only give a simple example:

```
examples\N-phenylpyrrole.fch
18 // Electron excitation analysis
1
examples\N-phenylpyrrole_ext.out // The output file of excited state calculation
2 // Select the second transition mode
-1 // By default, transition magnetic dipole moment density is not calculated by option 1 for
saving time, we select this option to make option 1 also calculate magnetic dipole moment density
1
2 // Medium quality grid
```

After the calculation is finished, from screen you can find the transition magnetic dipole moment evaluated based on the grid data:

```
Transition magnetic dipole moment in X/Y/Z: -0.503315 0.000548 -0.000758 a.u.
```

Then select option 9 and select the component, you will see the isosurface of transition magnetic dipole moment density. You can also export the grid data as cube file in current folder by option 17.

#### **Part 5: Calculating Coulomb attractive energy between hole and electron**

The Coulomb attractive energy ( $E_c$ ) has been introduced as theory 6 in Section 3.21.1.1. Here I show how to calculate it. Boot up Multiwfn and input

```
examples\N-phenylpyrrole.fch
18
1
examples\N-phenylpyrrole_ext.out
1 // The first transition mode
1 // Calculate hole and electron
1 // Low quality grid
18 // Calculate hole-electron Coulomb attractive energy
```

Even if low quality grid is used, the cost of  $E_c$  is still high, you need to wait very patientialy.

The cost is proportional to square of the number of grids, therefore if you use medium quality grid instead, the cost will be excessively expensive. Once the calculation is finished, you will find  $E_c$  on screen, the value of the 1st transition is -0.211870 a.u. (If you use medium quality grid, the result will be -0.212691. Clearly, low quality grid is adequate for producing reliable  $E_c$ ). Similarly, we calculate  $E_c$  for all other transitions, the results are

```
S0→S1: -0.211870 a.u.  
S0→S2: -0.229754 a.u.  
S0→S3: -0.199335 a.u.  
S0→S4: -0.182067 a.u.  
S0→S5: -0.144489 a.u.
```

You can find  $E_c$  closely relates with the S and D index that we calculated earlier, the underlying reason is easy to understand. For example, S0→S2 has large S and small D, implying the hole and electron distribution are essentially the same, evidently their Coulomb attraction must very strong, this explains why the  $E_c$  (-0.229754 a.u.) is quite negative. In contrast, S0→S5 has very small S and very large D, which imply very low degree of similarity between hole and electron distributions, this is the reason why the corresponding  $E_c$  (-0.144489 a.u.) is not so negative as S0→S2.

#### **Part 6: Calculating contribution of each atom to hole and electron**

It is possible to calculate contribution of each atom to hole or electron distribution in Multiwfn. To do this, it is best to make use of fuzzy analysis module (you may also use basin analysis module to realize AIM partition of hole or electron distribution). Here I illustrate how to decompose hole distribution of S0→S5 transition to atomic contributions.

```
Boot up Multiwfn and input  
examples\N-phenylpyrrole.fch  
18  
1  
examples\N-phenylpyrrole_ext.out  
5 // The 5th transition mode  
1 // Calculate hole and electron  
2 // Medium quality grid  
10 // Export hole distribution as cube file hole.cub in current folder  
1 // Total
```

Now quite Multiwfn. Set "iuserfunc" in settings.ini to -1, so that the user-defined function corresponds to interpolated function based on grid data (see Section 2.7 for detail). Then boot up Multiwfn and input

```
hole.cub  
15 // Fuzzy analysis module  
1 // Integrate a real space function over each atomic space  
100 // User-defined function
```

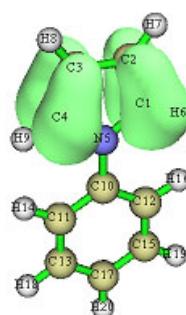
The result corresponding to pyrrole moiety is shown below

Atomic space	Value	% of sum	% of sum abs
1(C )	0. 31123048	31. 155665	31. 155665
2(C )	0. 13948638	13. 963256	13. 963256

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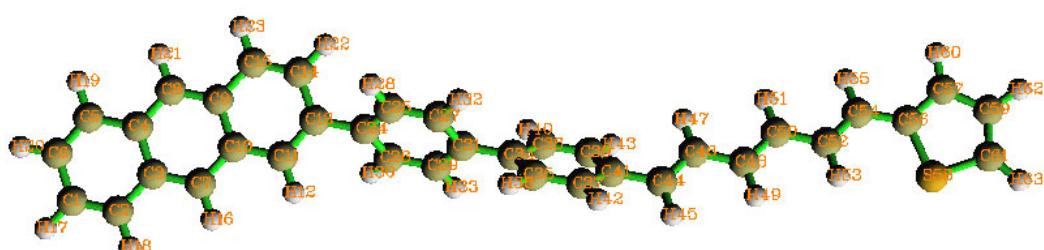
3(C )	0. 13953801	13. 968425	13. 968425
4(C )	0. 31123654	31. 156272	31. 156272
5(N )	0. 04320178	4. 324706	4. 324706
6(H )	0. 00738105	0. 738879	0. 738879
7(H )	0. 00309722	0. 310047	0. 310047
8(H )	0. 00309738	0. 310062	0. 310062
9(H )	0. 00737876	0. 738649	0. 738649

From above data we can find, for example, C4 contributes 31.16% to the hole. Please compare the data with the isosurface map of hole shown below, it is clear that the quantitative data well describes the actual hole distribution.



### 4.18.2 Plot transition density matrix of large-size conjugated molecule as color-filled map

Plotting transition density matrix (TDM) as color-filled map is especially useful for visually studying spatial span and primary sites of electron transitions, the basic principle has given in Section 3.21.2. Here we use this approach to study below molecule:



This molecule contains four fragments: anthracene, biphenyl, 1,3,5-Hexatriene and thiophene. Since this system is relatively large, in order to reduce computational cost, we use semi-empirical method ZINDO (strictly speaking what we will use should be called as ZINDO/S, also known as INDO/S) to calculate electron transition. You can also use other methods, such as CIS, TDHF, TDDFT, etc.

First, run tdm.gjf provided in "examples" folder by Gaussian to produce tdm.out. The keyword "density=transition=1" in route section means the TDM between S0 (ground state) and S1 (the first singlet excited state) will be passed to L601 module, while IOp(6/8=3) tell L601 to

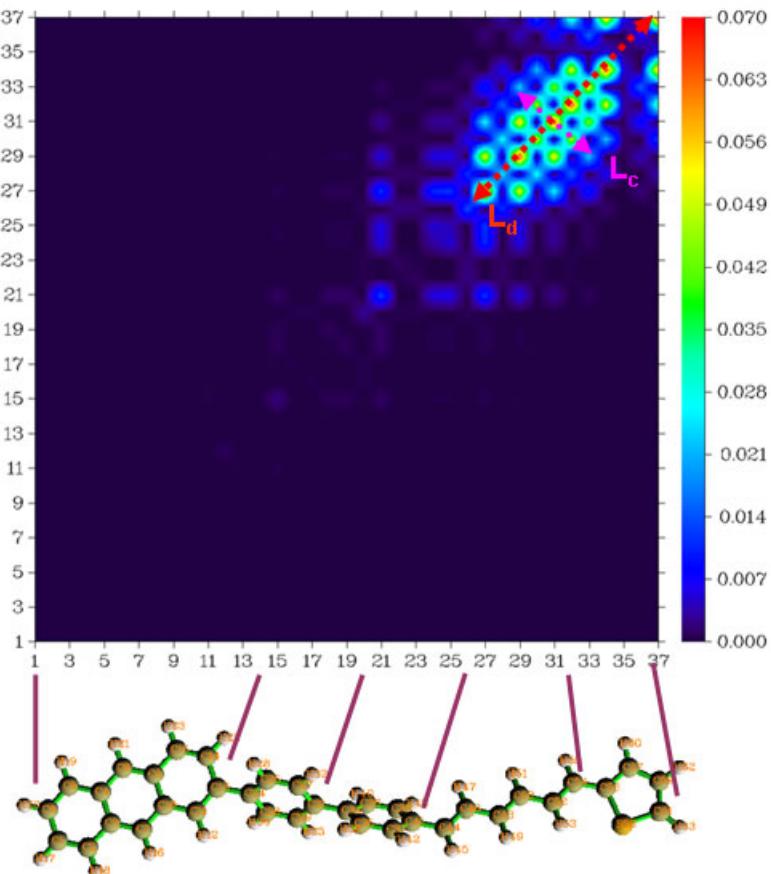
write the received TDM to output file. Then we use formchk to convert tpmat.chk to tpmat.fch.

Boot up Multiwfn and input following commands

```
xxx\tdmat.fch // The path of .fch file
18 // Electron excitation analysis
2 // The function used to plot TDM
xxx\tdmat.out // The path of .out file
1 // Show graph on screen
```

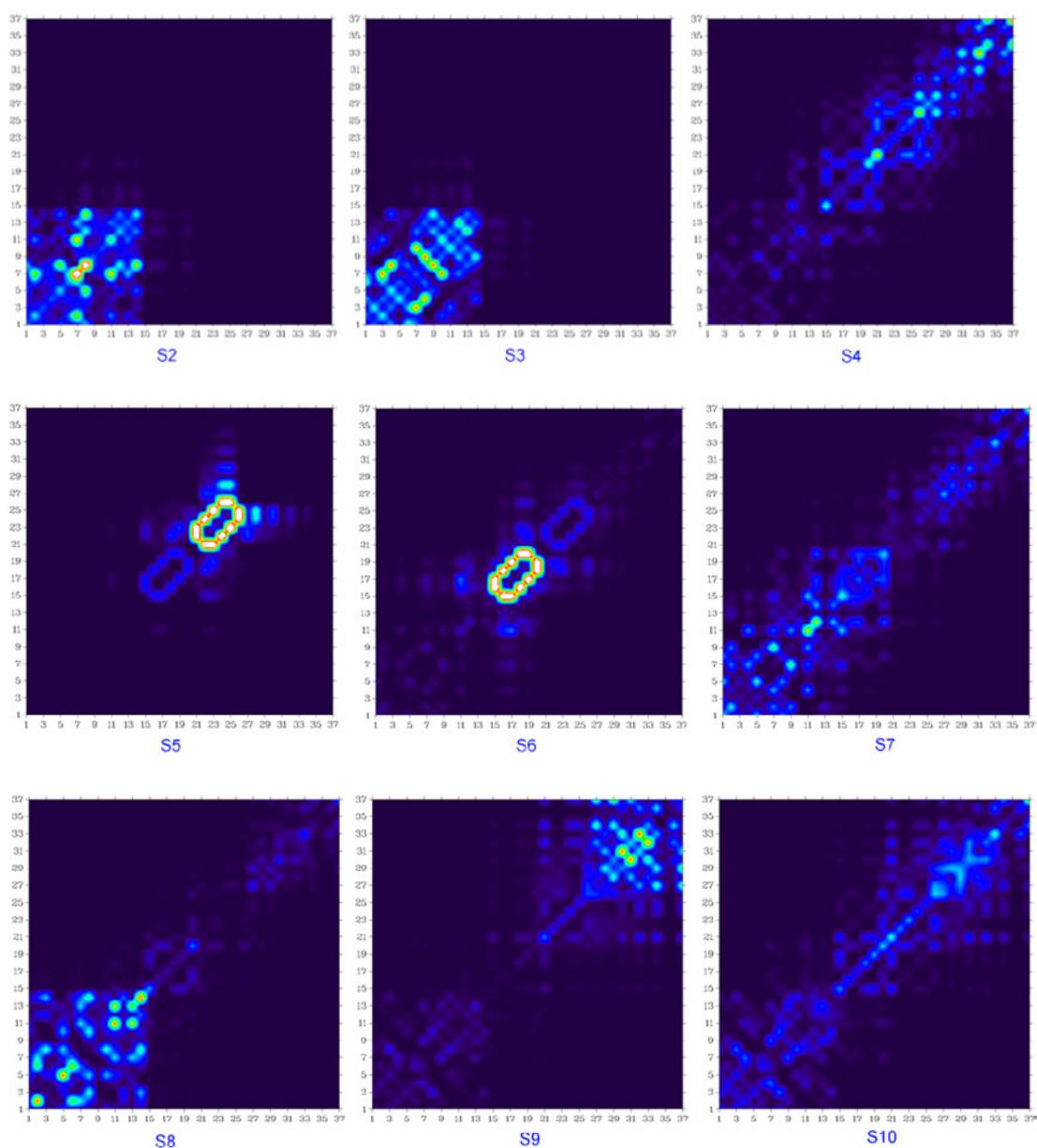
You will see the color-filled map shown below. Labels in abscissa and ordinate correspond to indices of heavy atoms, for clarity, the correspondence between labels and atoms is marked on the plot. Hydrogens are ignored by default, since usually they have little contribution to the transitions we are interested in.

From this graph we can understand which atoms are mainly affected by the electron transition and which atom pairs are strongly coherent when electron transits. A large value in diagonal term corresponds to large charge variance of corresponding atom. While a large value in non-diagonal term denotes that strong hole-electron coherence presents between corresponding two atoms. From the graph corresponding to S0→S1 transition we can clearly see that the transition only involves 1,3,5-Hexatriene and thiophene parts (spanned by red arrow in the graph, the length is denoted by  $L_d$ ), while anthracene and biphenyl almost didn't participated in. We can also find that most heavy atoms in 1,3,5-Hexatriene and thiophene are evidently coherent with surrounding atoms, the spatial span is indicated by pink two-way arrow with length of  $L_c$  in the graph.



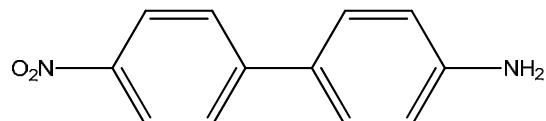
#### 4 Tutorials and Examples

TDM map between S0 and S1, S2 ... S10 are shown below. They can be easily obtained by repeating above procedure, only if X in the keyword "density=transition=X" is changed to corresponding state. (while .fch file is unnecessary to be regenerated, the utilized information in .fch file are identical to all states) Obviously, the electron transitions from S0 to S2, to S3 and to S8 of present system essentially reflect the local transitions within anthracene. Since anthracene is a high delocalization system, relatively widespread coherence span can be observed. S0 to S5 and to S6 correspond to the local transitions occurred within the respective two benzene rings, the coherence between atoms in each benzene ring is very strong, however the coherence between the two benzene is much weaker. S0 to S4, to S7 and to S10 are the transition modes involving large spatial range.



### 4.18.3 Analyze charge-transfer during electron excitation based on electron density difference

In this instance we will analyze charge-transfer (CT) between the first singlet excited state and ground state of the molecule shown below in ethanol solvent, which will be referred to as P2. The related theory has been introduced in Section 3.21.3. The discussions in this example are somewhat related to the ones involved in Section 4.18.1, however the methods employed in this section are purely based on electron density difference.



Since the .wfn files corresponding to the excited and ground state are huge, they are not provided. Instead, the input files of Gaussian for generating the two .wfn files are provided in "example" folder (extP2.gjf and basP2.gjf). I assume that the corresponding .wfn files are produced at "CT" subfolder in current folder. I would like to remind you once again, the geometries in the wavefunction files of the two states must be exactly identical, otherwise the result will be meaningless!

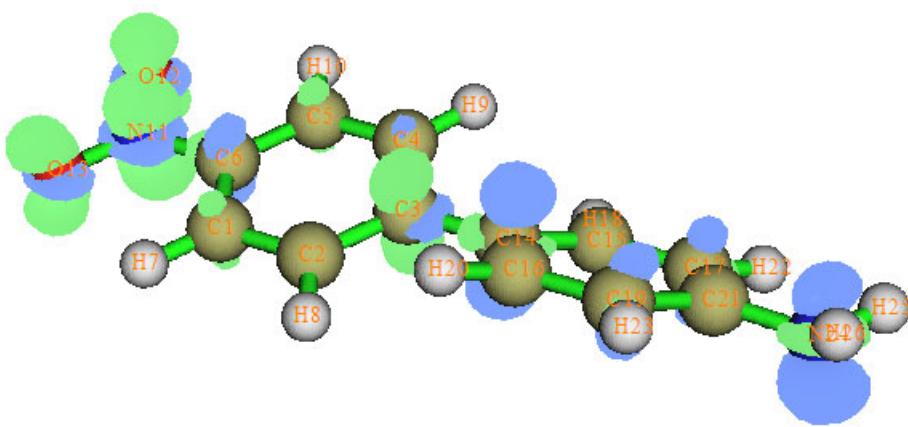
First, we calculate grid data of electron density variation  $\Delta\rho$ . Boot up Multiwfn and input:

```
CT\extP2.wfn // Excited state wavefunction file
5 // Generate grid data
0 // Set custom operation
1 // Only one file will be dealt with
-,CT\basP2.wfn // Ground state wavefunction file. Corresponding density will be subtracted
```

from the excited one to generate  $\Delta\rho$

```
I // Electron density
2 // If the system is much larger than present one, more grid points is required.
```

Once the calculation is normally terminated, you can choose option -1 to view the electron density variation before and after excitation (Default value is too large, 0.005 is recommended as isovalue). Green and blue regions correspond to positive and negative regions, respectively, and thus represent increase and decrease in electron density due to the excitation.



However this difference graph is not intuitive, positive and negative parts intertwined together, we will see that  $C_+$  and  $C_-$  functions make the picture much clearer.

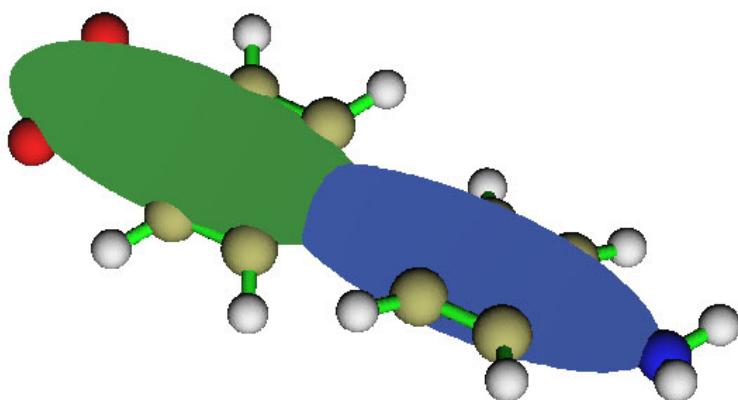
```
0 // Return to main menu
18 // Electron excitation analysis
3 // The routine for analyzing CT
```

The following information are displayed immediately. Note that if positive and negative parts of transferred charge are obvious unequal, that means the grid setting used in generating  $\Delta\rho$  is too coarse, and you need to calculate again with finer grid setting.

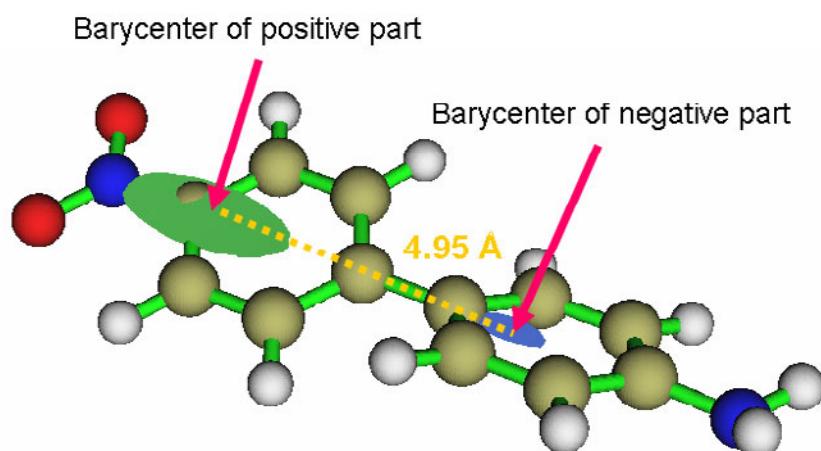
```
Transferred charge (positive and negative parts): 0.844 -0.844
Barycenter of positive part in x,y,z (Bohr): -5.024 -0.001 0.000
Barycenter of positive part in x,y,z (Angstrom): -2.659 -0.001 0.000
Barycenter of negative part in x,y,z (Bohr): 4.335 -0.018 -0.055
Barycenter of negative part in x,y,z (Angstrom): 2.294 -0.009 -0.029
Distance of CT in x,y,z (Bohr): 9.359 0.017 0.055 Norm: 9.359
Distance of CT in x,y,z (Angstrom): 4.953 0.009 0.029 Norm: 4.953
Dipole moment variation (a.u.): 7.896 -0.014 -0.046 Norm: 7.896
Dipole moment variation (Debye): 20.070 -0.035 -0.117 Norm: 20.070
RMSD of positive part in x,y,z: 5.656 2.362 1.551 Total: 6.323
RMSD of negative part in x,y,z: 6.217 2.162 1.664 Total: 6.789
H index in x,y,z (Bohr): 5.936 2.262 1.608 Norm: 6.553
H index in x,y,z (Angstrom): 3.141 1.197 0.851 Norm: 3.468
t index in x,y,z (Bohr): 3.423 -2.245 -1.553 Norm: 4.378
t index in x,y,z (Angstrom): 1.811 -1.188 -0.822 Norm: 2.317
Overlap integral between  $C_+$  and  $C_-$ : 0.742365
```

These information are self-explained, if you are confused, recall Section 3.21.3.

By selecting option 1,  $C_+$  (green) and  $C_-$  (blue) functions can be shown up. The isovalue of the graph shown below is 0.0015.



If the isovalue is increased to 0.0024, the positions of barycenters can be approximately located.



From the graph it is evident that the direction of electron-transfer is from amino group side (electron donor) to nitryl group side (electron acceptor). However the barycenters are not located at the two substituents exactly, and especially the displacement at amino group side is non-negligible, it suggests that electron depletion zone is markedly shifted to nearby phenyl, also the actual electron donor is not amino group but phenyl. This finding parallels that phenyl is a weak electron donor.

Hint: If you would like to get better display effect of the C<sub>+</sub> and C<sub>-</sub> isosurfaces, you can use VMD program (freely available at <http://www.ks.uiuc.edu/Research/vmd/>) to display them, the procedure is: Boot up VMD first, drag Cpos.cub into VMD main window, and then drag Cneg.cub into it. Select "Graphics"- "Representations", choose the first term in "Selected Molecule", click "Create Rep" button to create a new representation (the existing representation is used to show molecular structure), change the "drawing method" to "isosurface", set "Draw" to "solid surface", change the isovalue to 0.0015, set "coloring method" to "ColorID" and choose "7 green". Now the isosurface of Cpos has been properly displayed. Next, choose the second term in "Selected Molecule", use the similar methods to set each options, but select "0 blue" in "ColorID", and use isovalue of -0.0015. Finally the graph will look like the one shown above. You can also set "Material" to "transparent" so that the overlap region of C<sub>+</sub> and C<sub>-</sub> can be clearly distinguished.

#### 4.18.4 Generate and analyze natural transition orbitals (NTOs)

In this section I illustrate how to use Multiwfn to perform the very popular natural transition orbital (NTO) analysis with uracil as example. Please first read Section 3.21.6 to acquire basic knowledge of NTO.

Before showing how to perform NTO analysis, I would like to let you apprehend why NTO analysis is meaningful. As an instance, we use Gaussian to perform TDDFT calculation at PBE0/6-31G\* level for singlet excited states of uracil, you will find below information

```
Excited State 3: Singlet-A"   6.0180 eV 206.02 nm f=0.0000 <S**2>=0.000
26 -> 30      0.54135
26 -> 31      -0.20634
28 -> 30      -0.15424
28 -> 31      0.36715
```

Clearly, in excitation of S<sub>0</sub>→S<sub>3</sub>, there is no dominant MO transition, the largest contribution of a single MO pair is merely  $0.541^2 \cdot 2 \cdot 100\% = 58.5\%$ , therefore it is impossible to identify the nature of this excitation by viewing only one MO pair. In such difficult cases, NTO analysis is often useful, because after transforming MOs to NTOs, commonly you will be able to find only one pair of NTO having eigenvalue very close to 1, transition between the two NTOs in this pair faithfully represents the real character of the electronic excitation.

The input files needed for NTO analysis are the same as those needed for hole-electron analysis exemplified in Section 4.18.1. Assume that you are a Gaussian user and you want to study electronic excitation from ground state to the lowest three singlet excited states for uracil at TD-PBE0/6-31G\* level, what you need to do is carrying out a normal TDDFT calculation with these keywords: # PBE1PBE/6-31G\* TD IOp(9/40=4), also you need to make Gaussian generate corresponding .fch file. The input file, output file and.fch file have already been provided in "examples\NTO" folder. The keyword IOp(9/40=4) is very important, without it the NTO result will be evidently inaccurate, the meaning of this IOp has been mentioned in Section 4.18.1.

Now we start to carry out NTO analysis. Boot up Multiwfn and input

*examples\NTO\uracil.fch*

18 // Electronic excitation analysis

6 // Generate NTOs

*examples\NTO\uracil.out* // Gaussian calculated three lowest excited states, you can analyze any one of them

3 // Study transition from ground state (S<sub>0</sub>) to the 3rd excited state (S<sub>3</sub>)

Now Multiwfn loads transition information of S<sub>0</sub>→S<sub>3</sub> from the Gaussian output file and generate NTOs, the eigenvalues of occupied and virtual NTOs are shown below

The highest 10 eigenvalues of occupied NTOs:

```
0.000006  0.000007  0.000015  0.000016  0.000024
0.000063  0.000121  0.000582  0.134025  0.865529
```

The highest 10 eigenvalues of virtual NTOs:

```
0.865529  0.134025  0.000582  0.000121  0.000063
0.000024  0.000016  0.000015  0.000007  0.000006
```

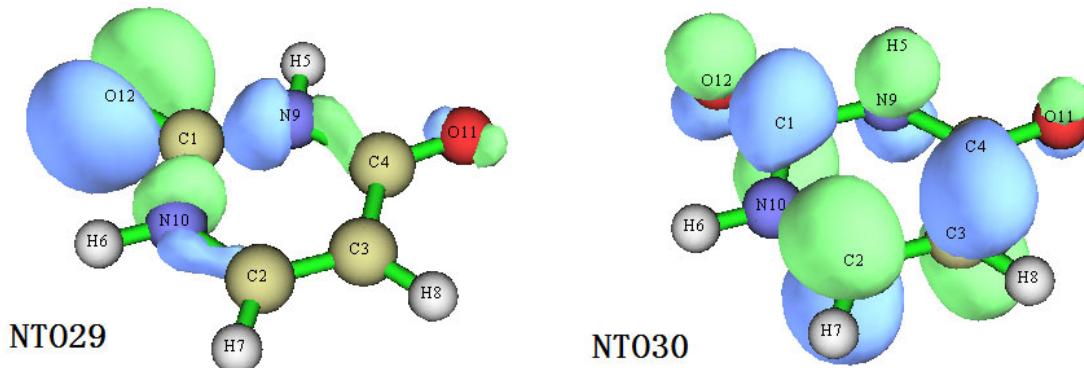
It can be seen that, the eigenvalues of occupied and virtual NTOs have one-to-one correspondence,

the largest eigenvalue is 0.8655, that means that NTO pair contributes as high as 86.55% of the S0→S3 transition. So, if we would like to characterize the nature of this transition, we can only study the occupied NTO and virtual NTO in this NTO pair.

Now you can select if outputting .fch or .molden file containing the NTOs. We choose "2 Output NTO orbitals to .fch file" and input the path to output, such as C:\S3.fch. After the .fch has been successfully generated, you can reboot Multiwfn and load the S3.fch, in main function 0 you can visualize the NTOs, the orbital energies now correspond to NTO eigenvalue. To plot the two NTOs in the NTO pair with 86.55% contribution, in the GUI of main function 0 you can select "orbital info." - "Show up to LUMO+10" in the menu, in the text window you will find output like below

Orb:	27 Ene(au/eV):	0. 000582	0. 0158 Occ: 2. 000000 Type: A+B
Orb:	28 Ene(au/eV):	0. 134025	3. 6470 Occ: 2. 000000 Type: A+B
Orb:	29 Ene(au/eV):	0. 865529	23. 5522 Occ: 2. 000000 Type: A+B
Orb:	30 Ene(au/eV):	0. 865529	23. 5522 Occ: 0. 000000 Type: A+B
Orb:	31 Ene(au/eV):	0. 134025	3. 6470 Occ: 0. 000000 Type: A+B
Orb:	32 Ene(au/eV):	0. 000582	0. 0158 Occ: 0. 000000 Type: A+B

We can see that the occupied NTO with index of 29 and the virtual NTO with index of 30 constitute the NTO pair with eigenvalue of 0.8655, there we select corresponding index in the GUI to visualize them, the isosurfaces are shown below



Undoubtedly, this S0→S3 excitation can be regarded as transition from lone pair of O12 to anti-bonding  $\pi$  orbital of the uracil ring, at least we have 86.55% confidence to say that. From NTO eigenvalues we notice that NTO28→NTO31 transition also has small contribution (13.40%) to the excitation, please plot corresponding orbitals and discuss their characteristic.

Note that the NTOs can also be subjected to quantitative analyses. For example, you can enter main function 8 and use suitable options to analyze their orbital composition at quantitative level, or you can use subfunction 11 of main function 100 to evaluate overlap extent and centroid distance between selected two NTOs.

Sometimes we want to perform NTO analysis for a batch of excitations, for example, we want to generate a batch of .fch files that respectively contain NTOs of S0→S1, S0→S2 and S0→S3 transitions, although you can manually do this in the interactive interface of Multiwfn, a more efficient and clever way is employing shell script. If you are a Linux user, we can run below shell script to yield S1.fch, S2.fch and S3.fch, which contain NTOs corresponding to S0→S1, S0→S3 and S0→S3. This script is very easy to understand as long as if you have basic level of knowledge about shell programming.

```

#!/bin/bash
cat << EOF > allNTO.txt
18
6
examples/NT0/uracil.out
EOF
for ((i=1; i<=3; i=i+1))
do
cat << EOF >> allNTO.txt
$i
2
S${i}.fch
6
EOF
done
./Multiwfn examples/NT0/uracil.fch < allNTO.txt
rm ./allNTO.txt

```

This script is also provided as "examples\NT0\allNTO.sh". If you do not make any modification to the script, this script should be copied to the Multiwfn folder and run as "./allNTO.sh" in Multiwfn folder, then S1.fch, S2.fch and S3.fch will be yielded at the same folder. In practical studies, you should properly modify the script according to actual situation, the range of the excitations to be studied is determined by "i=1;i<=3".

Note that NTO analysis has both advantage and disadvantage with respect to the hole-electron analysis, this point has been mentioned at the end of Section 3.21.6. For many systems and excitations, even if NTO transformation has been applied, there are still no NTO pair with predominant contribution, in this case you have to use hole-electron analysis to facilitate discussion of excitation characteristic. The drawback of hole-electron analysis is that it is unable to present orbital phase information like NTO analysis, and it takes more computational cost.

## 4.100 Other functions, Part 1

### 4.100.1 Visual study of weak interaction by RDG and DORI method

This is a very very important application of Multiwfn, the theory has been detailed in *J. Am. Chem. Soc.*, **132**, 6498 and my blog article *Visual research of weak interaction by Multiwfn* (in Chinese, see <http://sobereva.com/68>), so below I only sketch key points. Some additional discussions and ways to improve plotting quality can be found in <http://sobereva.com/291>.

#### Use isosurface to represent weak interaction region

The first thing is to find a way to distinguish weak interaction region from other regions. From the table below we can know if only the regions where the value of reduced density gradient (RDG) function is in the range of 0 to medium are reserved, then “around nuclei” and “edge of molecule” regions will be shielded. The RDG function is defined as

$$\text{RDG}(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}$$

	Around nuclei	Around chemical bond	Weak interaction region	Edge of molecule
$ \nabla\rho(\mathbf{r}) $	Large	0~Minor	0~Small	Very small~Small
$\rho(\mathbf{r})$	Large	Medium	Small	0~Small
RDG( $\mathbf{r}$ )	Medium	0~Minor	0~ Medium	Medium ~Very large

Then from remained regions, if we only extract the region where  $\rho(\mathbf{r})$  is small rather than middle, the region “around chemical bond” will be shielded and only weak interaction region is eventually remained. Now I use phenol dimer to exemplify this analysis method. Boot up Multiwfn and input following commands

*examples\PhenolDimer.wfn*

5 // Generate grid data

13 // RDG function

7 // Use middle point of two atoms as center of grid data, this way to define spatial scope is very suitable for weak interaction analysis

1,14 // The indices of the two atoms are set to 1 and 14, because from molecular structure (see below graph) we can estimate that the weak interaction region is between C1 and C14

40,40,40 // The weak interaction region is small, so  $40*40*40=64000$  grid is fine enough

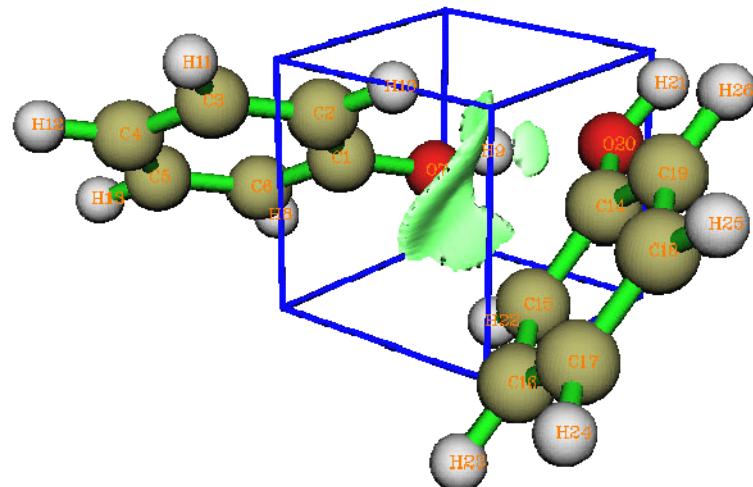
3,3,3 // Extension distance in all directions are 3 Bohr, so the volume of spatial scope is  $(2*3)^3=216$  Bohr<sup>3</sup>. This extension value is generally too small, but enough for present study.

4 // After Multiwfn finished the calculation of grid data, set isovalue for viewing RDG isosurface

0.5 // Set isovalue to 0.5, this is recommended value for most cases, if too small, then isosurface is too small, if too big, then unwanted “Around nuclei” and “Around chemical bond” region will appear

-1 // Show the isosurface

You will get below graph:

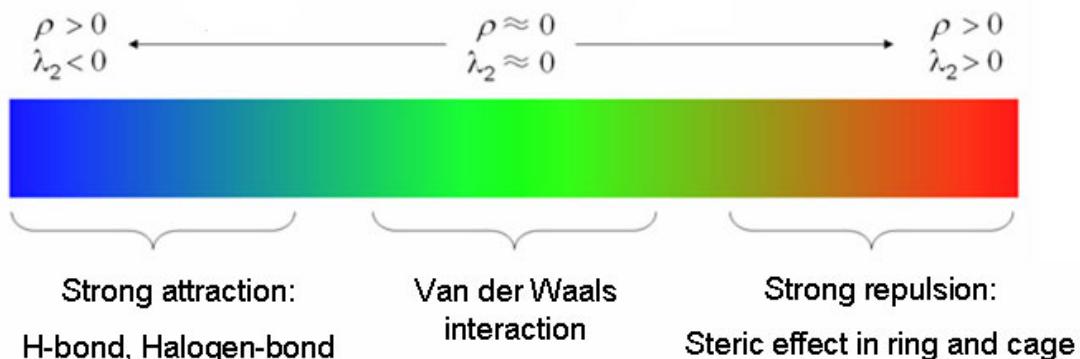


The isosurface represents the weak interaction region between phenol dimer very clearly. Notice that by default, RDG function is set to an arbitrary large value (100.0) where electron density is larger than or equal to 0.05, so that the isosurfaces in the regions “around chemical bond” will be shielded. The threshold is determined by “RDG\_maxrho” parameter in settings.ini, 0.05 is suitable for most cases.

The cubic blue frame shows spatial scope of grid data, only appears when “Show data range” is selected in GUI window. Because the extension distance from center of grid data is set to 3.0 Bohr, so the side length is  $2 \times 3 = 6$  Bohr.

### Discriminate weak interaction types by filling color to RDG isosurface

In Bader’s AIM theory, the (3,-1) type critical point indicates electron density is aggregated at this point, appears in chemical bond path or between the atoms which have attractive interaction; while (3,+1) type critical point indicates electron density is depleted at this point and displays steric effect (also called nonbond overlap), generally appears in the center of ring system. The criterion for distinguishing (3,-1) and (3,+1) is the second largest eigenvalue of Hessian matrix of electron density (called  $\lambda_2$  here), if  $\lambda_2$  exceed zero, then (3,+1), else (3,-1). Besides, the strength of weak interaction has positive correlation with electron density  $\rho$  in corresponding region, van der Waals interaction regions always have very small  $\rho$ , while the regions correspond to strong steric effect and hydrogen bond always have relative large  $\rho$ . So we can define a real space function  $\text{sign}(\lambda_2(\mathbf{r}))\rho(\mathbf{r})$ , that is the sign of  $\lambda_2$  multiples  $\rho$ . If we use different colors to represent this function value as below and fill them to RDG isosurfaces, we can not only know where weak interaction region is, but also know the interaction type.



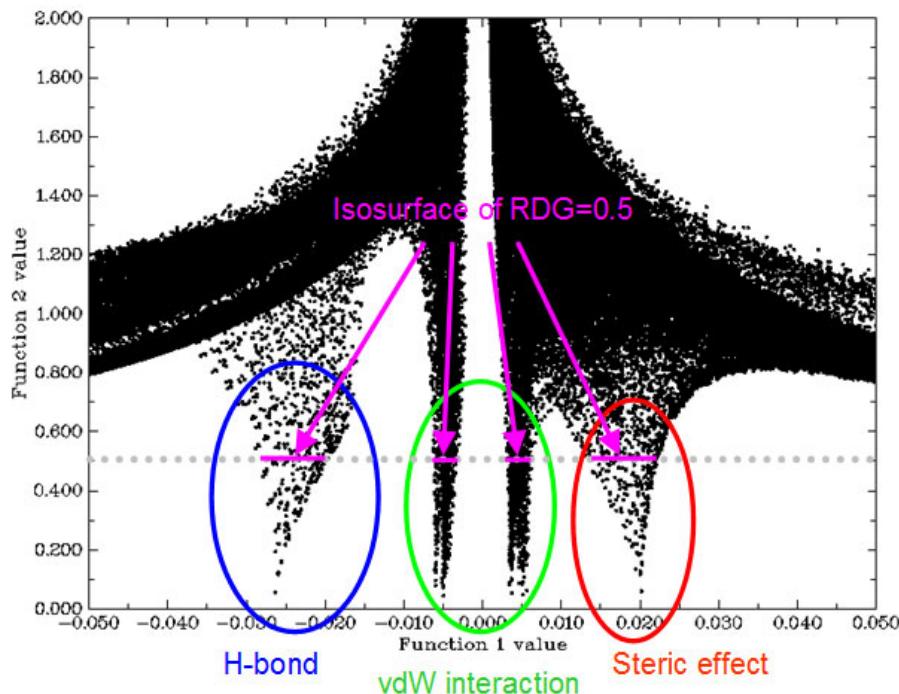
Unfortunately, current Multiwfn does not support plotting color-filled isosurface graph, I recommend you to generate grid data for  $\text{sign}(\lambda_2)\rho$  and RDG simultaneously by subfunction 1 of function 100 of Multiwfn, and then plot the graph by VMD, which is a free software and can be downloaded at <http://www.ks.uiuc.edu/Research/vmd>. I again use phenol dimer as example, this time I do not only show you the characteristic of weak interaction region, but also ring center region, so the spatial scope of grid data should be set to cover entire dimer.

Boot up Multiwfn and input following commands

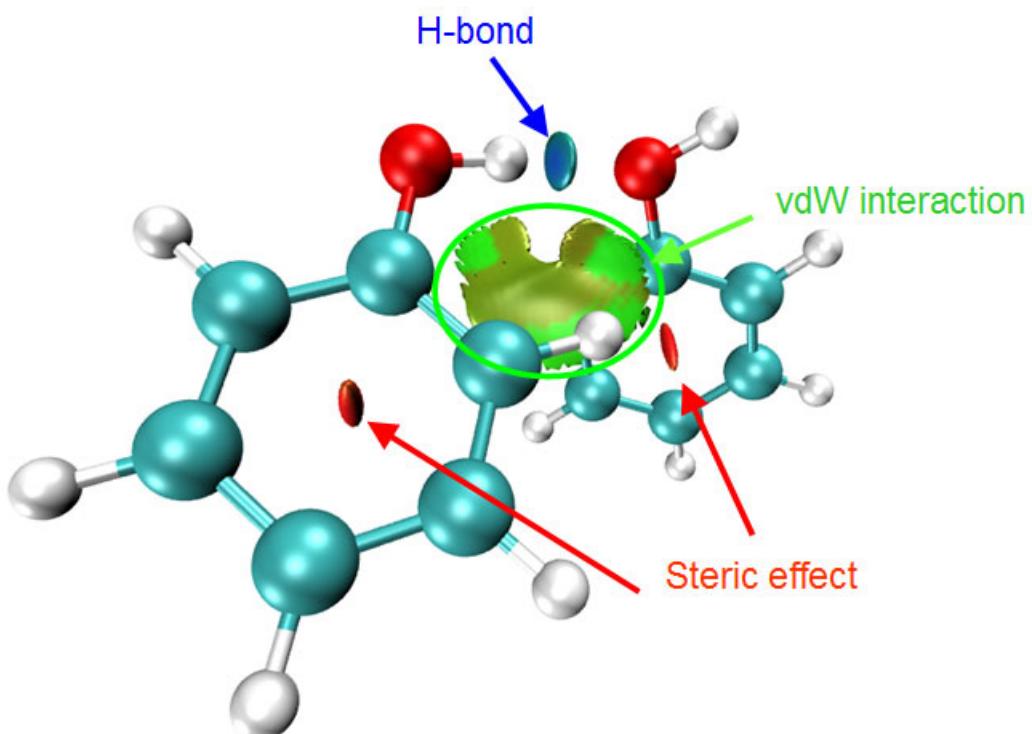
```
examples\PhenolDimer.wfn
100 // Other functions
1 // Generate grid data for two real space functions in same spatial scope
15,13 // Define sign(λ₂)ρ as function 1 and RDG as function 2
-10 // Set extension distance in all directions
0 // Because weak interaction regions only appear in internal region of present system, we do
not need to leave a buffer region at system boundary, so we set the extension distance to 0 Bohr
here
```

2 // Medium quality grid (totally about 512000 points). Because the spatial scope is larger than last example, we need more grid points, otherwise the the RDG isosurface may look discrete

I first show you the characteristics of different kinds of regions via scatter graph, I think it will be helpful to understand the underlying mechanism. Select option -1, a scatter graph pops up (you can also select option 1 to export this graph as file). The X-axis and Y-axis are  $\text{sign}(\lambda_2)\rho$  and RDG functions respectively, each point in the graph corresponds to each grid point. There are four spikes, and the points in their peaks are just the critical points in AIM theory. If you draw a horizontal line, then the segments crossing the spikes just correspond to the RDG isosurfaces. So RDG analysis method can be seen as an extension of AIM theory for visual study. The spikes can be classified into three types, I marked them by blue, green and red circle, see below.



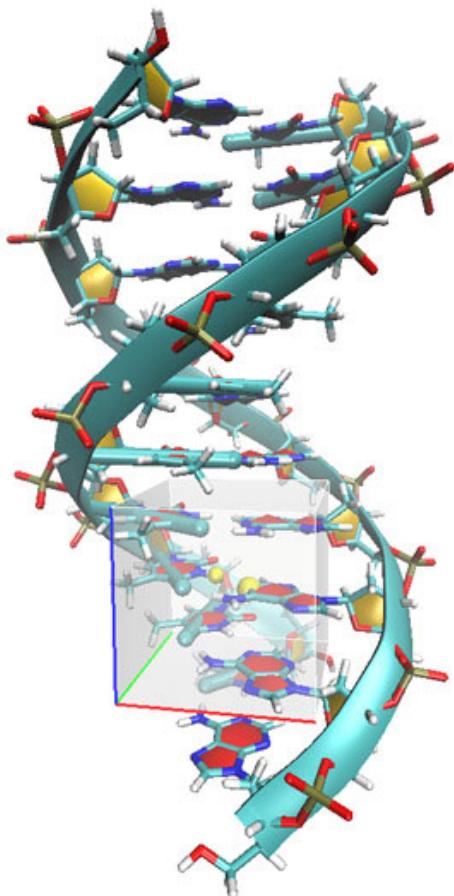
Now, select option 3 to export grid data of  $\text{sign}(\lambda_2)\rho$  and RDG to func1.cub and func2.cub in current directory, then copy them and the RDGfill.vmd file in “examples” folder to VMD install directory. The RDGfill.vmd is a plotting script of VMD. Then boot up VMD (here I use version 1.9.2), select “file”-“Load state”, choose “RDGfill.vmd”, you will see the graph below in OpenGL window. The default RDG isosurface is 0.5, and color range is -0.035 to 0.02, you can manually edit the RDGfill.vmd to change the default values, current values are suitable for general cases. (for present example, I suggest enabling "Display"- "Light 3", otherwise some parts of the isosurfaces will be in shadow and the color cannot be faithfully exhibited)



From the color-filled RDG isosurface, we can identify different type regions by color. Recall the color scale bar I showed you, the more blue means the stronger interactive interaction, the elliptical slab between oxygen and hydrogen shows light blue color, so we can conclude that there is a hydrogen bond, but not strong. The interaction region marked by green circle can be identified as vdW interaction region, because the filled-color is green or light brown, that means the density electron in this region is low. Obviously, the regions in the center of rings show strong steric effect, since they are filled by red.

### Promolecular approximation

Calculation of wavefunction and grid data for macrosystem is very time-consuming, however, the electron density can be approximately constructed by superposing electron densities of free-stated atoms (so-called “Promolecular approximation”), at this time the results of RDG analysis are shown to be still reasonable, the B3LYP/6-31G\* densities of free-stated atoms (for first three rows) are built-in data of Multiwfn. To active promolecular approximation, simply use function 14 instead of function 13 and use function 16 instead function 15 when you selecting real space function. Since only atom coordinate information is required when promolecular approximation is used, you can use .pdb file as input. As an example, let's do RDG analysis for a DNA molecule with 10 base-pairs, what we are interested in is only the region in the box, see below.



Boot up Multiwfn and input:

*examples\DNA.pdb*

100

1

16,14 // sign( $\lambda_2$ ) $\rho$  and RDG function with promolecular approximation

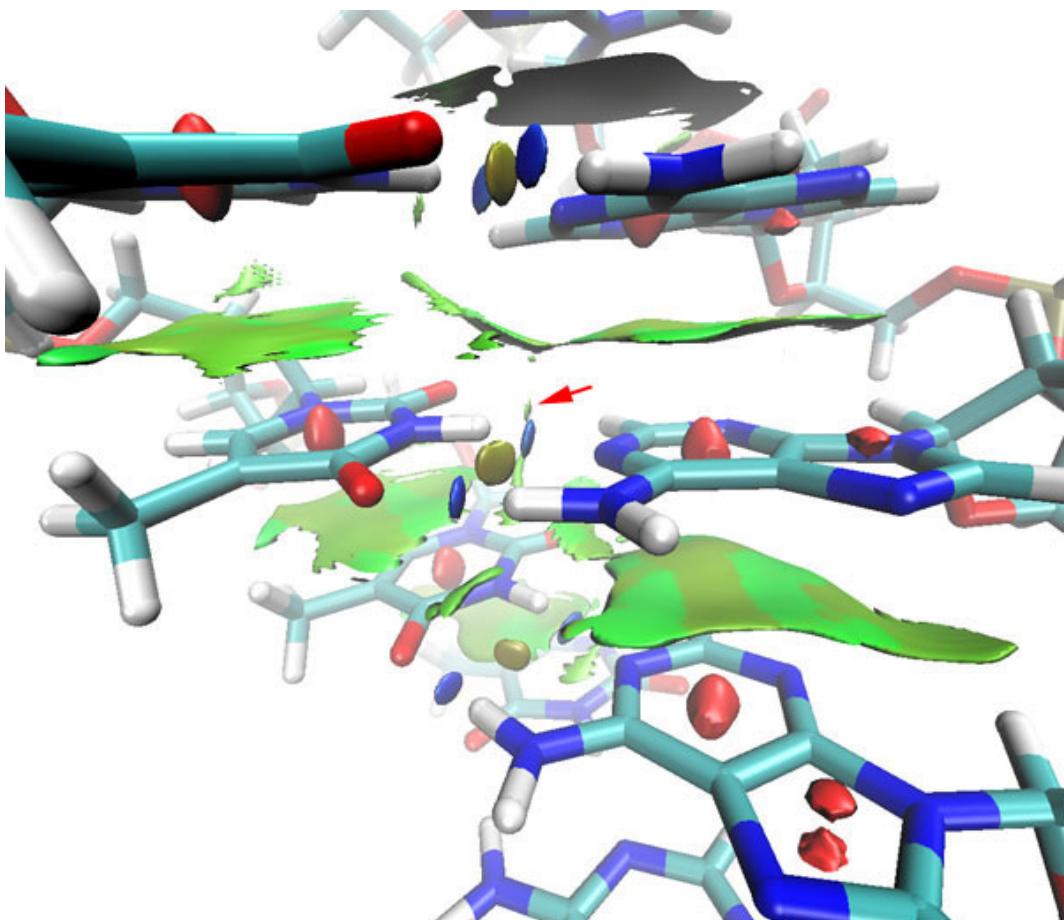
7

84,565 // Use middle point of atom 84 and 565 as center. You can view molecule structure in main function 0 in advance to find two proper atoms used to define center

120,120,120 // Because the spatial scope of grid data is large, we need more grid points

9,9,9 // Set the extension distances in all directions to 9 Bohr

When calculation is finished, export func1.cub and func2.cub and then plot the graph by VMD as the procedure described in last section. From the graph you will see the default isovalue 0.5 is not suitable for plotting RDG isosurface when promolecular approximation is used, so you need to adjust it manually, choose “Graphics”-“Representation”, select the representation whose style is “Isosurface”, then reset isovalue by inputting expected value in text box or dragging scale bar, for present system I recommend 0.25. For better visualization, you’d better adjust “cue mode” and “Cue Start/End” in “Display”-“Display settings...”. Finally, you will get the graph below



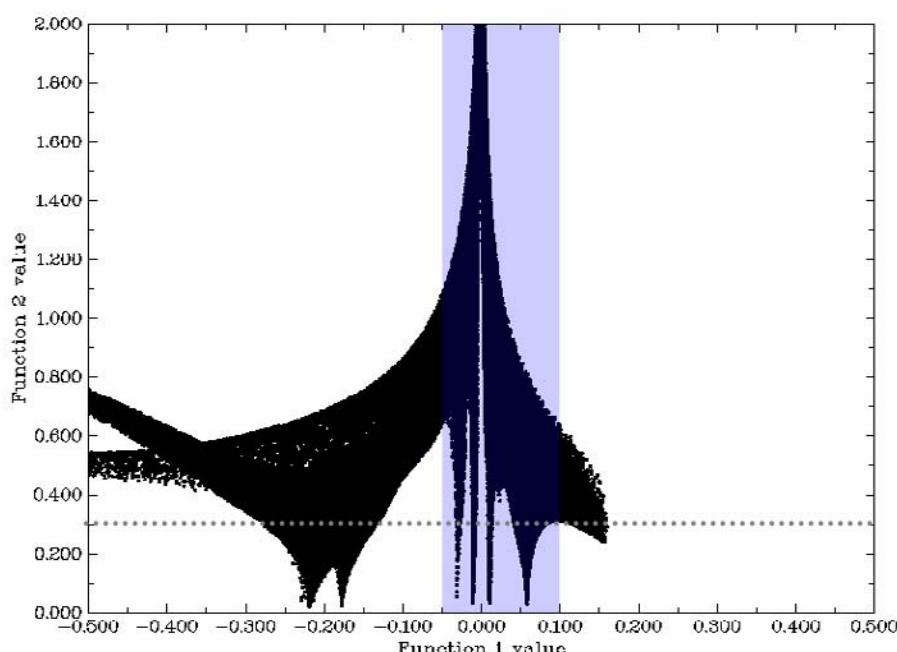
It is clear that there are  $\pi$ - $\pi$  stacking interactions between neighbour base pairs (big pieces), and there are two strong hydrogen bonds within each base-pairs. The region pointed by red arrow seems to be hydrogen bond because it connects hydrogen and oxygen, however since the filled-

color is green, we can conclude that this is only vdW interaction.

Notice that, by default RDG value will be set to 100.0 where  $\rho$  is larger than 0.1 if promolecular approximation is used, this value may not be suitable for certain circumstance, you can set the default threshold by “RDGprodens\_maxrho” in settings.ini.

### Interactively set RDG value where $\text{sign}(\lambda_2)\rho$ is in specific range

Multiwfn allows you to interactively set RDG value where  $\text{sign}(\lambda_2)\rho$  is in specified range. Here I use phenol dimer under promolecular approximation as example. Firstly, set “RDGprodens\_maxrho” to 0.0 to disable automatic truncation, then generate grid data of RDG and  $\text{sign}(\lambda_2)\rho$  for present system, after the calculation is finished, if you set X-axis range from -0.5 to 0.5 and then plot scatter graph, you will see (blue box and dash line are added by external plotting tools)



In above scatter plot, the blue box corresponds to weak interaction regions. Assume that you want to plot the RDG=0.3 isosurfaces only for weak interaction regions, you should first screen the region outside the blue box, otherwise the dashed line will intersect with the spikes around  $\text{sign}(\lambda_2)\rho=-0.2$  (corresponding to chemical bond regions) and the small tail at rightmost the graph, resulting in unnecessary isosurfaces. So we choose option -3, input -0.05, 0.1 and 100 in turn, then draw scatter graph again, you will find only the region where  $\text{sign}(\lambda_2)\rho$  is within -0.05~0.1 is preserved, and then if you plot the RDG=0.3 isosurface, only weak interaction region will be revealed.

### Simultaneously reveal covalent and non-covalent interactions

Sometimes ELF and RDG are used in combination to simultaneously investigate covalent and non-covalent interactions, see *J. Chem. Theory Comput.*, **8**, 3993 (2012) for example. Is it possible to study both kinds of interactions by *single* real space function? The answer is yes. In *J. Chem. Theory Comput.*, **10**, 3745 (2014) the authors proposed a function named density overlap

regions indicator (DORI), it is found that when properly choosing an isosurface, both covalent and non-covalent interaction regions can be well exhibited, and  $\text{sign}(\lambda_2)\rho$  can also be mapped on to DORI isosurfaces to facilitate analysis of the nature of interactions. Here I use phenol dimer as instance to show how to do this, most steps are identical to RDG analysis.

DORI is the 20th user-defined function, so before booting up Multiwfn, you should set "iuserfunc" in settings.ini to 20. Then boot up Multiwfn and input

examples\PhenolDimer.wfn

100

1

15,100 // As seen here, user-defined function is chosen as "function 2", which corresponds to DORI currently

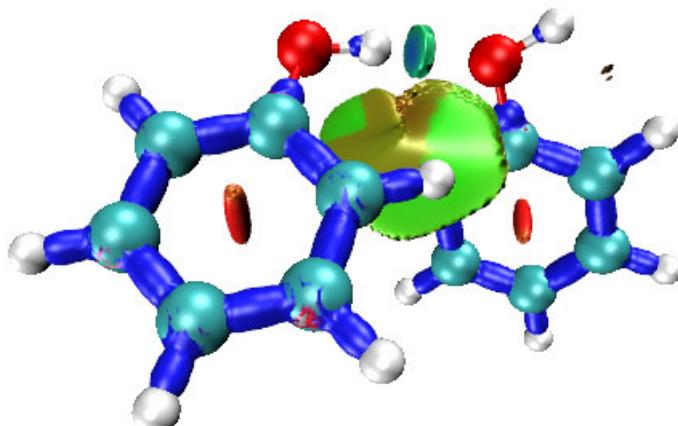
-10

0 // Remove extension distance

2 // Medium quality grid

3 // Export cube file

Move func1.cub, func2.cub and examples\DORIfill.vmd to VMD folder. Then boot up VMD and input *source DORIfill.vmd* in console window, you will immediately see



The graphic effect is clearly satisfactory. The weakly interaction regions are exhibited almost the same as RDG, while the strong chemical bonding regions are nicely portrayed as blue isosurfaces. Note that the most suited isovalue of DORI must be different for different systems, the default isovalue is 0.95, you can modify it in the .vmd script file, or manually adjust it in Graphics - Representations panel of VMD.

Finally, please note that Multiwfn is capable of integrating any real space function within isosurface defined by any real space function, therefore you can study such as volume and the number of electrons within isosurfaces of RDG or DORI to study weak interactions at quantitative level. Illustrative examples are given in Section 4.200.14.

#### 4.100.4 Calculate kinetic energy and nuclear attraction potential energy of phosgene by numerical integration

I suggest you read Section 3.100.4 first, the aim of this example is to show you the usefulness and universality of numerical integration. In quantum chemistry program, kinetic energy and nuclear attraction potential energy integration are evaluated analytically, analytical method has advantage in both speed and accuracy. In Multiwfn you can evaluate them by general numerical integration function. Local kinetic energy (or called “kinetic energy density”) is a built-in function, we first integrate this function in whole space to get total kinetic energy. Boot up Multiwfn and input:

```
examples\COCl2.wfn // HF/6-31G* wavefunction
100
4 // Integrate a function in whole space
6 // Hamiltonian kinetic density K(r)
```

The result is 1031.1092, which is very close to the Gaussian outputted value 1031.1107.

Because I do not want the list of real space function becomes lengthy, so rarely used functions such as local nuclear attraction potential energy are not chosen as built-in function, however you can still easily make these functions available by hacking source code, please consult Appendix 2. First, search “function userfunc” in function.f90, change the default content, namely userfunc=1.0D0, to `userfunc = -nucesp(x,y,z)*fdens(x,y,z)`, then recompile Multiwfn, redo above procedure but select function 100 as integrand, you will get nuclear attraction potential energy -2839.1668, the value outputted by Gaussian is -2839.1629, evidently they are rather close. If you want to obtain nuclear attraction potential energy contributed from a specific orbital, use subfunction 26 of main function 6 to set occupation number of other orbitals to zero, and then do the integration as before.

To further illustrate the flexibility of numerical integration function in Multiwfn, assume that you want to calculate expectation of  $r^2$  operator, you can modify the content of “userfunc” routine to `userfunc = (x*x+y*y+z*z)*fdens(x,y,z)`, then recompile Multiwfn and redo the integration, you will get 444.6523, which is in excellent agreement with the Gaussian outputted value 444.6524 (behind “Electronic spatial extent (au): <R\*\*2>”).

Tip: You may have already noticed that the two lines of the codes colored by blue above have presented in “userfunc” routine, and they correspond to iuserfunc==12 and iuserfunc==3 respectively. So actually you needn’t to modify and recompile the source code of Multiwfn, by simply changing “iuserfunc” parameter in settings.ini from the default value 0 to 12 and 3 respectively, the user defined real space function will be equivalent to the two functions. For more about the built-in real space functions in “userfunc” routine, see Section 2.7.

#### 4.100.8 Perform simple energy decomposition by using combined fragment wavefunctions

The principle of the simple energy decomposition has been introduced in Section 3.100.8, please read it first. Here we try to use this method to analyze components of interaction energy between  $\text{NH}_3$  and  $\text{BH}_3$  in the adduct  $\text{NH}_3\text{BH}_3$  at HF/6-31G\* level. The Gaussian input and output files involved in this section can be found in “EDA” subdirectory in “example” folder. The Gaussian used here is G09 E.01.

(1) Perform structure optimization task for  $\text{NH}_3\text{BH}_3$ , and then create a new input file with the optimized coordinate, named  $\text{NH3BH3.gjf}$ .

(2) Duplicate  $\text{NH3BH3.gjf}$  as  $\text{NH3.gjf}$  and  $\text{BH3.gjf}$ , then remove  $\text{BH3}$  fragment in  $\text{NH3.gjf}$ , and remove  $\text{NH3}$  fragment in  $\text{BH3.gjf}$ . Add "pop=full nosymm" keywords in both  $\text{NH3.gjf}$  and  $\text{BH3.gjf}$ .

(3) Run the input file of the two fragments by Gaussian respectively to generate  $\text{NH3.out}$  and  $\text{BH3.out}$ .

(4) Boot up Multiwfn, input following commands

$\text{NH3.out} \text{ //Fragment 1}$

$100$

$8$

$2 \text{ // There are two fragments in total}$

$\text{BH3.out} \text{ //Fragment 2}$

Multiwfn generates  $\text{new.gjf}$  in current folder, this is the Gaussian input file for  $\text{NH}_3\text{BH}_3$  with fragment-combined wavefunction as initial guess.

(5) Make sure "nosymm" keyword is presented in  $\text{new.gjf}$ . In order to output SCF energy in each iteration, change "#" to "#P". "pop=full" keyword can be deleted.

(6) Run  $\text{new.gjf}$  by Gaussian to generate  $\text{new.out}$ .

From  $\text{NH3.out}$ ,  $\text{BH3.out}$  and  $\text{new.out}$ , following information can be found

$E(\text{NH3}) = -56.184295 \text{ a.u.}$

$E(\text{BH3}) = -26.368199 \text{ a.u.}$

$E(\text{NH3BH3}) = E_{\text{SCF\_last}} = -82.611817 \text{ a.u.}$

$E_{\text{SCF\_1st}} = -82.535276 \text{ a.u.}$

PS: If you don't know where to find  $E_{\text{SCF\_1st}}$ , search below information from  $\text{new.out}$ :

Cycle 1 Pass 1 Diag 1:

$E = -82.5352762791642$

DIIS: error= 5.16D-02 at cycle 1 NSaved= 1.

The  $E_{\text{SCF\_1st}}$  is the SCF energy in the first cycle of SCF process.

According to the equations shown in Section 3.100.8, we can calculate each energy term:

$$\Delta E_{\text{tot}} = E(\text{NH3BH3}) - E(\text{NH3}) - E(\text{BH3}) = -0.059323 \text{ a.u.} = -155.75 \text{ KJ/mol}$$

$$\Delta E_{\text{orb}} = E_{\text{SCF\_last}} - E_{\text{SCF\_1st}} = -0.076541 \text{ a.u.} = -200.96 \text{ KJ/mol}$$

$$\Delta E_{\text{steric}} = \Delta E_{\text{cls}} + \Delta E_{\text{Ex}} = \Delta E_{\text{tot}} - \Delta E_{\text{orb}} = 0.017218 \text{ a.u.} = 45.20 \text{ KJ/mol}$$

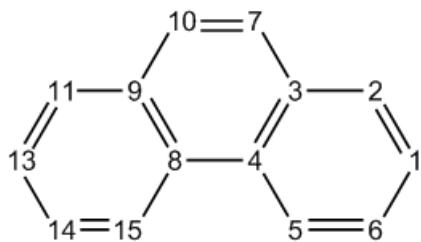
namely the total interaction energy between  $\text{NH}_3$  and  $\text{BH}_3$  is  $-155.75 \text{ KJ/mol}$ , the orbital interaction energy  $-200.96 \text{ KJ/mol}$  stabilized the adduct, while the steric energy, which is the sum of electrostatic and exchange repulsion energy, destabilized the adduct by  $45.20 \text{ KJ/mol}$ .

In present system, compared to other energy components the dispersion interaction can be safely neglected, so we did not discuss it. However if the system you studied is the complex bounded by weak interaction, you must evaluate the dispersion component in total interaction energy, see the discussion in Section 3.100.8 on how to do this.

### 4.100.13 Calculate HOMA and Bird aromaticity index for phenanthrene

HOMA is the most prevalently used aromaticity index based on geometry equalization, see Section 3.100.13 for detail. Here we use HOMA to study which ring of phenanthrene has stronger aromaticity.

Since calculation of HOMA only requires molecular coordinate, you can simply use .pdb or .xyz as input file. Of course, other files containing molecular coordinate, such as .wfn and .fch files are acceptable too. The geometry in present instance is optimized under B3LYP/6-31G\* level.



Boot up Multiwfn and input following commands

*examples/phenanthrene.pdb*

100

13

0 // Start the calculation

You will see the default parameters are printed, they are taken from *J. Chem. Inf. Comput. Sci.*, **33**, 70, you can also change these parameters by yourself via option 1 before the calculation.

Now we input the atom indices in the ring that we are interested in, we calculate HOMA for the central ring first, so input 3,4,8,9,10,7, the input order must be consistent with atom connectivity. You will immediately obtain the result shown below

Atom pair	Contribution	Bond length(Angstrom)
3(C) -- 4(C):	-0.065698	1.427111
4(C) -- 8(C):	-0.210455	1.458000
8(C) -- 9(C):	-0.065698	1.427111
9(C) -- 10(C):	-0.096016	1.435282
10(C) -- 7(C):	-0.033673	1.360000
7(C) -- 3(C):	-0.096016	1.435282

HOMA value is 0.432442

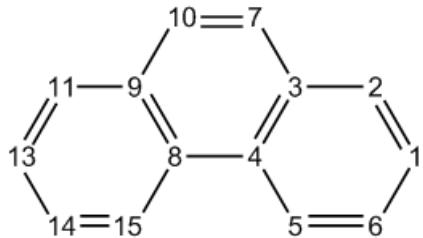
Obviously, C4-C8 deviates to ideal bond length 1.388 most significantly, giving rise to large negative contribution to HOMA, in other words, significantly breaked aromaticity. The HOMA value is calculated as 1 plus the contributions from all bonds in the ring.

Then input 8,15,14,13,11,9 to calculate HOMA for the boundary ring, the result is 0.855126. Since this value is much closer to 1 than the one for central ring, HOMA suggests that the two boundary rings have stronger aromaticity.

Bird index is another quantity used to measure degree of aromaticity, see Section 3.100.13 for a brief description. Now choose option 2 to calculate Bird index for the two rings, you will find the value for boundary ring is more close to 100 than the central ring. Likewise HOMA, Bird index also indicates that the two boundary rings have stronger aromaticity.

#### 4.100.14 Calculate LOLIPOP for phenanthrene

In this instance, we use LOLIPOP (Localized Orbital Locator Integrated Pi Over Plane) index to evaluate which ring of phenanthrene has stronger  $\pi$ -stacking ability. For detail about LOLIPOP, see Section 3.100.14 and the paper *Chem. Commun.*, **48**, 9239.



Boot up Multiwfn and input following commands

*examples/phenanthrene.wfn*

100

14

1 // Specify  $\pi$  orbitals

36,40,43,44,45,46,47 //These orbitals are  $\pi$  orbitals. You can find out  $\pi$  orbitals by visualizing orbital isosurfaces via main function 0 or by function 22 of main function 100

0 // Start the calculation

8,9,11,13,14,15 // The indices of the atoms in the ring you are interested in. This ring is boundary ring

Wait for a while, from screen we can see that the LOLIPOP value is 8.233.

0 // Start the calculation again

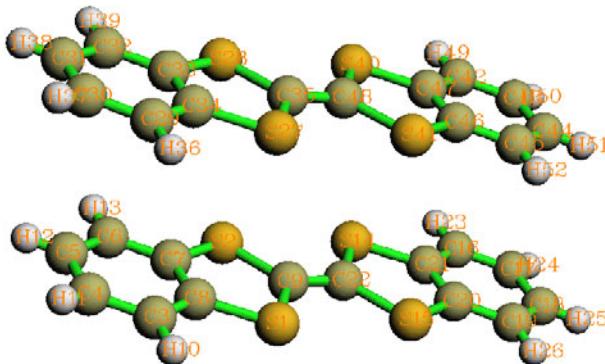
7,3,4,8,9,10 // Central ring

The LOLIPOP value is 6.183

Since smaller LOLIPOP value corresponds to stronger  $\pi$ -stacking ability, we can expect that the tendency of forming  $\pi$ -stacking structure for central ring is stronger than for boundary ring.

#### 4.100.15 Calculate intermolecular orbital overlap integral of DB-TTF

Intermolecular orbital overlap integral is important in discussions of intermolecular charge transfer, see Section 3.100.15 for introduction. In this example, we calculate HOMO-HOMO and LUMO-LUMO overlap integrals between the two DB-TTF (Dibenzotetrathiafulvalene) monomers in below dimer. The dimer structure was extracted from CSD (Cambridge Structural Database). The wavefunction level we used is PW91PW91/6-31G\*, MO78 and MO79 correspond to HOMO and LUMO, respectively.



First, we construct a Gaussian input file for dimer according to the structure. *iop(3/33=1) nosymm guess(only)* should be present in route section. *IOP(3/33=1)* tells Gaussian to output overlap matrix in original basis; *nosymm* instructs Gaussian to do not adjust the coordinate to standard orientation; *guess(only)* is specified because we do not require converged wavefunction of the dimer. The input file is provided as *examples\intermol\DB-TTFdimer.gjf*. Run it by Gaussian, and then we obtain *DB-TTFdimer.out*.

Next, we extract the first and the second monomer coordinates in turn from the dimer input file to construct two Gaussian input files for the two monomers, named as *DB-TTF1.gjf* and *DB-TTF2.gjf*, the two files can also be found in *examples\intermol* folder. *nosymm* and *pop=full* should be specified in route section. Use Gaussian to run the two files to yield *DB-TTF1.out* and *DB-TTF2.out*.

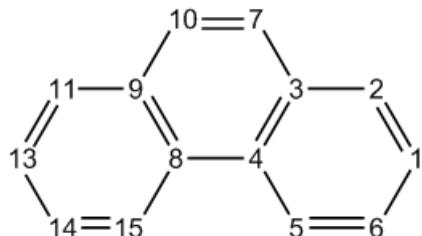
After that, boot up Multiwfn, and input below commands:

```
DB-TTFdimer.out
100
15 // Then Multiwfn will read overlap matrix (in original basis) from DB-TTFdimer.out
DB-TTF1.out // Multiwfn will read MO coefficients of monomer 1 from the file
DB-TTF2.out // Multiwfn will read MO coefficients of monomer 2 from the file
```

Now, input such as *i,j* then the intermolecular orbital overlap integral between MO *i* in monomer 1 and MO *j* in monomer 2 will be printed. To obtain the integral between HOMO-HOMO, input 78,78, we immediately get -0.01389242; Then input 79,79, we will find the integral between LUMO-LUMO is 0.00906935.

#### 4.100.18 Yoshizawa's electron transmission route analysis for phenanthrene

In this example, we will use Yoshizawa's formula (*Acc. Chem. Res.*, **45**, 1612) to analyze favourable electron transimission routes for phenanthrene. Related theory, requirement of input file and program options have been introduced in Section 3.100.18. The numbering scheme of the carbons is shown below.



Boot up Multiwfn and input following commands:

*examples\phenanthrene\_NAOMO.out* //The Gaussian output file containing "NAOMO" information

2 // Select YZ plane, which is the molecular plane

Then program will detect which atom has expected  $p_z$  atomic orbitals, and load their expansion coefficients in all MOs.

Now we select 1, and input 2,11 to check the transmission probability between 2 and 11. From the output we can know that the transmission probability is 0.855879. The contributions from each MO are also shown. From the output we also know that the probability will be 2.144432 if only HOMO and LUMO are considered. Although Yoshizawa's paper said that in common one only need to take HOMO and LUMO into account, it seems that this approximation is not true in quantitative level. The distance route 5.674656 Angstrom is the distance between atom 2 and 11.

Next, we examine which transport routes are the most favourable. Suppose that this time we only want to consider HOMO and LUMO, so we choose option -1 and input 47,48. Then choose option 2, you will see

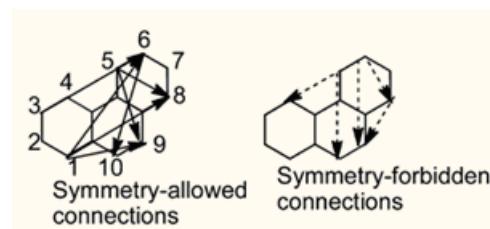
Note: The routes whose absolute value < 0.010000 will not be shown

Note: The routes whose distance < 0.0000 or > 9999.0000 Angstrom will not be shown

Atom	7 -- Atom	10	Value and distance:	3.743670	1.359562
Atom	6 -- Atom	10	Value and distance:	3.098919	5.081382
Atom	7 -- Atom	14	Value and distance:	3.098919	5.081382
Atom	7 -- Atom	11	Value and distance:	-2.831680	3.720990
Atom	2 -- Atom	10	Value and distance:	-2.831680	3.720990
Atom	6 -- Atom	14	Value and distance:	2.565337	5.765892
...					
Atom	6 -- Atom	9	Value and distance:	-0.016585	4.927289
Atom	3 -- Atom	14	Value and distance:	-0.016585	4.927289
Atom	2 -- Atom	4	Value and distance:	-0.014931	2.456189
Atom	8 -- Atom	11	Value and distance:	-0.014931	2.456189

The routes are ranked by transmission probability (absolute value). If we ignore the atoms linking three carbons and the duplicated routes due to symmetry, the most favourable four routes are 7-10, 6-10, 7-11, 6-14. This conclusion is completely in line with below graph in Yoshizawa's paper!

Note that Yoshizawa stated that connection 9-10 (corresponding to 7-10 in our numbering scheme) is predicted to be the best route from the rule, but it is too close to construct a metal-molecule-metal junction for connection, so the route was not marked on his graph.



Now we check the feasible routes started from atom 2. Choose option 3, and input 2, you will see

```
To atom    10  Value and distance (Angstrom): -2. 831680   3. 720990
To atom    14  Value and distance (Angstrom): -2. 344569   6. 206600
To atom    11  Value and distance (Angstrom):  2. 144432   5. 674656
To atom     5  Value and distance (Angstrom): -1. 571512   2. 787501
...

```

Evidently, 2-10 is the most favourable route.

#### 4.100.19 ELF analysis on the promolecular wavefunction combined from fragment wavefunctions

Before reading this section please read Section 3.100.19 first.

It is usually interesting to analyze the characteristic of promolecular wavefunction, which corresponds to the state without any electron transfer and polarization due to the interaction between the fragments constituting the system. Commonly, we can use "custom operation" in main function 3, 4 and 5 to realize this purpose, see Section 3.7 for introduction of custom operation and some illustrative applications in Sections 4.5.4 and 4.5.5. For example, we want to study electron density distribution of promolecular state of a complex  $AB$ , by using custom operation, we can very conveniently instruct Multiwfn to calculate electron density of  $A$  and that of  $B$  respectively, and then sum them up as electron density of the promolecule state. However, this process is not applicable to non-linear real space functions such as ELF; that is to say, ELF of promolecular state of  $AB$  is not equal to the sum of ELF of  $A$  and ELF of  $B$ , the result is completely meaningless. For such cases, we should combine fragment wavefunctions first as promolecular wavefunction, and then calculate ELF for it to obtain the ELF distribution in promolecular state.

Below I will show how to use Multiwfn to produce promolecular wavefunction for  $\text{COBH}_3$  based on fragment wavefunctions of  $\text{CO}$  and  $\text{BH}_3$ , and then discuss the corresponding ELF character. The .wfn files used below and the corresponding Gaussian .gjf files can be found in "examples\genpromol" folder.

Boot up Multiwfn and then input

```
examples\genpromol\COBH3\CO.wfn      // The path of wavefunction file of fragment 1
100
```

```
19 // Generate promolecular .wfn file from fragment wavefunctions
```

```
2 // Two fragments in total
```

```
examples\genpromol\COBH3\BH3.wfn      // The path of wavefunction file of fragment 2
```

Now the promolecular wavefunction file of  $\text{COBH}_3$  has been outputted to promol.wfn in

current folder.

Let's plot ELF for this promolecular wavefunction. Reboot Multiwfn and input

*promol.wfn*

4 // Draw plane map

9 // ELF

1 // Color-filled map

[Press ENTER button]

2 // XZ plane

0 // Y=0

Interestingly, even in the promolecular state, from the resultant graph it looks as if the carbon and boron have been bonded to each other. In order to make clear how the relaxation of electron distribution affects the ELF character of COBH<sub>3</sub>, we decide to draw difference map of ELF between the actual state and promolecular state.

Reboot Multiwfn and input

*examples\genpromol\COBH3\COBH3.wfn* // Wavefunction file of actual state of COBH<sub>3</sub>

4 // Draw plane map

0 // Custom operation

1 // Deal with only one file

*-,promol.wfn* // Subtracting property of COBH3.wfn by that of promol.wfn

9 // ELF

1 // Color-filled map

[Press ENTER button]

2 // XZ plane

0 // Y=0

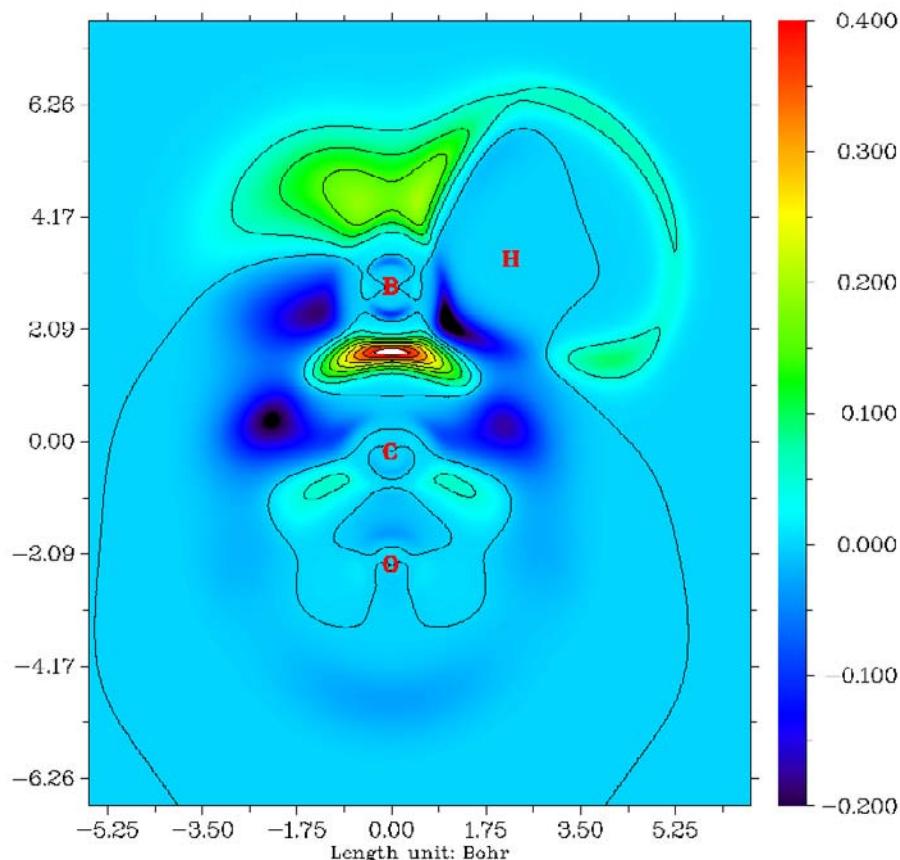
Close the graph and then input

1

-0.2,0.4 // Set the color scale from -0.2 to 0.4, since as you can see from the command-line window, in this plane the data range is from -0.248 to 0.436

2 // Enable showing contour lines

-1 // Show the graph again



From this difference map of ELF, it is very clear that after electron relaxation, the electron localization character between the C-B bond enhanced evidently.

Next I will show how to create promolecular wavefunction when open-shell fragments are involved.  $\text{CH}_3\text{NH}_2$  is taken as example, the two fragments are  $\text{CH}_3$  and  $\text{NH}_2$  free-radicals. Boot up Multiwfn and input

```
examples\genpromol\CH3NH2\CH3.wfn
```

```
100
```

```
19
```

```
2
```

```
examples\genpromol\CH3NH2\NH2.wfn
```

```
n // Do not flip spin of orbitals of  $\text{CH}_3$ 
```

$y$  // Flip spin of orbitals of  $\text{NH}_2$ . If you do not understand why the spin should be flipped, you can consult the corresponding CDA example in Section 4.16.2.

Now you have promolecular wavefunction of  $\text{CH}_3\text{NH}_2$  in current folder. Try to plot ELF for it and compare the result with actual state (i.e. examples\genpromol\CH3NH2\CH3NH2.wfn)

## 4.200 Other functions, Part 2

### 4.200.1 Visually studying weak interaction in molecular dynamics simulation by aRDG method

If you are not familiar with RDG analysis method, you should first read the introduction given in Section 4.100.1. The theory exemplified in this section is a generalization of RDG analysis method (known as aRDG method), so that the weak interaction can also be revealed in fluctuation environment, e.g. molecular dynamics (MD) or Monte Carlo simulation. The basic principle of aRDG is proposed in *J. Chem. Theory Comput.*, **9**, 2226, and I have also briefed it in Section 3.200.1.

In this example I will show how to use Multiwfn to visually study the weak interaction between waters in the MD simulation of bulk water system. You can use any program to perform the MD, as long as you know how to convert the trajectory to .xyz trajectory. Here I assume that you are a GROMACS 4.5 user. The detailed steps of the MD process are given below, all of the related files can be found in "examples\aRDG" folder.

#### Generating MD trajectory by GROMACS

First, build a file named "emptybox.gro", which records a blank box, and the side length in each direction is 2.5nm. Then run below command to fill the box with waters.

```
genbox -cp emptybox.gro -cs spc216.gro -o water.gro
```

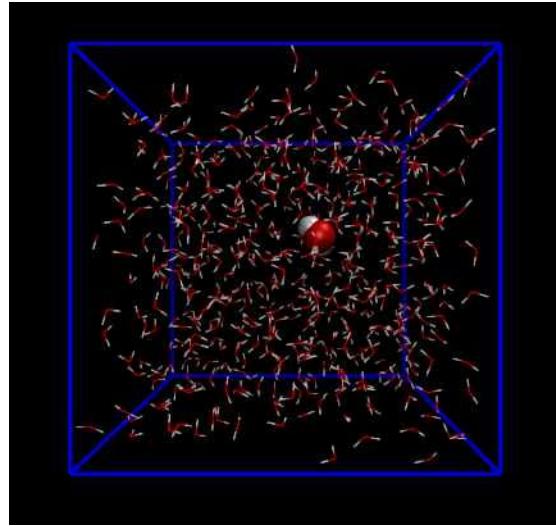
Run below command and select "GROMOS96 53a6 force field" to obtain the top file of the bulk water system. SPC/E water model is employed.

```
pdb2gmx -f water.gro -o water.gro -p water.top -water spce
```

Then carry out NPT MD by 100ps to equilibrate the bulk water at 298.15K, 1atm environment.

```
grompp -f prmdp -c water.gro -p water.top -o water-pr.tpr
mdrun -v -deffnm water-pr
```

Using VMD program to load water-pr.gro, select a water close to the center of the box. We select the water with resid index of 101, which is highlighted in below graph. Note that the two hydrogens in this water have index of 302 and 303, and the index of the oxygen is 301.



This water will be freezed in the following MD simulation. In order to do so, we generate index file, namely inputting below commands

```
make_ndx -f water-pr.gro
ri 101
q
```

Run following command to do 1ns equilibrium MD simulation at 298.15K, the trajectory will be saved every 1ps, and finally we will obtain 1000 frames. The water with resid index of 101 is freezed via the keyword "freezegrps = r\_101". Note that NVT ensemble instead of NPT is used, because NPT process will scale the coordinate of the atoms, which somewhat destroys the effect of freezing.

```
grompp -f mdmdp -c water-pr.gro -p water.top -o water-md.tpr -n index.ndx
mdrun -v -deffnm water-md
```

Load "water-pr.gro" and "water-md.xtc" into VMD in turn, select "File"- "Save Coordinate..." option and set the file type as xyz, then set "Selected atoms" as "all", input 1 and 1000 in the "First" and "Last" window respectively, then click "Save" button to convert the GROMACS trajectory to wat.xyz.

### Generating grid data by Multiwfn

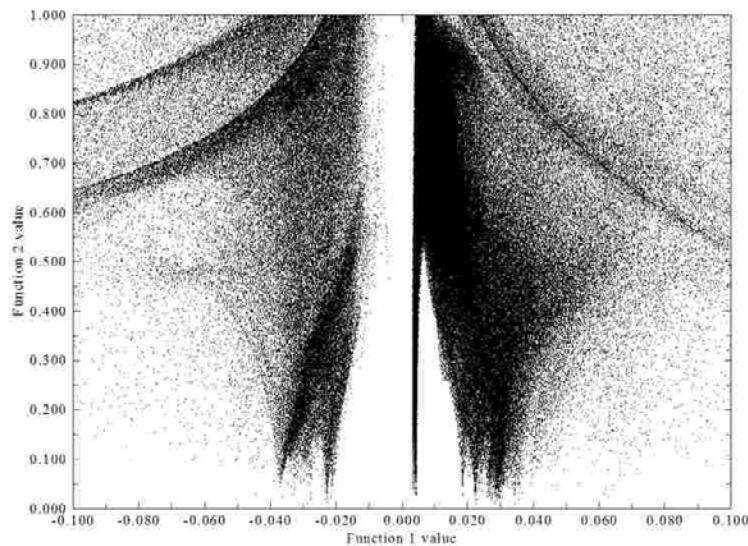
Boot up Multiwfn and input following commands

```
wat.xyz
200 // Main function 200
I // aRDG analysis
1,1000 // The range of the frames to be analyzed
7
301,301 // Using atom 301 (the oxygen of the freezed water) as the box center of the grid
data
80,80,80 // The number of grid points in each side
4.5,4.5,4.5 // Extend 4.5 Bohr in each side
```

Now Multiwfn starts to calculate electron density, its gradient and Hessian of each frame,

then their average quantities will be obtained, and finally Multiwfn calculates average RDG and average sign(lambda2)rho. The whole process is time-consuming; at a common Intel 4-cores computer about half an hour will be consumed. (Note that the electron density I referred here is produced by promolecular approximation, which is constructed by simply superposing the density of the atoms in their free-state)

After the calculation is finished, you can select option 1 to check the scatter plot between average RDG (X-axis) and average sign(lambda2)rho (Y-axis), see below, there is also option used to export the corresponding data points to plain text file.



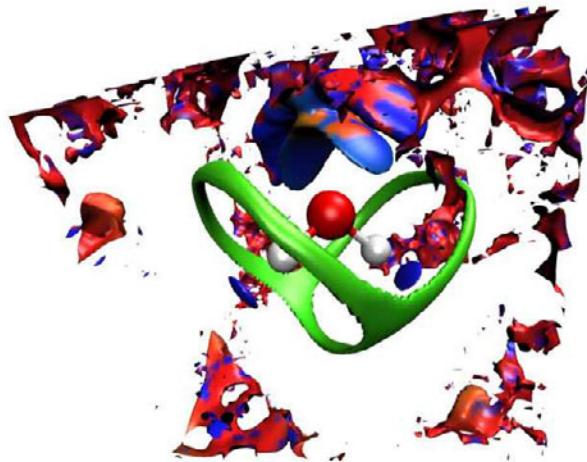
Select 6 to export the grid data of average RDG and average sign(lambda2)rho as avgRDG.cub and avgsl2r.cub in current folder, respectively.

Since we wish to check the stability of weak interaction, we also select 7 to export thermal fluctuation index to thermflu.cub in current folder. Note that this process requires recomputing electron density of each frame, and thus is time-consuming.

### Analysis

Copy avgRDG.cub, avgsl2r.cub, thermflu.cub as well as avgRDG.vmd and avgRDG\_TFI.vmd in "examples\aRDG" folder to the directory of VMD program.

Simply boot up VMD and input *source avgRDG.vmd* in its console window, the average RDG isosurface will be shown up with isovalue of 0.25, meantime the average sign(lambda2)rho is mapped on the isosurface by various color. In order to make the graph clearer, one should screen unrelated atoms, that is enter "Graphics-Representation", then select the entry whose "style" is "CPK", and input *serial 301 302 303* in the "Selected Atoms" box and then press ENTER button. Now only the water with resid index of 101 presents in the graph. After proper rotation and translation of view, you will see



Unfortunately, around the water of interest, there are large amount noisy isosurfaces, which somewhat messed up the graph, thus it is better to shield them. This aim can be achieved by main function 13 of Multiwfn, the steps are described below.

Write a plain text file named index.txt, whose content is

```
3      // The number of atoms
301 302 303    // The index of the atoms
```

Then boot up Multiwfn and input

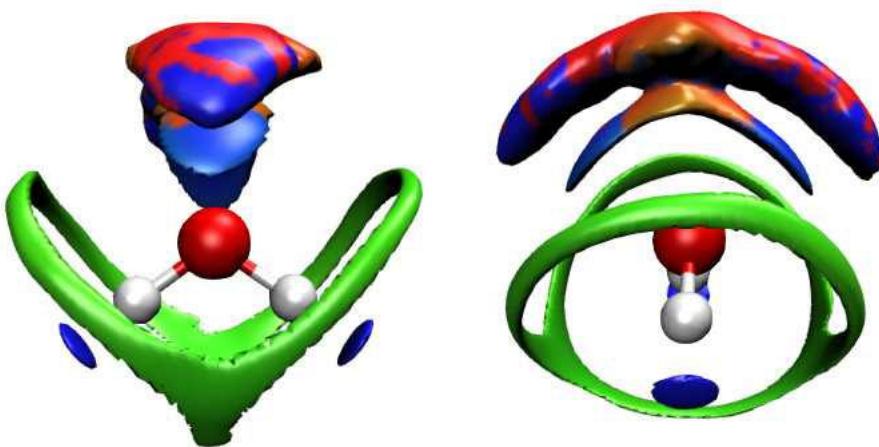
```
avgRDG.cub
13 // Process grid data
13 // Set the value of the grid points far away from specific atoms
```

1.5 // If the distance between a grid point and any atom recorded in index.txt is longer than 1.5 times of vdW radius of corresponding atom, then the value of the grid point will be set as given value

100 // The given value is 100, which is arbitrary, as long as larger than the isovalue of the RDG isosurfaces (0.25)

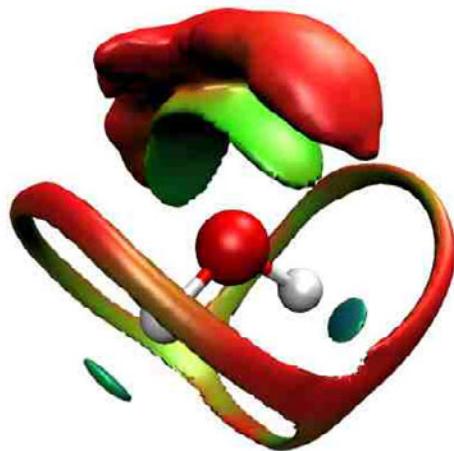
```
index.txt // Which specifies the atoms of interest
0 // Export the updated grid data to a new cube file
avgRDG.cub // The name of the new cube file
```

Copy the newly generated avgRDG.cub to the folder of VMD program to overlay the old one, then use the script avgRDGvmd again to plot the graph, after some adjustments you will see (for clarity, the view of two sides are shown at the same time)



The graph we obtained this time is very clear. The color scale is from -0.25 to 0.25, corresponding to the color variation of Blue-Green-Red. More blue denotes electrostatic interaction or H-bond effect in corresponding region is stronger, and more red suggests more intensive steric effect. Green region implies low electron density, corresponding to vdW interaction. From the graph one can see that there are two blue ellipses near the two hydrogens, rendering that in the MD process, strong H-bonds are formed due to the O-H group. The slender green isosurface exhibits in which direction this water prefers to interact with other waters by vdW interaction. There is a big lump of isosurface above the oxygen, on which the red color appears in the middle part, while blue color occurs at the two ends; the latter reflects that the two lone pairs of the oxygen act as H-bond acceptors during the simulation, while the former reveals the repulsive interaction zone between waters. Note that if we set the isosurface of RDG smaller (e.g. 0.18), then this isosurface will be dissected as two, which perhaps correspond to the two coordination shells of the water.

Next, we study the stability of the weak interactions. First disable present isosurfaces, and then input the command `source avgRDG_TFI.vmd` in the console window, after some adjustments you will see



The color scale is 0~1.5, still corresponding to the color transition of Blue-Green-Red. More blue (red) means the thermal fluctuation index (TFI) is smaller (larger), and hence the weak

interaction in corresponding region is more stable (unstable). The graph shows that it is stable that the water behaves as H-bond donor, while the stability of the water acting as H-bond acceptor is slightly weaker; the vdW interaction region is totally red, rendering that vdW interaction is evidently unstable compared to hydrogen bonding.

#### 4.200.4 Study iso-chemical shielding surface (ICSS) and magnetic shielding distribution for benzene

Iso-chemical shielding surface (ICSS) denotes isosurface of magnetic shielding value, which presents intuitive picture on aromaticity. If you are familiar with NICS, you can also simply view ICSS as the isosurface of NICS with inverted sign. Please see Section 3.200.4 for more information. In this example we will study benzene, since this is a planar system, we will plot ICSS<sub>ZZ</sub> instead of ICSS, namely only the component of magnetic shielding tensor perpendicular to molecular planar will be taken into account. ICSS<sub>ZZ</sub> must be more physically meaningful than ICSS, just like NICS<sub>ZZ</sub> is a better aromaticity index than NICS (proved in *Org. Lett.*, **8**, 863). Meanwhile I will also show how to plot magnetic shielding value in a line and in a plane.

Note that Multiwfn itself is incapable of calculating magnetic shielding tensor and requires Gaussian to do that.

Before running Multiwfn, you should prepare a Gaussian input file of standard single point task for present system, which later will be taken as template. This file has already been provided as "examples\ICSS\benzene.gjf". Meantime, you should prepare a file containing the structure of corresponding system, for benzene this file is provided as "examples\ICSS\benzene.pdb"

Boot up Multiwfn and input below commands

```
examples\ICSS\benzene.pdb      // Note that molecular plane is in XY plane
200  // Other functions (Part2)
4   // Generate grid data of ICSS or related quantities
-10 // Change extension distance, because the default value is somewhat too small for this molecule
12 // 12 Bohr of extension distance
1 // Low quality grid, magnetic shielding tensor at 130910 points will be calculated by Gaussian later. Since present system is not very small, using medium or better quality grid will be expensive
n // Do not skip the step of generating Gaussian input file, because this is the first time we carry out analysis and thus currently we do not have Gaussian input/output files in hand
examples\ICSS\benzene.gjf // The path of template input file
```

Now Multiwfn generates a lot of Gaussian input files of NMR task in current folder based on the template file. The files are named as NICS0001.gjf, NICS0002.gjf ... NICS0017.gjf. Run these files by Gaussian.

Note: If these files cannot be runned by your Gaussian normally, please check the tail of the output file, there are two common reasons:

(1) The %mem is too small to finish the task, you need to set %mem in the template .gjf file to a large value and retry.

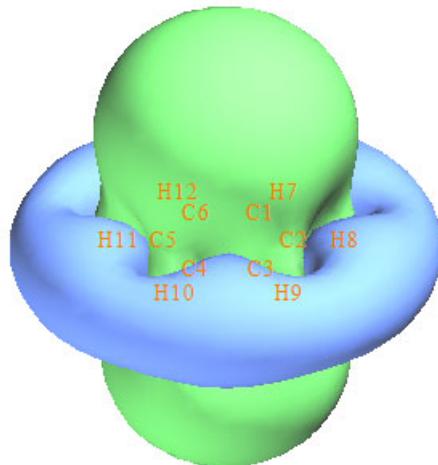
(2) The "NICSnptlim" in settings.ini is too large, you should properly reduce it and try again. The reason is that in Gaussian there is a limit on the number of Bq atoms, and it is somewhat dependant of the version of Gaussian and your computer. Beware that for G09 D.01 and may be some later versions, you should always add "guess=huckel" keyword, otherwise due to memory allocation bug the NICSnptlim has to be reduced to a very

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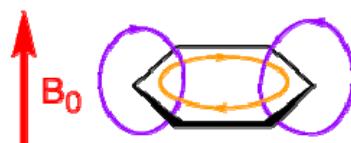
small value to make Gaussian run normally; in this case the overall computational cost will be quite high.

Hint: You can make use of the script "examples\runall.sh" (for Linux) or "examples\runall.bat" (for Windows), which invokes Gaussian to run all .gif files in current folder to yield output files with the same name but with .out suffix.

Assume that the output files (NICS0001.out, NICS0002.out...) have been placed in "C:\benzene" folder, in the window of Multiwfn input C:\benzene\NICS and then input 5 to select ZZ component, Multiwfn will load these output files and convert magnetic shielding tensors to grid data of ICSS<sub>ZZ</sub>. After that you can see a new menu, you can directly visualize isosurface of the grid data by option 1, export it as cube file by option 2 or re-select the property you are interested in, for example ICSS or ICSS<sub>XX</sub>. The isosurface of ICSS<sub>ZZ</sub>=2.0 is shown below



As you can see, the green isosurface (positive Z-component shielding value), completely covers the region above and below the benzene ring, suggesting that due to the induced ring current originated from the globally delocalized  $\pi$ -electrons, the Z-direction external magnetic field is largely shielded in these regions, this observation implies the strong aromaticity of benzene. From below scheme we can understand the ICSS<sub>ZZ</sub> more deeply; in the cylindrical region perpendicular to and through the benzene, the direction of induced magnetic field (purple arrows) is exactly opposite to external magnetic field ( $B_0$ ), this is why in this region Z-component of magnetic shielding value is large.



You can also see, blue isosurface (negative Z-component shielding value) presents in the outlier region of benzene, exhibiting de-shielding effect. This is mostly because the induced magnetic field is parallel to  $B_0$  and thus enhances  $B_0$  in this region.

If you properly rotate viewpoint, you will clearly find the C-H bond is also completely covered by the green surface. The reason is that the  $\sigma$ -electrons involved in the C-H bonding form conspicuous local induced ring current, so the external magnetic field is also strongly shielded around the C-H bond.

Now close the GUI window, and select 2 to export the grid data to ICSSZZ.cub in current folder.

Digression: Assume that you have obtained the Gaussian output files, and the Multiwfn instance has been terminated due to some reasons, but now you would like to re-analyze ICSS for this system, you should exactly repeat the steps what you have done before, the grid must be set in the same manner, then when Multiwfn asks you

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"If skip generating Gaussian input file of NMR task?", you should input "y", then the Gaussian input files will not be re-generated, and you can directly feed the Gaussian output files you have obtained into Multiwfn.

Next I will show how to plot magnetic shielding value in a line and in a plane. Since we already have grid data of ICSS<sub>ZZ</sub> in hand, magnetic shielding value at any point in a line/plane can be easily obtained by means of linear interpolation technique based on the grid data.

We first plot color-filled map for ICSS<sub>ZZ</sub> in the YZ plane with X=0. This plane is normal to benzene and crosses C4-H10 and C1-H7. Set "iuserfunc" in settings.ini to -I, and then boot up a new Multiwfn instance and input below commands

*ICSSZZ.cub*

4 // Plot plane map

100 //User-defined function, which now corresponds to the function interpolated by the grid data of ICSSZZ.cub

1 // Color-filled map

[Press Enter]

0 // Set extension distance of the plot

8

3 // YZ plane

0 // X=0

Now the graph pops up, close it and then input

4 // Show atom labels

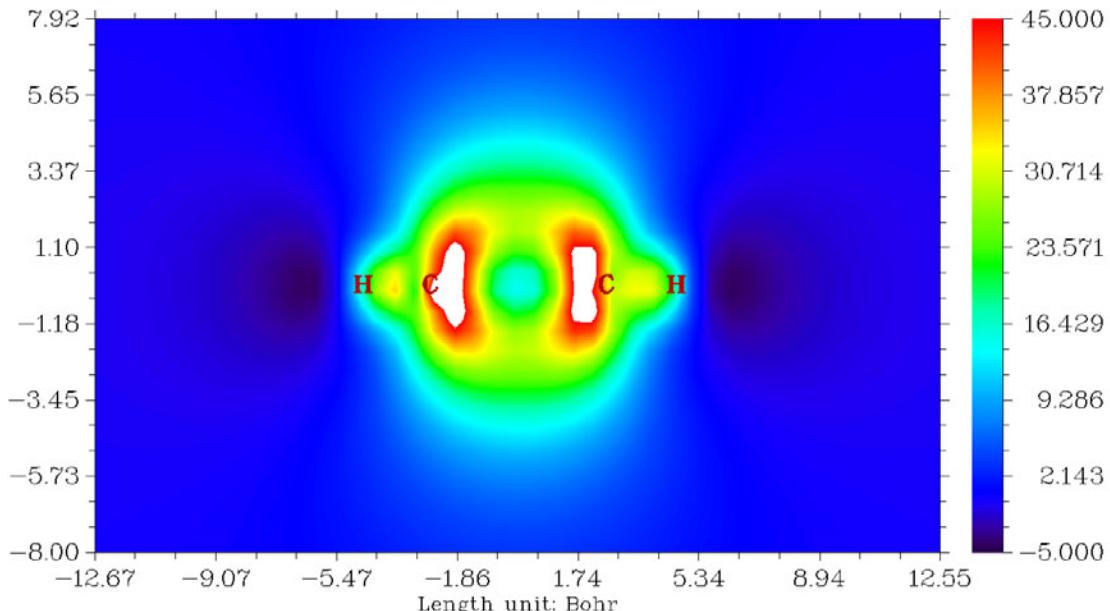
11 // Crimson text

1 // Change lower and upper limit

-5,45

-1 // Replot the map

Now you can see below map



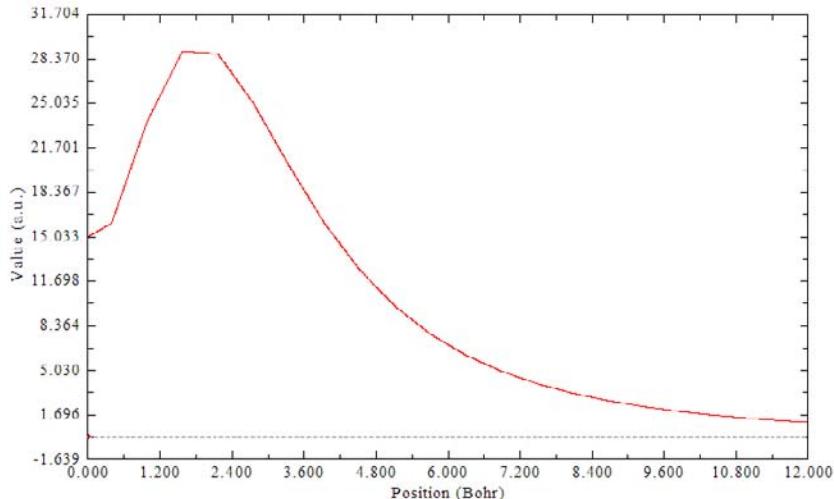
From the graph one can find that although Z-component of magnetic shielding in the center of benzene is an evident positive value, the magnitude is by far less than in the region above and below the ring plane. The reason is clear, that is benzene only has  $\pi$ -aromaticity, while its  $\sigma$ -electrons are not globally delocalized to form  $\sigma$ -aromaticity, so the shielding effect is relatively

weak in the plane due to lack of contribution of  $\sigma$ -ring current.

Next, we plot curve map to study the variation of magnetic shielding in the line perpendicular to ring plane and starting from ring center. Choose -5 to return to main menu and input

```
3 // Plot curve map
100
2 // Input coordinate of two points to define a line
0,0,0,0,0,12 // The line starts from ring center (0,0,0) and ends at 12 Bohr above the ring
plane
```

You will immediately see

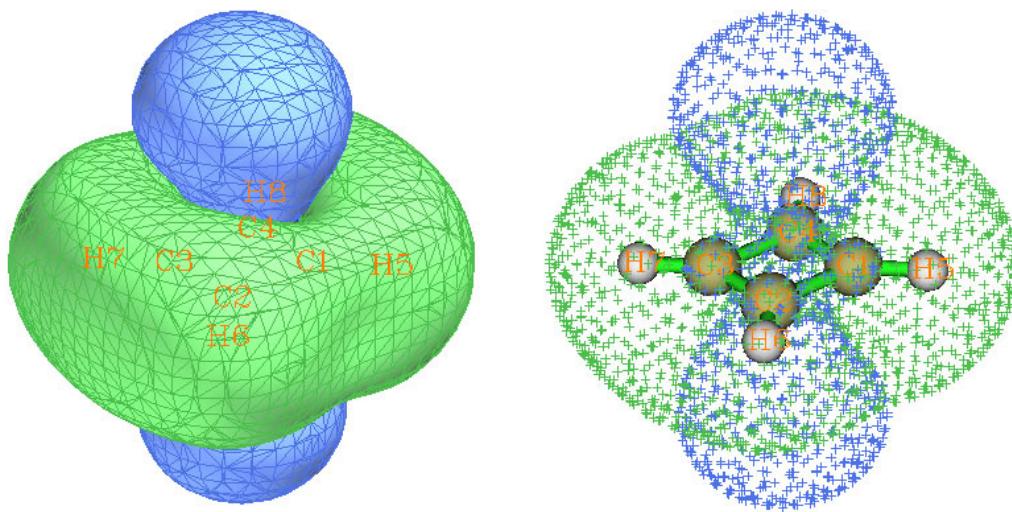


It can be seen that the maximum of Z-component of magnetic shielding value occurs about 1.8 Bohr above the ring plane.

Probably you have noticed that in some regions the curve map and plane map are not smooth enough, this is because the grid of ICSSZZ.cub is relative coarse (the grid spacing is large). If we use denser grid when calculating ICSS<sub>ZZ</sub>, the graphs will be improved. Also beware that since the extension distance used in the calculation of grid data of ICSS<sub>ZZ</sub> is only 12 Bohr, when we plot curve or plane map based on the interpolated data of ICSS<sub>ZZ</sub>, the spatial range involved in the map should not be too large. For example, we cannot plot the curve map from (0,0,0) to (0,0,20).

ICSS is very useful for discussing aromaticity and anti-aromaticity, many instances can be found in the original paper of ICSS (*J. Chem. Soc. Perkin Trans. 2*, **2001**, 1893), and in some applicative papers, such as *J. Phys. Chem. A*, **116**, 5674 (2012). AFAIK, ICSS<sub>ZZ</sub> is first proposed by me in this manual and has not been discussed in any literature yet.

I strongly recommend the users do some more practices about plotting and analyzing ICSS/ICSS<sub>ZZ</sub>, I provided some ideal exercise systems in "examples\ICSS" folder, including azulene, cyclobutadiene, cycloheptatriene, porphyrin, propane and pyracylene; among them cyclobutadiene is the most simple one. Below is the ICSS=0.5 isosurface of cyclobutadiene showing in two representations; from the graph it is clear that this system shows strong anti-aromaticity character, the  $4n$   $\pi$ -electrons cause evident de-shielding effect in the cylindrical region perpendicular to and through the ring, this situation is in complete contrast to benzene.



I wrote a very detailed post to discuss ICSS, in which all systems in "examples\ICSS" folder are involved, see "Using Multiwfn to study aromaticity by drawing iso-chemical shielding surfaces" (in Chinese, <http://sobereva.com/216>).

#### 4.200.5 Plot radial distribution function of electron density

Multiwfn is capable of plotting radial distribution function (RDF) for any real space function, see Section 3.200.5 for detail. This function is particularly useful for studying electronic structure character of sphere-like system.

This section consists of two parts. In part 1, we will plot RDF for electron density of fullerene ( $C_{60}$ ); while in part 2, I will show how to plot RDF of electron density for a Rydberg orbital to characterize it quantatively.

##### Part 1: RDF of electron density for fullerene

Since .wfn file of fullerene at B3LYP/6-31G\* level is large, I only provide the corresponding Gaussian input file for you (C60.gjf in example folder), please properly modify and run it by Gaussian to produce C60.wfn.

Boot up Multiwfn and input:

*C60.wfn*

200 // Other functions (Part 2)

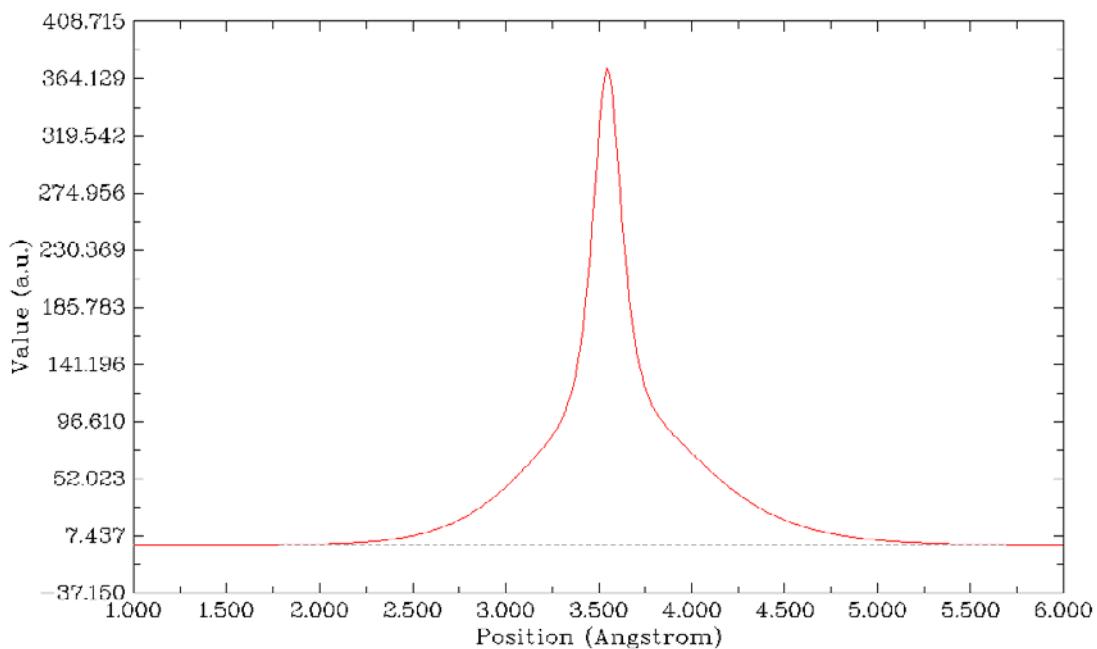
5 // Plot RDF for a real space function

3

1,6 // Set the lower and upper limit of RDF to 1.0 and 6.0 Angstrom, respectively

0 // Calculate RDF and its integration curve

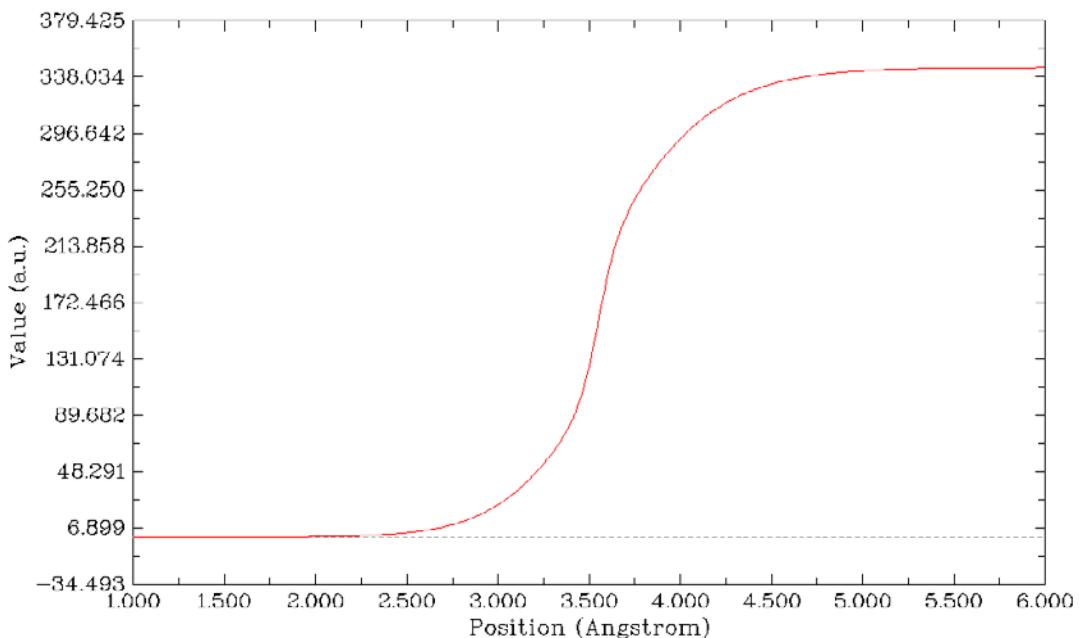
After the calculation is finished, select option 0, below RDF map will be shown on the screen, the X-axis corresponds to radial distance



As you can see, the peak of RDF is about 3.5 Å, this is because the distance between nucleus of carbons and the sphere center is 3.545 Å. It is known that electron density has maximum at nuclear position for any atom except for hydrogen.

If you carefully examine the RDF curve, you will find that the curve on the right side of the peak is slightly higher than that on the left sight. The reason is that the amount of  $\pi$  electrons at outer side of fullerene is richer than inner side. You can also draw and analyze ELF isosurface map to confirm this point.

You can also choose option 2 to plot integration curve of RDF, as shown below



Probably you have noticed that after the calculation there is a prompt on screen:

```
Integrating the RDF in the specified range is      344.9321931513
```

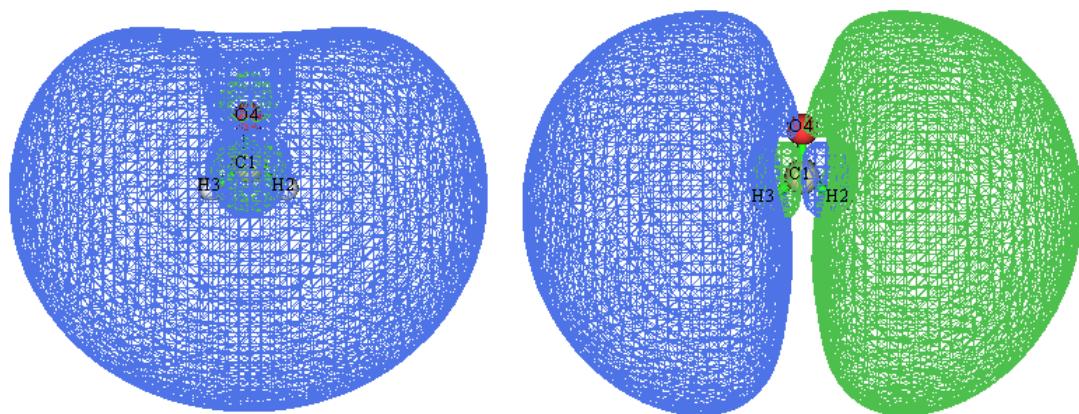
which means integrating the RDF from  $r=1.0$  to  $r=6.0$  Å yields 344.932, it also corresponds to the value of integration curve at  $r=6.0$ . This value deviates evidently from our expectation, namely the number of electrons in current system (360). One reason is that the default number of integration points is not large enough (500 and 2030 for radial and angular parts, respectively. You can manually increase them), while another reason is more important, that is the size of current system is too large, using single-center integration method is too difficult to yield very accurate result, at least for integrating electron density.

### Part 2: Using RDF of electron density to quantitatively characterize Rydberg orbital for acetone

Rydberg orbitals denote the spatially very diffuse MOs, their orbital shapes are akin to atomic orbitals, since electrons in Rydberg orbitals can be regarded as weakly bounded by a small cation core, which behaves as an atomic nucleus. In order to faithfully represent the diffuse character of Rydberg orbitals, basis set with substantial diffuse functions must be employed, e.g. aug-cc-pVTZ.

The example file we used below is formaldehyde calculated at B3LYP/aug-cc-pVTZ level by Gaussian. We will first visualize Rydberg orbitals as isosurfaces, and then calculate RDF of electron density corresponding to these orbitals to characterize them quantitatively.

Since Rydberg orbitals are very diffuse, in order to avoid truncating their isosurfaces when viewing them by main function 0, we should enlarge "aug3D" in settings.ini first, here we set it to 12. After that, boot up Multiwfn, input *examples\H2CO\_aVTZ.fch*, then enter main function 0, change isovalue to a much smaller value than default, e.g. 0.01, and then randomly examine some virtual MOs. You will find a lot of virtual MOs show very diffuse character, for example, MO10 and MO11:



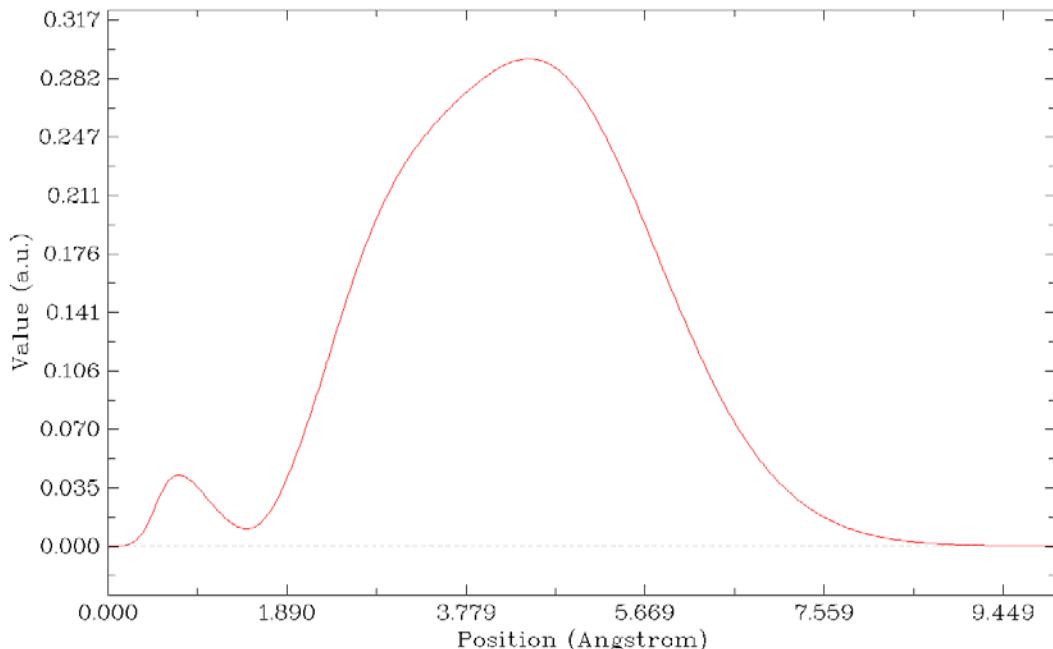
The main distribution region of both of them are far from the molecule. MO10 is almost spherically symmetric, thus is can be denoted as *s* type of Rydberg orbital. While MO11 has two phases, they equally distribute at the two sides, the overall shape is very close to atomic *p* orbitals, therefore MO11 can be identified as *p* type of Rydberg orbital.

How to quantitatively demonstrate that the main distribution region of these Rydberg orbitals is far from the molecular center? One of the best way is plotting RDF of electron density corresponding to these orbitals. Here we plot this kind of RDF map for MO11. We close the GUI of main function 0, and then input below commands:

```

6 // Modify wavefunction
26 // Modify orbital occupation number
0 // Select all orbitals
0 // Select occupation number of all orbitals to zero
11 // Select orbital 11
2 // Set occupation number of orbital 11 to 2.0 (assume it is doubly occupied)
q // Return
-1 // Return to main menu
200
5 // Plot RDF
3 // Set lower and upper limit of radial plotting
0,10 // From 0 to 10 Å
4 // Set angular number of integration points. The default value is unnecessarily high for
present purpose, therefore we set it to a smaller value to reduce computational time
302 // 302 angular points
0 // Calculate RDF for electron density (which is the default real space function)
1 // Plot the RDF map

```



From the map it can be seen that the global maximum peak is at about 4.6Å, indicating that the major distribution region of this orbital wavefunction is very far from origin (in present .fch file, Cartesian origin corresponds to molecular center), and thus MO11 can be unambiguously identified as a Rydberg orbital.

Please also plot such a RDF map for a regular valence virtual MO, e.g. MO9, which is  $\pi^*$  orbital. Where is its peak position?

## 4.200.8 Calculate polarizability and hyperpolarizability for NH<sub>3</sub> via sum-over-states (SOS) method

In this example I will show how to use Multiwfn to calculate polarizability and hyperpolarizability based on sum-over-states (SOS) method for HF molecule. Please make sure that you have read Section 3.200.8.

As introduced in Section 3.200.8, SOS calculation requires information of a large amount of electronic states, including electric dipole moments, excitation energies, and transition dipole moments between these states. Commonly these information can be obtained by ZINDO, CIS, TDHF and TDDFT calculations. In this example we use the very popular CIS method. According to my experiences, the more expensive methods TDHF and TDDFT, which can produce more accurate excitation energies, do not necessarily give rise to better (hyper)polarizability than CIS when used in combination with SOS technique.

We use Gaussian program to carry out the CIS calculation. However, Gaussian itself cannot output enough information for SOS calculation. Though for CIS (and ZINDO) there is a keyword *alltransitiondensities*, which makes Gaussian output transition density moment between each pair of excited states, however electric dipole moment of all states still cannot be obtained in a single run. Fortunately, we can use the very powerful electron excitation analysis module of Multiwfn to generate all information needed by SOS based on the output file of Gaussian CIS/TDHF/TDDFT task.

First, run "examples\NH3\_SOS.gjf" to produce output file of Gaussian CIS task (NH3\_SOS.out), and use formchk utility to convert the checkpoint file to NH3\_SOS.fch.

Since the SOS results converge often slow with respect to the number of excited states taken into account, we produce as high as 150 excited states in this example to substantially avoid truncation error. Of course, employing higher number of excited states needs more computational time in both of the CIS calculation and the subsequent SOS calculation in Multiwfn. In most practical studies, 100 states is generally large enough, and even 70 is often enough to provide usable results. Calculation of hyperpolarizability, especially the high-order ones, has very stringent requirements on the quality of basis-set, abundant diffuse functions are absolutely indispensable. In this example we employ def2-TZVPPD (J. Chem. Phys., 133, 134105), which is a high-quality basis-set optimized for calculation of molecular response properties. Since this is not a built-in basis-set in current version of Gaussian, it was picked from EMSL website (<https://bse.pnl.gov/bse/portal>). The keyword IOp(9/40=5) is important, because in the ZINDO/CIS/TDHF/TDDFT task by default Gaussian only outputs the transition coefficients whose absolute values are larger than 0.1, while IOp(9/40=5) lowers the criterion to 0.00001, so that much more coefficients can be outputted, and thereby we can obtain accurate transition dipole moments by Multiwfn at next step. Worthnoting, you can also use TDHF or TDDFT instead of CIS, for example you can write #P TD(nstates=150) CAM-B3LYP/gen IOp(9/40=5).

Boot up Multiwfn and input below commands

```
C:\gtest\NH3_SOS.fch
18 // Electron excitation analysis module
5 // Calculate transition dipole moments between all excited states
C:\gtest\NH3_SOS.out
3
```

The file SOS.txt generated in current folder contains all information needed by SOS (hyper)polarizability calculation. This file can be directly used by SOS module of Multiwfn.

Reboot Multiwfn and input

```
SOS.txt
200 // Other function (Part 2)
7 // Calculate (hyper)polarizability by sum-over-states (SOS) method
```

## 4 Tutorials and Examples

Note that all units used in the SOS module are atomic units.

Select 1 and input 0 to calculate static polarizability  $\alpha(0;0)$  first, the result is

Polarizability tensor:

	1	2	3
1	14.610682	0.000000	0.000000
2	0.000000	14.610682	0.000000
3	0.000000	0.000000	14.552483

Isotropic polarizability: 14.591283

Polarizability anisotropy (definition 1): 0.058199

Eigenvalues: 14.552483 14.610682 14.610682

Polarizability anisotropy (definition 2): 0.029100

As can be seen, not only the polarizability tensor, but also some related quantities are outputted. Their definitions can be found in Section 3.100.20. The isotropic average polarizability we obtained here is 14.59, which is in perfect agreement with the experimentally determined value 14.56 ! (*Mol. Phys.*, **33**, 1155)

Then we calculate dynamic polarizability  $\alpha(-\omega;\omega)$  and assume the frequency of external field to be 0.0719 a.u. Select option 1 again, input 0.0719, from the output we can see the dynamic isotropic polarizability at  $\omega=0.0719$  is 14.86, which is slightly larger than the static counterpart.

Next, we calculate first hyperpolarizability and consider the static case  $\beta(0;0,0)$ . Select option 2 and input 0,0. Only the  $\beta$  component along the dipole moment direction, namely  $\beta_{||}$ , is what we are particularly interested in, since only this quantity can be determined experimentally. From the output we find  $\beta_{||}(0;0,0)$  is -38.98. The corresponding experimental value is not available, however this value is close to the highly accurate value calculated by CCSD(T) method (-34.3, see *J. Chem. Phys.*, **98**, 3022).

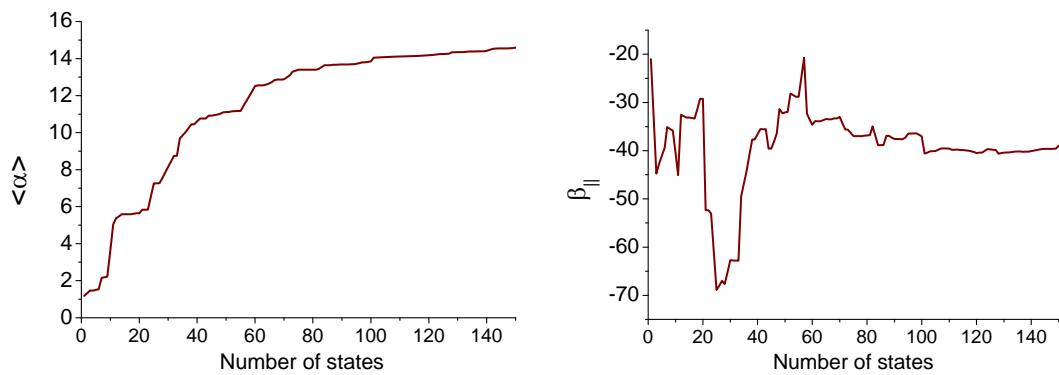
Now we calculate  $\beta(-2\omega;\omega,\omega)$  at  $\omega=0.0656$  a.u. Select option 2 again and input 0.0656, 0.0656 to set the frequency of both two external fields as 0.0656 a.u. This time the  $\beta_{||}$  value is -49.69, which is again in excellent agreement with the experimentally determined value  $-48.9 \pm 1.2$  (see A. Hernández-Laguna et al. (eds.), *Quantum Systems in Chemistry and Physics*, Vol. 1, p111)

Note: Although in this example the agreement between our SOS/CIS calculations and the reference values is surprisingly good, this is not always hold for other systems. The SOS/CIS method sometimes severely overestimates  $\beta$  value!

Finally, we tentatively calculate second hyperpolarizability  $\gamma$ . Select 3 and input 0,0,0 to assume static electric fields. Since calculation of  $\gamma$  is evidently more time-consuming than  $\beta$ , Multiwfn does not automatically use all states but allow you to set the number of states to be taken into account. Larger value in principle gives rise to better result, but of course more time will be consumed in the calculation. Here, we input 150 to use all states. After a while, the result is shown on screen, the average of  $\gamma$  is 928.74. Beware that this value may be inaccurate (reference value is not available, so I am not sure if this is a good result), one of the main reasons is that the basis-set we used in the electron excitation calculation is not large enough. Accurate calculation of  $\gamma$  usually requests a basis-set like d-aug-cc-pVTZ (or a even better one), which has an additional shell of diffuse functions compared to the commonly used aug-cc-pVTZ.

Multiwfn is also capable of calculating third hyperpolarizability  $\delta(-\omega;\omega_1,\omega_2,\omega_3,\omega_4)$  where  $\omega=\omega_1+\omega_2+\omega_3+\omega_4$ , but we do not do this in present example, because this quantity is fairly unimportant, and the calculation is terribly expensive when the number of states in consideration is large; moreover, a sky-high quality of basis-set must be employed in the calculation...

A very important point in SOS calculation is that the number of states used must be high enough; in other words, if  $n$  states are involved in your SOS studies, the variation of the (hyper)polarizability with respect to the number of states have to be converged before  $n$ , otherwise  $n$  must be enlarged. By using Multiwfn we can readily examine if the convergence condition is satisfied. Here we check the convergence of static  $\beta$ . Select option 6 and input 0,0, after a while, the result is exported to "beta\_n.txt" in current folder, the meaning of each column is clearly indicated on screen. Use your favourite tool to plot the data in "beta\_n.txt". If you are an Origin user, you can directly drag this file into Origin window and plot the data as curve maps. You can also similarly use option 5 and 7 to study the convergence of  $\alpha$  and  $\gamma$ . Below graphs show the variation of static  $\beta_{||}$  as well as static isotropic average polarizability  $\langle\alpha\rangle$  with respect to the number of states.



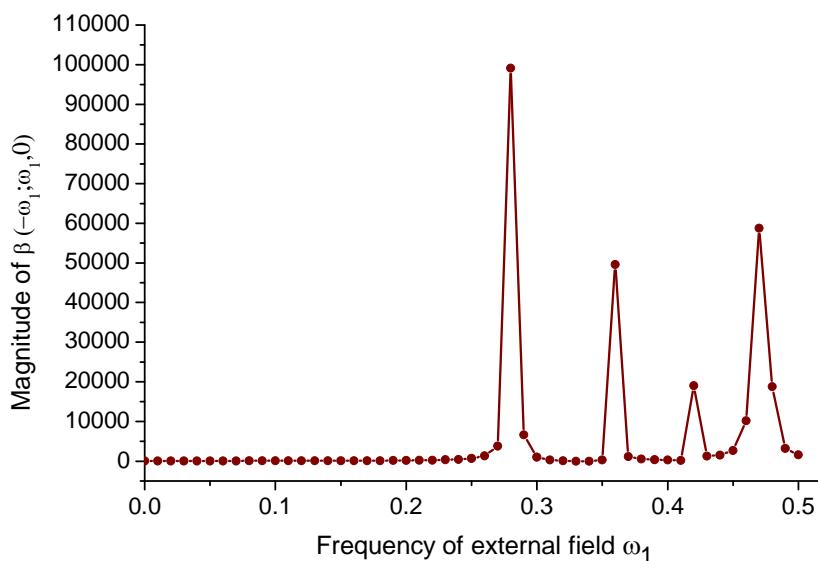
It is clear that both of the two quantities have basically converged at  $n=100$ . Since we employed 150 states in our calculations, the error due to the truncation of states can be safely ignored. From the graph one can also see that if the number of states is truncated at 70, the results are still qualitatively correct.

In the SOS module of Multiwfn one can also easily study the variation of dynamic (hyper)polarizability with respect to the frequency of external fields. For example, we investigate the variation of  $\beta(-\omega_1;\omega_1,0)$  as  $\omega_1$  varies from 0 to 0.5 a.u. with stepsize of 0.01. Write a plain text file, each row corresponds to a pair of  $\omega_1$ ,  $\omega_2$  ( $\omega_2$  is fixed at zero in this example), for example

```
0.00 0
0.01 0
0.02 0
...
0.5 0
```

Tips: For convenience, you can utilize Microsoft Excel program to generate frequency list, and save the table as .txt file (you can select such as "Text (tab delimited)", but do not choose "Unicode text").

Then choose option 16, input the path of the plain text file, the  $\beta$  will be calculated at each pair of frequencies, the result will be outputted to "beta\_w.txt" in current folder; the meaning of each column of the data is clearly indicated on screen. The data can be directly plotted as curve map by Origin, like below:



#### 4.200.12 Calculate energy index (EI) and bond polarity index (BPI)

In this section I will illustrate how to calculate EI and BPI indices, which were defined in *J. Phys. Chem.*, **94**, 5602 (1990). If you are not familiar with these two quantities, please read Section 3.200.12 first. The geometry and wavefunction involved in this example were produced at HF/6-31G\* level, which is the one used in above mentioned paper.

We will calculate BPI for C-N bond of  $\text{CH}_3\text{NH}_2$ , before this we first need to calculate reference EI value for C and N atoms, which correspond to EI of C in ethane and N in  $\text{H}_2\text{N}-\text{NH}_2$ , respectively. Boot up Multiwfn and input

```
examples\EI_BPI\ethane.fch
200
12
1 // C1 atom
```

You will see the EI value for C in reference molecule ethane is -0.667639 a.u. Reboot Multiwfn and input

```
examples\EI_BPI\N2H4.fch
200
12
1 // N1 atom
```

You can see the EI value for N in reference molecule  $\text{H}_2\text{N}-\text{NH}_2$  is -0.718126 a.u.

Next we calculate EI for C and N in  $\text{CH}_3\text{NH}_2$ . Reboot Multiwfn and input

```
examples\EI_BPI\CH3NH2.fch
200
12
1 // C1, the result is -0.693374 a.u.
5 // N5, the result is -0.698092 a.u.
```

The BPI<sub>CN</sub> in  $\text{CH}_3\text{NH}_2$  is computed as

$$\begin{aligned}
 \text{BPI}_{\text{CN}} &= (\text{EI}_{\text{C}} - \text{EI}_{\text{C}}^{\text{ref}}) - (\text{EI}_{\text{N}} - \text{EI}_{\text{N}}^{\text{ref}}) \\
 &= -0.693374 + 0.667639 + 0.698092 - 0.718126 \\
 &= -0.046
 \end{aligned}$$

As a comparison, use *examples\EI\_BPI\F2.fch* to calculate reference value for F, the result should be -0.992542 a.u., and use *examples\EI\_BPI\CH3F.fch* to calculate EI for C and F in CH<sub>3</sub>F molecule, the result should be -0.750302 and -0.885961, respectively. Then compute the BPI<sub>CF</sub> value as -0.750302+0.667639+0.885961-0.992542= -0.189. Since BPI<sub>CF</sub> in CH<sub>3</sub>F is evidently more negative than BPI<sub>CN</sub> in CH<sub>3</sub>NH<sub>2</sub>, it can be concluded that C-F bond in CH<sub>3</sub>F is more polar than C-N bond in CH<sub>3</sub>NH<sub>2</sub>.

Via EI index we can also evaluate the so-called group electronegativity, which is often more useful than atomic electronegativity. Here we calculate electronegativity for -CH<sub>3</sub> group, which is simply the negative of EI<sub>C</sub> for CH<sub>3</sub> radical. Boot up Multiwfn and input

```
examples\EI_BPI\CH3.fch // Optimized and produced at UHF/6-31G*
```

```
200
```

```
12
```

```
1 // Carbon atom
```

The result is -0.630656 a.u., corresponding to electronegativity of CH<sub>3</sub> group of 0.631. Then we use *examples\EI\_BPI\F.fch* to calculate group electronegativity for -F, the result is 0.957. It is clear that -F group has much higher electronegativity, and thus has stronger capacity to attract electrons than -CH<sub>3</sub> group due to its lower average energy per valence electron.

### 4.200.13 Localizing molecular orbital of 1,3-butadiene by Pipek-Mezey method

This section illustrates the use of Pipek-Mezey (PM) localization function of Multiwfn with *trans*-1,3-butadiene as example. Before reading this section please read Section 3.200.13 first to gain some basic knowledges.

The input file is *examples\butadiene.fch*, which was yielded at B3LYP/6-31G\*\* level. You can first visualize its MOs via main function 0, you will find all MOs except for inner-core ones are highly delocalized, none of them have direct correlation with classical concept of chemical bond theory. Now we perform orbital localization to transform them to more chemically meaningful orbitals. Boot up Multiwfn and input

```
examples\butadiene.fch
```

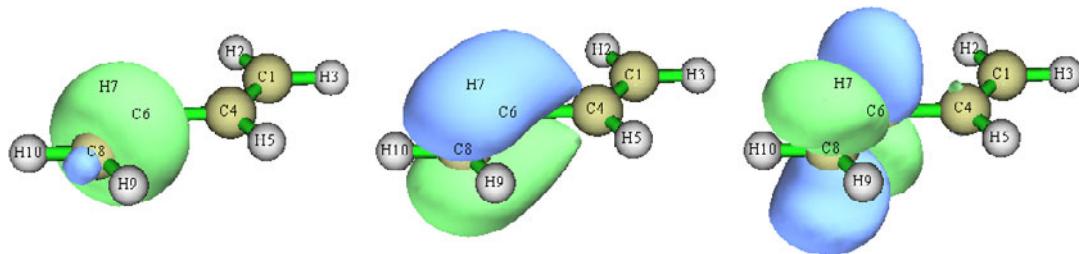
```
200
```

```
13 // Pipek-Mezey orbital localization
```

```
1 // Perform localization for both occupied and unoccupied MOs
```

Since this system is small, convergence of localization iteration promptly achieved. After that Multiwfn automatically exports the localized orbitals as new.fch in current folder and then load it. Now, the orbital coefficients in memory have been completely updated to localized orbitals. You may use different ways to characterize them, for example, we enter main function 0 to visualize these orbitals, you will find all orbitals show strong localization character, in particular the

occupied ones. Below are screenshot of three localized orbital involving C6-C8, the first two are occupied, and they correspond to  $\sigma$  bond and  $\pi$  bond, respectively; the third one is unoccupied, it can be ambiguously identified as anti- $\pi$  bond orbital.



It is also possible to obtain energy for the localized MOs, you should provide Fock matrix (strictly speaking, Kohn-Sham matrix in current case). To realize this for present system, we enter main function 100 and choose subfunction 2, and then select option 10 to write current molecular geometry as a Gaussian input file. We properly modify it to make Gaussian output NBO .47 file, which contains Fock matrix, and we need to ensure that the calculation level is identical to the .fch we used (i.e. B3LYP/6-31G\*\*). The .gjf file after modification is provided as butadiene\_47.gjf in "examples" folder. Run it by Gaussian, you will find *BUTADIENE.47* at C:\, search \$FOCK in this file, and extract all content between \$FOCK and the \$END next to it into a plain text file named *butadiene\_FOCK.txt* (this file is also provided in "examples" folder).

We have finished preparation. Now reboot Multiwfn and input

*examples\butadiene.fch*

200

13

-4 // Allow Multiwfn to generate and print energy for localized orbitals

*examples\butadiene\_FOCK.txt*

2

After convergence finished, Multiwfn evaluates energy of the localized MOs and sort orbitals according to their energies from low to high. The information of the highest occupied localized orbitals and lowest unoccupied localized orbitals are shown below

14	Energy (a.u.):	-0.27507273	Type: A+B	Occ: 2.0
15	Energy (a.u.):	-0.27507273	Type: A+B	Occ: 2.0
16	Energy (a.u.):	0.21859103	Type: A+B	Occ: 0.0
17	Energy (a.u.):	0.21859121	Type: A+B	Occ: 0.0

Please plot them in main function 0 to try to identify their characters.

#### 4.200.14 Integrate real space function within reduced density gradient (RDG) isosurfaces to study weak interaction

Before reading this, please read Section 4.100.1 to understand how to use reduced density gradient (RDG) to reveal weak interaction regions. In this section, I show the possibility of characterizing weak interaction by integrating domains enclosed by RDG isosurfaces.

##### System 1: Phenol dimer

First, we use phenol dimer as example. Boot up Multiwfn and input

*examples\phenoldimer.wfn*

```
200 // Main function 200
```

```
14 // Integrate real space functions within isosurfaces of a real space function
```

Here we want to study RDG domains defined as regions enclosed by isosurface of RDG=0.5; in other words, these domains composed of grid points where RDG<0.5. Therefore, we select option 2 and choose "13 Reduced density gradient", and then select option 3 and input criterion, namely <0.5 (In fact, RDG<0.5 is the default setting and you do not need to manually do these steps). Next, input below commands:

```
1 // Start calculation grid data and generate domains
```

```
-10 // Adjust extension distance
```

*0 // Set extension distance to zero to avoid wasting of grid points at boundary area, where RDG isosurfaces commonly do not occur*

```
2 // Medium quality grid (i.e. grid spacing=0.1 Bohr), generally this is accurate enough
```

Now Multiwfn starts calculation of grid data for the selected real space function (i.e. RDG), and then identifies individual RDG domains according to the criterion of RDG<0.5. Finally, four domains are found, the number of grid points constituting the domains are shown as the last column:

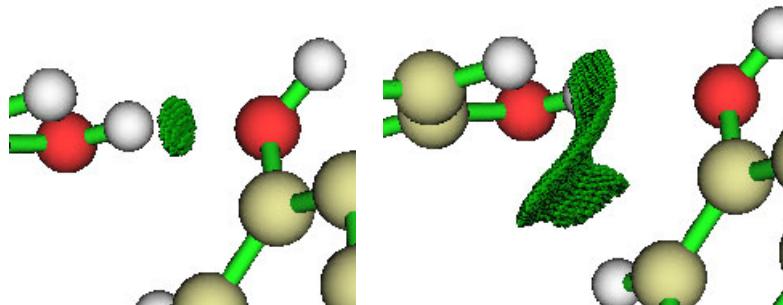
Domai n:	1	Gri ds:	208
----------	---	---------	-----

Domai n:	2	Gri ds:	290
----------	---	---------	-----

Domai n:	3	Gri ds:	200
----------	---	---------	-----

Domai n:	4	Gri ds:	2597
----------	---	---------	------

To visualize them, select "3 Visualize domains". In the GUI, you can select domain index at right-bottom list. The 2nd and 4th domains are shown below:



If you have read Section 4.100.1, you must know these domains correspond to H-bond and van der waals (vdW) interactions between the two phenols, respectively. We can study properties of these domains in terms of integrating specific real space functions in them. The real space function to be integrated can be selected by option 4, it is default to electron density, which is just the one we want to integrate in the domains. So we directly select option 1 and input 2, then integral of electron density in domain 2 is shown on the screen:

```
Integrat ion resul t: 0. 6932973049E-02 a. u.
```

```
Vol ume: 0. 290000 Bohr^3 ( 0. 042974 Angstrom^3 )
```

```
Average: 0. 2390680362E-01
```

```
Maxi mum: 0. 2766231164E-01 Mi ni mum: 0. 1994457517E-01
```

Similarly, we do this for domain 4:

```
Integrat ion resul t: 0. 1181667175E-01 a. u.
```

```
Vol ume: 2. 597000 Bohr^3 ( 0. 384836 Angstrom^3 )
```

```
Average: 0. 4550123895E-02
```

## 4 Tutorials and Examples

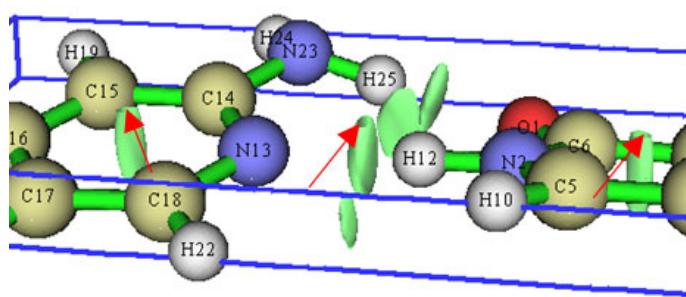
Maxi mum: 0. 6217203920E-02 Mi ni mum: 0. 3102088666E-02

From the output we know the number of electrons involved in the domains corresponding to H-bond and vdW interactions are 0.006933 and 0.011817, respectively. They can be interpreted as overlapping electrons and are closely related to strength of same type of interactions (see discussion in Section 5.2 of DORI original paper *J. Chem. Theory Comput.*, **10**, 3745 (2014)). However, since these two domains correspond to different type of weak interactions, the magnitude of overlapping electrons is not positively correlated to their strengths, namely we are unable thus to say that the vdW interaction between the two phenols is stronger than the intermolecular H-bond. The "Volume" in the output denotes volume of the domain, we can find that vdW interaction involves much wider spatial region than H-bond. "Average" correspond to average value of real space function in the domain, from this quantity one can easily infer that the strength of interaction per contact region of H-bond must be significantly higher than that of vdW interaction, since as shown above, their average values are 0.0239 and 0.0045, respectively, the former is much larger than the latter.

### System 2: 2-pyridoxine 2-aminopyridine

Intermolecular H-bonds of 2-pyridoxine 2-aminopyridine (PP) has been investigated in Section 4.2.1 by means of AIM analysis, while this time we will analyze them by means of  $q_{\text{int}}$  index. This index was proposed in *J. Phys. Chem. A*, **115**, 12983 (2011) for judging interaction of H-bond at various intermolecular distance, please check Section 3.200.14 for its definition. Commonly, the more negative of the  $q_{\text{int}}$  index, the more stable the interaction.

$q_{\text{int}}$  index is defined based on integrating domains enclosed by RDG=0.6 isosurfaces, therefore we need to first calculate RDG grid data and generate corresponding domains. Note that it is not always appropriate to set extension distance of RDG grid data to zero. For present system, if you calculate RDG grid data by main function 5 with extension distance of zero, you will see some RDG isosurfaces are truncated by box boundary, as shown below and highlighted by red arrows. In this case domain integrating module of Multiwfn does not work.



Therefore, when we calculate RDG grid data for this case, extension distance should be set somewhat larger than zero, 3 Bohr is safe enough for avoiding unexpected truncation. Extension distance should also never be set to a too large value, otherwise the number of grid points to be calculated will be very high and thus very time-consuming.

Boot up Multiwfn and input below commands:

*examples\2-pyridoxine\_2-aminopyridine.wfn*

200

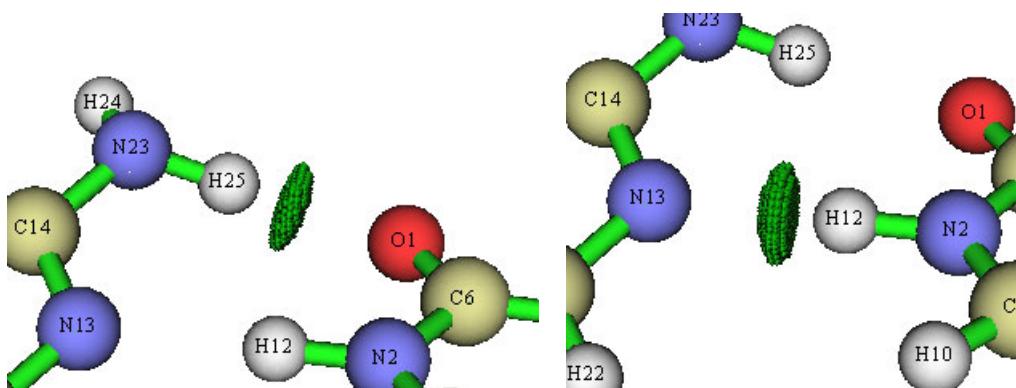
14

```

3 // Change the default criterion of defining domain
<0.6
1 // Start calculation of grid data
-10 // Change extension distance
3 // 3 Bohr of extension distance
2 // Medium quality grid

```

Now visualize resulting domains. Domain 2 and 4 are shown below, clearly they correspond to H-bond of N23-H25.....O1 and N2-H12.....N13, respectively.



Now select "5 Calculate  $q_{\text{bind}}$  index for a domain" and input 2, the resulting  $q_{\text{int}}$  and related details of the domain are shown below

```

q_att:      0. 00490957 a. u.
q_rep:      0. 00005590 a. u.
q_bind:     -0. 00485367 a. u.

Volume (I ambda2<0):    0. 599000 Bohr^3
Volume (I ambda2>0):    0. 010000 Bohr^3
Volume (Total):          0. 609000 Bohr^3

```

Similarly, we obtain results for domain 4

```

q_att:      0. 00805204 a. u.
q_rep:      0. 00037346 a. u.
q_bind:     -0. 00767858 a. u.

Volume (I ambda2<0):    0. 745000 Bohr^3
Volume (I ambda2>0):    0. 052000 Bohr^3
Volume (Total):          0. 797000 Bohr^3

```

Since the  $q_{\text{bind}}$  corresponding to N2-H12.....N13 (-0.007678) is much more negative than that of N23-H25.....O1 (-0.004854), the former should be stronger than the latter.

Since both the interactions are H-bond, it is also possible to simply compare the number of electrons contained in the domains to estimate their relative strength. We choose "2 Perform integration for all domains" to print out integral of electron density (the default real space function) in all domains:

Domain	Integral (a. u.)	Volume (Bohr^3)	Average
1	0. 1212147834E-03	0. 111000	0. 1092025076E-02
2	0. 1647945811E-01	0. 609000	0. 2705986553E-01
3	0. 1714432107E-02	0. 319000	0. 5374395319E-02
4	0. 2618188584E-01	0. 797000	0. 3285054685E-01

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```
5    0. 8932587581E-02      0. 412000  0. 2168103782E-01  
6    0. 7764521413E-02      0. 394000  0. 1970690714E-01
```

```
Integration result of all domains: 0. 6119409984E-01 a.u.
```

```
Volume of all domains: 2. 642000 Bohr^3 0. 391504 Angstrom^3
```

Not only the integration value of domain 2 (0.01648) is evidently smaller than domain 4 (0.02618), but also the average value of domain 2 (0.02706) is smaller than domain 4 (0.03285), therefore we have strong evidence to say N2-H12.....N13 is stronger than N23-H25.....O1.

With similar steps illustrated in this section, you can also integrate other real space functions such as potential energy density and spin density, in the domains enclosed by isosurfaces of other real space functions, e.g. DORI and ELF.

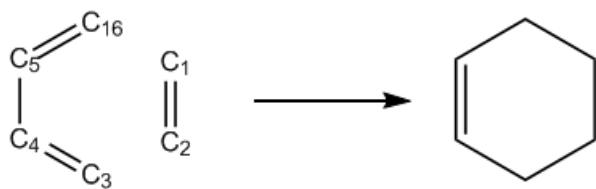
Note that the accuracy of integration in the domains is directly determined by grid setting, higher quality of grid leads to better accuracy. For example, when visualizing domains, if you found a domain only consists of very few grid points, and its profile is very coarse, then integration accuracy of this domain must be very low.

## 4.A Special topics and advanced tutorials

The contents in this Section involve more than one main functions of Multiwfn.

### 4.A.1 Study variation of electronic structure along IRC path

In this tutorial, I will briefly show you how to use Multiwfn to study variation of electronic structure along the IRC path of Diels-Alder adduction. We will study the variation of Mayer bond order, and will animate the deformation of ELF isosurface. With the similar fashion you can also easily investigate variation of other properties, such as atomic charges, electron density, aromaticity and so on.



Gaussian 09 A.02 are used throughout this tutorial. Unless otherwise specified, all calculations will be performed under Windows 7 64bit system. In this tutorial the files marked by crimson can be found in "examples\IRC" or "examples" folder.

Before starting this tutorial, you should setup running environment for Gaussian first, otherwise Gaussian cannot be properly invoked in Windows environment. The setup method is: Enter “control panel”-“System properties”-“Advanced”, click “Environment variables” button, then click “New” button in “User variables” frame, input GAUSS\_EXEDIR as variable name, input the install directory of Gaussian as variable value (e.g. d:\study\g09w\), assuming that g09.exe is in this folder). After that modify "PATH" environment variable to add the install directory of Gaussian into it.

#### 1 Perform IRC calculation

Run **DA\_IRC.gjf** by Gaussian to produce **DA\_IRC.out**. We will find this IRC path actually contains 18 and 13 points in the two directions, respectively. B3LYP/6-31+G\* is used in this calculation.

#### 2 Generate wavefunction file for each point of IRC

Write an input file of single point task of Gaussian (**DA\_SP.gjf**), which will be used as "template" later. The geometry in fact can be arbitrarily filled.

```
DO NOT write anything here (e.g. %chk)
#p B3LYP/6-31G* nosymm
```

```
DA adducti on
```

```
0 1
```

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```

C      -0. 26156800   1. 56679300   0. 69509600
C      -0. 26156800   1. 56679300  -0. 69509600
C      0. 50031400  -0. 43279300  -1. 43864500
C      -0. 26156800  -1. 32826500  -0. 70392000
C      -0. 26156800  -1. 32826500   0. 70392000
H      -1. 19341600   1. 44689700  -1. 23752300
H      -1. 19341600   1. 44689700   1. 23752300
H      0. 52507600   2. 08588200   1. 23621300
H      0. 38154400  -0. 37781200   2. 51847500
H      0. 38154400  -0. 37781200  -2. 51847500
H      1. 46467600  -0. 09643600  -1. 07409700
H      -1. 04094400  -1. 89294000  -1. 21418700
H      -1. 04094400  -1. 89294000   1. 21418700
H      1. 46467600  -0. 09643600   1. 07409700
H      0. 52507600   2. 08588200  -1. 23621300
C      0. 50031400  -0. 43279300   1. 43864500

```

**blank line**

**blank line**

Notice that the basis-set we used here (6-31G\*) is different to the one used in IRC task (6-31+G\*), because Mayer bond order does not work well when diffuse functions are presented. By the way, ignoring diffuse functions will not lead to detectable change of ELF isosurface. Also note that the "nosymm" keyword is specified, because if we do not do this Gaussian will automatically translate and rotate the molecule to put it to standard orientation, which may leads to discontinuity problem in the animation of ELF (You will see molecule suddenly jumps in certain frames of the animation).

**IRCsplit.exe** is a tool used to produce .wfn/.chk file for each point of IRC and SCAN tasks of Gaussian 09, **IRCsplit.f90** is the corresponding source code, by which you can compile Linux version of IRCsplit. Boot up IRCsplit.exe by double click its icon and then input

```

DA_IRC.out          //The file of the output file of the IRC task
DA_SP.gjf           //The template file used to generate single point input files
2                  //Only yield .chk files
c:\DA_IRCchk\DA    //The path and prefix of the finally generated .chk files
18,13              // The program detected that in DA_IRC.out there are 18 and 13 points in the
two directions of IRC, respectively. Here we extract all of them, together with the TS point

```

Now you can find DA\_SP0001.gjf, DA\_SP0002.gjf ... DA\_SP0032.gjf in current folder. Please manually check one of them to verify the reasonableness of these input files. Note that DA\_SP0014.gjf corresponds to the TS geometry.

Build a new folder "c:\DA\_IRCchk" and copy the .gjf files as well as the script **runall.bat** into it. Double clicking the icon of runall.bat, which will invoke Gaussian 09 to run all of the .gjf files.

Now you have DA0001.chk, DA0002.chk ... DA0032.chk in "c:\DA\_IRCchk" folder. Copy **chk2fch.bat** to this folder and run it, then the formchk utility in Gaussian package will be automatically invoked to convert all .chk files to .fch files.

### 3 Calculate Mayer bond orders for all IRC points

Mayer bond order of C1-C16 is the one we are particularly interested in, whose formation is the key process of the DA adduction. Since by default Multiwfn only outputs Mayer bond orders with value  $> 0.05$ , while C1-C16 must be very weak at the initial stage of DA adduction, we need to set "bndordthres" parameter in the settings.ini file in Multiwfn folder to 0.0, so that all of the bond orders larger than 0.0 can be outputted.

Write a plain text file (**MBObatch.txt**) and put it into Multiwfn folder, the content is

```
9          // Enter bond order analysis module
I          // Calculate Mayer bond order
```

Note: If you are confused why this file is written in such manner, please read Section 5.2 to study how to run Multiwfn in silent mode.

Then write a plain text file with .bat suffix (**MBObatchrun.bat**) and put it into Multiwfn folder, the content should be

```
for /f %%i in ('dir c:\DA_IRCchk\*.fch /b') do Multiwfn c:\DA_IRCchk\%%i <
MBObatch.txt > c:\DA_IRCchk\%%~ni.txt
```

**batchrun.bat** in fact is a Windows batch script. Double clicking its icon to run it, the .fch files in "c:\DA\_IRCchk\" folder will be sequentially loaded into Multiwfn, and the calculated Mayer bond orders will be exported to .txt files in the same folder.

### 4 Plot Mayer bond order

Now what we should do next is to extract the bond order of C1-C16 from the DA0001.txt, DA0002.txt ... DA0032.txt. The most convenient way is to utilize "grep" command in Linux. So we copy all of these .txt files to a folder in Linux system, then in this folder we run

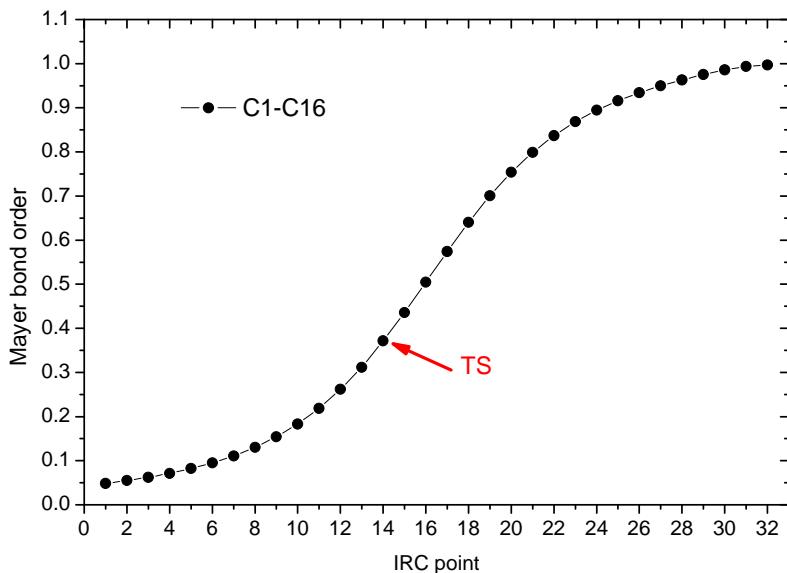
```
grep "1(C)    16(C)" * > out.txt
```

The **out.txt** file now contains C1-C16 bond order of all points in the IRC:

```
DA0001. txt: # 9:      1(C )  16(C )  0. 05929972
DA0002. txt: # 7:      1(C )  16(C )  0. 06877306
DA0003. txt: # 7:      1(C )  16(C )  0. 07926829
DA0004. txt: # 7:      1(C )  16(C )  0. 09089774
DA0005. txt: # 7:      1(C )  16(C )  0. 10380144
DA0006. txt: # 7:      1(C )  16(C )  0. 11815120
DA0007. txt: # 7:      1(C )  16(C )  0. 13417828
DA0008. txt: # 7:      1(C )  16(C )  0. 15218555
```

...

The last column is the values of Mayer bond order of C1-C16, you can plot them by your favorite program now, you will see

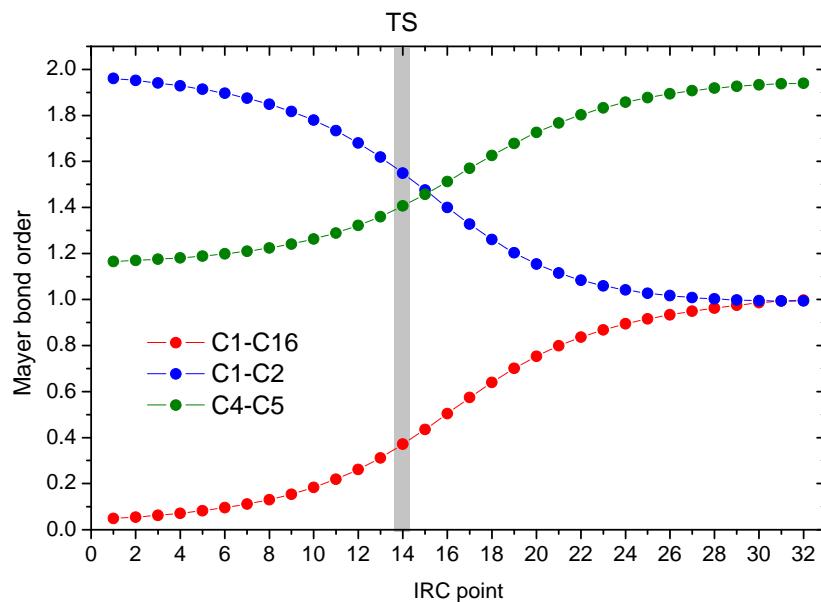


Clearly, C1-C16 become stronger and stronger as the reaction proceeds, its Mayer bond order gradually increases to 1.0 (typical single bond).

With the same method, we also calculate the Mayer bond order of C1-C2 and C4-C5, namely run below commands

```
grep "1(C )      2(C )" * > out2.txt
grep "4(C )      5(C )" * > out3.txt
```

Plot the data in **out.txt**, **out2.txt** and **out3.txt** together, you will see



This graph vividly shows that the C1-C2 smoothly becomes to a single bond from a double bond during the DA adduction, and the reaction increases the double-bond character of C4-C5 significantly.

## 5 Make animation of ELF isosurface

Next we make animation to study how the ELF isosurface varies during the DA adduction.

Create a plain text file ELFbatch.txt in Multiwfn folder with below content

```
5      // Generate grid data
9      // ELF
2      // Medium quality grid
2      // Export the grid data to ELF.cub in current folder
```

Create a script file named ELFbatchrun.bat, whose content is

```
for /f %%i in ('dir c:\DA_IRCchk\*.fch /b') do (
Multiwfn c:\DA_IRCchk\%%i < ELFbatch.txt
rename ELF.cub %%~ni.cub
)
```

Run **ELFbatchrun.bat**, Multiwfn will sequentially load the .fch files in "c:\DA\_IRCchk" and export the corresponding ELF grid data to DA0001.cub, DA0002.cub ... DA0032.cub in current folder.

We use VMD 1.9.1 program (freely available at <http://www.ks.uiuc.edu/Research/vmd/>) to render isosurface for these cube files. Move all of the cube files to VMD folder, and create a plain text file named **isoall.tcl** in the VMD folder, the content is

```
set isoval 0.88
axes location off
color Display Background white
for {set i 1} {$i<=32} {incr i} {
set name DA[format %04d $i]
puts "Processing $name.cub..."
mol default style CPK
mol new $name.cub
#translate by -0.100000 0.20000 0.000000
#scale to 0.30
rotate y by 50
rotate z by 90
rotate x by -30
rotate y by -20
mol addrep top
mol modstyle 1 top Isosurface $isoval 0 0 0 1 1
mol modcolor 1 top ColorID 3
render snapshot $name.bmp
mol delete top
}
```

This file essentially is a VMD script, in which the command *set isoval 0.88* means the isosurface of 0.88 will be plotted, the default view point is adjusted by *scale*, *rotate* and *translate* commands. *for {set i 1} {\$i<=32} {incr i}* means the file from DA0001.cub to DA0032.cub will be processed.

Now boot up VMD, and input the command *source isoall.tcl* in its command line window,

then you will have DA0001.bmp, DA0002.bmp ... DA0032.bmp.

There are numerous programs that can convert single-frame graphic files to animation, such as Atani, Premiere, Vegas, Ulead Video Studio, Videomach, etc. Here we use ImageMagick tool in Linux to do this, and we choose gif as the animation format, since gif animation can be directly embedded into webpages.

Copy all of the .bmp files to Linux system, and run below command in the corresponding folder:

```
convert -delay 12 -colors 100 -monitor *.bmp ELF_IRC.gif
```

in which *-delay* controls the time interval between each frame in the animation, and *-colors* determines the number of colors used, the larger the value, the more smoothly the color changes, but the larger the animation file. You can run *convert --help* to study more arguments of this tool

If the the resultant ELF\_IRC.gif cannot be properly displayed on your system, use your webpage explorer or advanced image explorers (e.g. IrfanView) to open it. The deformation of ELF isosurface in this animation very intuitively exhibits how the new bonds are formed and how the characteristic of existing bonds changed.

#### 4.A.2 Calculate spin population

As there are many ways to calculate atomic charges (see Section 3.9 for introduction and 4.7 for examples), there are various ways to calculate spin population. Spin population is defined as the population number of alpha electrons minus that of beta electrons. Spin population is a key quantity for characterizing electronic structure of open-shell systems, i.e. radicals and antiferromagnetic systems. From spin population we can clearly know where the spin electrons are mainly distributed. Moreoever, we can discuss contribution from different regions (atomic orbitals, atoms or fragments) to the total magnetic dipole moment **m** due to electron spin. If spin population of a region is *x*, then its contribution to **m** will be  $x^*\mu_B$ , where the Bohr magneton  $\mu_B=e^*\hbar/(2m_e)$  (*e*: electron charge,  $m_e$ : mass of electron) represents the magnetic moment produced by a single electron. Note that in chemical systems the movement of electron in orbitals and nuclear spins also have contributions to **m**, but the magnitude is evidently weaker and thus can often be neglected.

In Multiwfn, the spin population defined in many different ways can be calculated by three modules, they are briefly discussed below.

**(1) Population analysis module (main function 7).** In this module, if you select Mulliken population analysis, alpha, beta and spin population of each basis function, shell and angular moment orbitals will be outputted. If you select Löwdin and modified Mulliken population analysis, only the alpha/beta/spin population of each atom will be shown. Do not use these methods when diffuse basis functions are presented in your basis-set, otherwise the result may or may not be reliable.

**(2) Fuzzy atomic spaces analysis module (main function 15).** After you entered this module, select option 1 and choose electron spin density, the spin population of each atom will be shown. They are calculated by integrating electron spin density in fuzzy space of each atom. By default the fuzzy atomic space defined by Becke is employed, so the result can be called Becke spin population. If before calculation you selected option -1 to switch to Hirshfeld or Hirshfeld-I fuzzy atomic space, then the result will correspond to Hirshfeld or Hirshfeld-I spin population. All

the Becke, Hirshfeld and Hirshfeld-I methods are reliable in all cases. For more detail you can consult Section 3.18.

**(3) Basin analysis module (main function 17).** In this module, you can use AIM method to calculate spin population. Please consult Section 4.17.1 on how to perform integration of real space function in AIM atomic basins. If electron spin density is chosen to be the integrand, then the result will correspond to AIM spin population. In general I do not suggest using this method, because the computational cost is evidently higher than using population analysis module and fuzzy atomic spaces analysis module.

Overall, if you only need to calculate atomic spin population, using fuzzy atomic spaces analysis module is recommended. However, if more detailed information are requested, such as spin population in different angular moment orbitals, please use Mulliken population analysis.

### 4.A.3 Study aromaticity

Aromaticity is a fundamental concept in organic chemistry and wavefunction analysis realm. Previously I wrote a post to thoroughly discuss the methods for studying aromaticity, see "The methods for measuring aromaticity and their calculations in Multiwfn" (in Chinese, <http://sobereva.com/176>). Multiwfn support a very large number of methods for investigating aromaticity, they are summarized in below table and will be briefly introduced in turn. There are also many other methods, such as induced ring current, ARCS, magnetic susceptibility exaltation, aromatic stabilization energy (ASE), CiLC; they will not be mentioned since they are not directly related to the capacity of Multiwfn.

	Method	Principle	Year	Pop.	Reliab.	Univ.	Ref.	Anti-arom.	Sep. σ/π	Cost	Value
1	Molecular orbital	Hückel	1951	++	0	0	N	Y	Y	0	+
2	AdNDP	Hückel	2008	+	0	+	N	Y	Y	0	+
3	NICS	Magnet.	1996	+++	++	++	N	Y	Y	+	+++
4	ICSS	Magnet.	2001	0	++	++	N	Y	Y	+++	+
5	HOMA	Geom.	1972	+	+	0	Y	Y	N	--	+
6	Bird	Geom.	1985	--	0	-	Y	?	N	--	-
7	Multi-center BO	Delocal.	1990	+	+++	++	N	N	Y	0	+++
8	ELF-σ/π	Delocal.	2004	+	0	-	N	Y	Y	0	+
9	PDI	Delocal.	2003	0	+	0	N	N	Y	0	+
10	ATI	Delocal.	2005	--	+	0	N	N	Y	-	0
11	PLR	Delocal.	2012	--	+	0	N	N	Y	0	0
12	ΔDI	Delocal.	2003	--	-	-	N	N	Y	0	--
13	FLU, FLU-π	Delocal.	2005	0	+	0	Y/N	N	Y	0	+
14	RCP properties	ρ	1997	-	0	0	N	N	?	-	0
15	Shannon aromaticity	ρ	2010				N	Y	N	-	
16	EL index	ρ	2012	--	-	-	Y	Y	N	-	--

In the table, "+++", "++", "+", "0", "-", and "--" correspond to very high, high, relatively high, normal, relatively low and low, respectively. "Y" and "N" stand for "Yes" and "No", respectively. The meaning of each column are given below.

**Principle:** The principle behind the method. "Hückel" = Hückel rule; "Magnet." = Magnetic

properties; "Geom." = Molecular geometry; "Delocal." = Electron delocalization character; " $\rho$ " = Electron density distribution.

**Year:** The year that the method was first time proposed.

**Pop.:** Popularity in recent years.

**Reliab.:** Reliability, measuring if the method is able to faithfully reveal aromaticity.

**Univ.:** Universality. A method with high universality must be able to be applied to a wide variety of kinds of systems and situations, such as the rings containing heteroatoms and transition metals, non-equilibrium geometry (e.g. transition state of Diels-Alder adduction), excited state, etc.

**Ref.:** If the method relies on reference systems. A universal method must avoid this feature.

**Anti-arom.:** If the method is also able to measure anti-aromaticity.

**Sep.  $\sigma/\pi$ :** If the method can be used to separately discuss  $\sigma$  and  $\pi$  aromaticity.

**Cost:** The computational cost to apply the method.

**Value:** The overall value. This is the most important descriptor.

Next, the methods presented in above table will be briefed sequentially, and how to realize them in Multiwfn will also be mentioned.

**1. Molecular orbital (MO):** The famous Hückel  $4n+2$  and  $4n$  rule for determining aromaticity character was first explicitly presented in *J. Am. Chem. Soc.*, **73**, 876 (1951). For a molecule, if there are totally  $4n+2$  electrons in  $\pi$  ( $\sigma$ ) MOs, and this set of MOs share the similar delocalization pattern, then the ring involved in these MOs will show  $\pi$  ( $\sigma$ ) aromaticity. If there are  $4n$  electrons, then the ring should possess anti-aromaticity. Note that for Möbius type of molecule, the  $4n+2$  and  $4n$  rule are inverted.

In order to use the Hückel rule to determine aromaticity, one should first pick out proper MOs by visualizing MO isosurfaces, you can use main function 0 for this purpose. If the system is exactly planar, you can directly make use the function introduced in Section 3.100.22 to find out the indices of all  $\pi$  MOs.

**2. AdNDP (Adaptive natural density partitioning):** The MO method shown above commonly is only applicable to the molecule containing only one ring. When there are multiple rings, such as phenanthrene, the MOs are useless, since MOs in general delocalize over the whole molecule and thus cannot be used to study local aromaticity of different rings. The AdNDP method, which was proposed in *Phys. Chem. Chem. Phys.*, **10**, 5207 (2008), is able to overcome this difficulty. AdNDP has been carefully introduced in Section 3.17, and many examples are given in Section 4.14.

**3. NICS (Nucleus-independent chemical shift):** NICS uses the negative value of magnetic shielding value at ring center to measure its aromaticity. This is the most popular aromaticity index nowadays, it was originally proposed in *J. Am. Chem. Soc.*, **118**, 6317 (1996) and reviewed in *Chem. Rev.*, **105**, 3842-3888. There are also a few variants, among them the best one is NICS(1)<sub>ZZ</sub>, see *Org. Lett.*, **8**, 863 (2006). For non-planar system, it is often difficult to calculate NICS(1)<sub>ZZ</sub>, in this case you will find the function introduced in Section 3.100.24 quite useful.

**4. ICSS (Iso-chemical shielding surface):** The original paper of ICSS is *J. Chem. Soc., Perkin Trans.*, **2**, 1893 (2001). This method analyzes aromaticity by visualizing isosurface of magnetic shielding value around the molecule. See Section 3.200.4 for introduction and Section 4.200.4 for example. The main drawback of this method is that calculating grid data of magnetic

shielding values is fairly time-consuming.

**5. HOMA (Harmonic oscillator measure of aromaticity):** HOMA measures aromaticity based on bond lengths in the ring of interest. See Section 3.100.13 for introduction and Section 4.100.13 for example.

**6. Bird index:** The same as above.

**7. Multi-center bond order (MCBO):** MCBO is an indicator of electron delocalization ability over a ring and is the aromaticity index I most strongly recommended. Larger MCBO value corresponds to stronger aromaticity. See Section 3.11.2 for introduction. Some applications of MCBO in aromaticity studies can be found in *J. Phys. Org. Chem.*, **26**, 473 (2013), *Phys. Chem. Chem. Phys.*, **2**, 3381 (2000) and *J. Phys. Chem. A*, **109**, 6606 (2005). It is straightforward to discuss  $\pi$  and  $\sigma$  aromaticities separately by MCBO, that is before calculating MCBO value, first set occupation number of all  $\sigma$  and  $\pi$  MOs to zero respectively by subfunction 22 of main function 100.

Note that the definition of MCBO in many literatures differ with that in Multiwfn by a constant coefficient. The calculation cost of MCBO for six-membered ring can be ignored, however the cost increases exponentially with the number of atoms in the ring.

**8. ELF- $\sigma/\pi$ :** The ELF calculated solely based on  $\pi$  orbitals and all other orbitals are referred to as ELF- $\pi$  and ELF- $\sigma$ , respectively. It was argued that the value of bifurcation point of ELF- $\pi$  (ELF- $\sigma$ ) is an indicator of  $\pi$  ( $\sigma$ ) aromaticity, some applications can be found in *J. Chem. Phys.*, **120**, 1670 (2004), *J. Chem. Theory Comput.*, **1**, 83 (2005) and *Chem. Rev.*, **105**, 3911 (2005). An example of calculating ELF- $\sigma/\pi$  is given in Section 4.5.3. I do not think ELF- $\sigma/\pi$  is a very ideal method for measuring aromaticity, mostly because this method often suffers from ambiguity (you will recognize this point if you have used this method to study many practical systems). Also note that the bifurcation values of ELF- $\sigma/\pi$  in a lot of literatures are incorrect; if you try, you will find it is impossible to reproduce their results at all. (So do not always believe literatures but believe in yourself!)

**9. PDI (Para-delocalization index):** This aromaticity index is only applicable to six-membered rings. PDI was first proposed in *Chem. Eur. J.*, **9**, 400 (2003) and reviewed in *Chem. Rev.*, **105**, 3911 (2005). Please check Section 3.18.6 for introduction of PDI and Section 4.15.2 for example of using PDI.

**10. ATI (Average two-center indices):** ATI was first proposed in *J. Phys. Org. Chem.*, **18**, 706 (2005). In fact ATI does not contain any new idea, it simply replaces the delocalization indices involved in PDI formula with corresponding Mayer bond orders, and according to the discussions in *J. Phys. Chem. A*, **109**, 9904 (2005), there is no essential difference between Mayer bond order and delocalization index in physical nature. If you would like to use ATI, you can directly calculate Mayer bond order by Multiwfn and then manually calculate ATI according to its formula.

**11. PLR (Para linear response index):** As ATI, PLR is also very akin to PDI. The only difference between PLR and PDI is that the delocalization indices in PDI are replaced with corresponding condensed linear response kernels. Original paper of PLR is *Phys. Chem. Chem. Phys.*, **14**, 3960 (2012). You can check Section 3.18.9 for introduction of PLR and Section 4.15.2 for example of using PLR.

**12.  $\Delta$ DI:** This method was proposed in *Chem. Eur. J.*, **9**, 400 (2003) for measuring aromaticity of 5-membered systems. Consider below case



The  $\Delta\text{DI}$  is simply defined as the difference of delocalization index (DI) between the formal C=C bond and the C-C bond. The DI can be either calculated by fuzzy atomic space analysis module or by basin analysis module (though the definition of atomic spaces are different in these two module, the results are similar in common). In fact, you can also use Mayer bond order instead of DI. I do not believe  $\Delta\text{DI}$  is reliable, since aromaticity is an overall property of a system, while the delocalization over C-X bond is completely ignored in  $\Delta\text{DI}$ .

**13. FLU and FLU- $\pi$  (Aromatic fluctuation index):** They were proposed in *J. Chem. Phys.*, **122**, 014109 (2005). See Section 3.18.7 for introduction and Section 4.15.2 for example.

**14. RCP properties:** In *Can. J. Chem.*, **75**, 1174 (1997) it was shown that the density and the curvature of density perpendicular to the ring plane at ring critical point (RCP) closely relate to aromaticity of the ring. The larger the density, or the more negative the curvature, the larger the aromaticity. You can use topology analysis module of Multiwfn to apply this method. Detail introduction can be found in Section 3.14.6, an example is given in Section 4.2.1.

**15. Shannon aromaticity:** This method was proposed in *Phys. Chem. Chem. Phys.*, **12**, 4742 (2010), which measures aromaticity based on electron density at bond critical points (BCP) in the ring. See Section 3.14.6 for introduction and the example given in Section 4.2.1.

**16. EL index:** The idea of EL index is quite similar to HOMA, the most prominent difference is that the bond lengths in HOMA formula are replaced with electron density ellipticity at BCPs in the ring. For more detail see the original paper *Struct. Chem.*, **23**, 1173 (2012). Electron density ellipticity at BCPs can be directly calculated by topology analysis module of Multiwfn. Since the ellipticity at BCP is usually unclear for strongly polar bonds, EL index may be unreliable for the ring containing heteroatoms. In addition, EL index shares the same drawback of HOMA, that is reference system is need. If reference system cannot be obtained, such as the case of metal clusters, this method does not work.

#### 4.A.4 Predict reactive sites

There are numerous methods able to predict reactive site of electrophilic, nucleophilic and radical reactions, and almost all of them are supported by Multiwfn. In this section, I will summary and briefly introduce the methods available in Multiwfn. The interested reader is highly recommended to take a look at *Acta Phys.-Chim. Sinica*, **30**, 628 (2014) (in Chinese, <http://www.whxb.pku.edu.cn/EN/abstract/abstract28694.shtml>), in which various methods for predicting electrophilic sites are carefully introduced and thoroughly compared. You may also find the slideshow "Predicting reactive sites" in "Related resources and posts" Section of Multiwfn website useful.

**1 Electrostatic potential (ESP).** If you are not familiar with ESP, please consult corresponding introduction in Section 2.6. Since electrophile (nucleophile) locally carries negative (positive) charge, and thus tends to be attracted to the region where ESP is negative (positive), the position and value of minima (maxima) of ESP on molecular vdW surface is often used to reveal favorable site of electrophilic (nucleophilic) attack. ESP analysis can be realized via quantitative

molecular surface analysis module, see Section 4.12 for detailed introduction and Section 4.12.1 for example. There are also alternative ways to study ESP; as illustrated in Section 4.12.3, the average of ESP on local vdW surface corresponding to each atom is also very useful, and this approach is more reliable and robust than analyzing ESP extrema on vdW surface. For planar system, one can also calculate and compare the ESP value above 1.6Å (approximately equal to vdW radius of carbon) of molecular plane from different atoms to examine their reactivities; to do this, you need to use main function 1, which directly outputs various real space function values at given points.

However, as shown in *Acta Phys.-Chim. Sinica*, **30**, 628 (2014), ESP is usually not a reliable property for predicting reactive sites.

**2 Average local ionization energy (ALIE).** If you are not familiar with ALIE, please consult corresponding introduction in Section 2.6. ALIE can be studied in analogous ways to ESP. The most common way to predict reactive sites in terms of ALIE is analyzing minima of ALIE on vdW surface, see Section 4.12.2 for example. Also, you can study average of ALIE on local vdW surface or evaluate ALIE above 1.6Å of molecular plane for planar system.

Note that ALIE analysis is applicable to electrophilic and radical attacks, but it is useless for nucleophilic attack. However, another similar real space function named local electron affinity (LEA) may be useful for this purpose, see *J. Mol. Model.*, **9**, 342 (2003). LEA can be studied in Multiwfn via user-defined function, see Section 2.7 for detail. According to my experience, LEA is not well defined and usually does not work well.

**3 Atomic charges.** It is easy to understand that favorable electrophilic and nucleophilic reactive sites should carry negative and positive atomic charges respectively, so that they can attract electrophile and nucleophile to attack them. Multiwfn supports a lot of methods to calculate atomic charges, see Section 3.9 for introduction and Section 4.7 for some instances. Among the available atomic charges, the best one for predicting reactive sites purpose may be Hirshfeld, interested readers are suggested to consult *J. Phys. Chem. A*, **118**, 3698 (2014). Do not use Mulliken charges, which may be the worst one, though it is the most popular charge model.

**4 Frontier molecular orbital (FMO) theory.** Atom with larger contribution to HOMO (LUMO) is more likely to be the preferential site of electrophilic (nucleophilic) attack. Multiwfn supports many kinds of methods to calculate molecular orbital composition, see Section 3.10 for introduction and Section 4.8 for examples. Commonly I suggest using Becke or Hirshfeld method. Mulliken method works equally well if no diffuse functions are presented. NAO method is also a good choice, but not suitable for analyzing virtual MOs. Besides, you can also directly visualize the isosurface of MOs by main function 0 to discuss their compositions.

**5 Fukui function and condensed Fukui function.** The Fukui function proposed in *J. Am. Chem. Soc.*, **106**, 4049 (1984) by Parr is the most prevalently used method for predicting reactive sites nowadays. Please consult Section 4.5.4 for introduction and illustration. Fukui function is a real space function, which is commonly studied by means of visualization of isosurface. In order to facilitate quantitative comparison between difference sites, one can calculate condensed Fukui function based on atomic charges, please consult Section 4.7.3. In addition, as demonstrated in Section 4.12.4, the Fukui function can also be investigated in combination with local quantitative molecular surface analysis technique.

**6 Dual descriptor and condensed dual descriptor.** As demonstrated in *Acta Phys.-Chim. Sinica*, **30**, 628, the dual descriptor proposed in *J. Phys. Chem. A*, **109**, 205 (2005) may be the

most robust method for predicting reactive sites, at least for electrophilic reaction. Like Fukui function, dual descriptor also has condensed version. Dual descriptor and the condensed version are introduced in Section 4.5.4 and 4.7.3, respectively.

#### 4.A.5 Study weak interactions

There are a lots of ways to characterize weak interactions, and most of them are supported by Multiwfn, here I give you a brief summary. If you can read Chinese, I suggest reading my post "An overview of the weak interaction analysis methods supported by Multiwfn" (<http://sobereva.com/252>), in which this topic is discussed more deeply and extensively.

(1) AIM topology analysis is a very popular method for studying both strong and weak interactions. Its use in weak interaction analysis is partially illustrated in Section 4.2.1.

(2) RDG analysis proposed in 2010 may be viewed as an extension of AIM analysis, this method rapidly became quite popular after it was proposed. The example of using RDG analysis is given in Section 4.100.1. RDG analysis is also able to be employed to study weak interaction in dynamic environment such as molecular dynamic simulation, see the introduction in Section 3.200.1 and the accompanied example in Section 4.200.1. Integrating domain of RDG is a useful way to discuss weak interactions quantitatively, examples are provided in Section 4.200.14.

(3) Electrostatic potential (ESP) analysis. ESP has been introduced in Section 2.6, this is a extremely important real space function for studying electrostatic dominated weak interactions. There are many different ways to carry out ESP analysis:

a) Visually studying ESP color-mapped molecular vdW surface, this analysis can be used to quickly figure out potential electrostatic interaction sites and qualitatively study interaction strength. See the end of Section 4.12.1 and *J. Mol. Model.*, **13**, 291 (2007) for example.

b) Studying ESP minima and maxima on molecular vdW surface. This can done by quantitative molecular surface analysis module, see Section 4.12.1 for example and Section 3.15 for more details. The value of these ESP extrema on vdW surface strongly correlate with electrostatic interaction energies, and you can find many papers have used this method, for example *Phys. Chem. Chem. Phys.*, **15**, 14377 (2013), *J. Mol. Model.*, **13**, 305 (2007), *Int. J. Quantum. Chem.*, **107**, 3046 (2007), *Phys. Chem. Chem. Phys.*, **12**, 7748 (2010), *J. Mol. Model.*, **14**, 659 (2008), *J. Mol. Model.*, **18**, 541 (2012), *J. Mol. Model.*, **15**, 723 (2009), Chapter 6 of book *Practical Aspects of Computational Chemistry* (2009).

c) Superposition analysis of ESP contour map. This method was proposed by Tian Lu in *J. Mol. Model.*, **19**, 5387 (2013), it is quite vivid, easy-to-use and powerful. It was demonstrated that stability of complex configurations can be fairly well predicted by this method. Section 4.4.4 showed how to plot ESP contour map.

d) In *J. Phys. Chem. A*, **118**, 1697 (2014), the authors showed that by making use of ESP at nuclear positions the electrostatic dominated intermolecular interaction energies can be very accurately predicted. See Section 4.1.2 for introduction and example.

(4) Atomic charge analysis. Atomic charge is a very simple and intuitive model for describing charge distribution and can be used to analyze the strength of electrostatic interaction between different sites. The functions for calculating atomic charges are introduced in Section 3.9, and some practical examples are given in Section 3.7.

(5) Bond order and delocalization index (DI) analysis. Commonly weak interactions are

dominated by electrostatic and/or vdW interactions, so bond order and DI analysis, which mainly reflect covalent character are often not useful in these cases. However, for "strong" weak interactions, such as low-barrier hydrogen bonds (LBHB) and charge-assisted halogen bonds, covalent contribution may be not negligible, and thus bond order and DI analysis can be applied. Bond order calculations are illustrated in Section 4.9. In Multiwfn, DI can be calculated based on fuzzy atomic space or AIM basin, the former is equivalent to fuzzy bond order, while the latter can be evaluated in basin analysis module, see example in Section 4.17.1.

**(6)** ELF analysis. In *Theor. Chem. Acc.*, **104**, 13 (2000), Fuster and Silvi defined CVI index based on ELF to classify strength of H-bonds. *J. Phys. Chem. A*, **115**, 10078 (2011) employed this method to study a large amount of resonance-assisted hydrogen bonds and find this index is in good correlation with other H-bond strength indices. CVI index can easily calculated in Multiwfn by plotting ELF curve between the two interacting atoms via main function 3. There are also other papers using ELF to study H-bonds, e.g. *Chem. Rev.*, **111**, 2597 (2011).

**(7)** Charge variation analysis. Weak interactions often accompanied by charge transfer and polarization, therefore studying how the electrons are transferred between or within molecules, as well as how the electron density is polarized due to the presence another molecule are important. There are many available ways to investigate these points:

**a)** Plotting difference map of electron density between complex and monomers. This is the most straightforward and intuitive way to study variation of electron density. The procedure is illustrated in Section 4.5.5.

**b)** Plotting charge displacement curve. After generating grid data of density difference, in order to quantitatively study the charge variation in a direction, you can plot charge displacement curve, see Section 3.16.14 for introduction and Section 4.13.6 for example.

**c)** Variation of atomic charges of monomers in their isolated states and in complex state can quantitatively and clearly show how the electrons are transferred between different atoms/fragments due to the interaction.

**d)** After generating grid data of electron density difference between complex and monomers, you can use basin analysis module to integrate basin of density difference to study amount of electron variation in various characteristic regions (e.g. the region corresponding to  $\sigma$ -hole). You can consult the example in Section 4.17.4.

**e)** Charge decomposition analysis (CDA). CDA is used to reveal underlying details of charge transfer, the amount of donation and back-donation of electrons between two fragments due to various complex MOs can be studied. In addition, the CDA module of Multiwfn can tell you how the fragment MOs are mixed and hence yield complex MOs. CDA is commonly applied to strong interaction, but it may be also useful for exploring weak interactions. The theory of CDA is introduced in Section 3.19, practical examples are given in Section 4.16.

**f)** Multiwfn has a function dedicated to analyze charge transfer in electron excitation based on electron density difference, many important quantities characterizing the transfer can be obtained, see Section 3.21.3 for introduction and 4.18.3 for example. Based on the grid data of electron density difference between complex and monomers, this function may be also useful for studying charge transfer due to weak interaction.

**(8)** Hirshfeld and Becke surface analysis. This kind of analysis is extremely useful for revealing weak interaction in molecular crystals, see the example in Sections 4.12.5 and 4.12.6 as well as theory introduction in Section 3.15.5.

(9) LOLIPOP index is useful for measuring  $\pi$ - $\pi$  stacking ability, see the introduction in Section 3.100.14 and the example in Section 4.100.14.

(10) Energy decomposition analysis is a kind of important approaches for characterizing the nature of weak interactions, physical components of total interaction energy can be separately obtained. Multiwfn is capable of performing very simple energy decomposition analysis, see Section 4.100.8 for example.

(11) Source function analysis is defined in the framework of AIM theory. Gatti et al. suggested using source function to study both strong and weak interactions. Introduction of source function can be found in Section 2.6, and tutorial of performing source function analysis is given in Section 4.17.5. A thorough review is Struct. & Bond., **147**, 193 (2010), in which H-bond analysis is involved.

(12) Mutual penetration distance of vdW surfaces. For the same kind of weak interaction, generally the larger the penetration of vdW surface, the stronger the interaction strength. For a non-covalently interacting atom pair AB, the difference between the distance of A-B and the sum of their non-bonded radii is termed as mutual penetration distance. The non-bonded atomic radius is the closest distance between a nucleus and the molecular vdW surface, and can be obtained by option 10 in post-process interface of quantitative molecular surface analysis module of Multiwfn.

(13) Atomic multipole moment analysis. The definition of atomic multipole moment can be found in Section 3.18.3. Atomic multipole moment measures the anisotropy distribution of electron density around an atom, which has important impact on interatomic electrostatic interactions. See Section 7.4.3 of the Bader's book *Atoms in molecules-A quantum theory* for illustrative examples. In Multiwfn, atomic multipole moment can be calculated by both fuzzy space analysis module and basin analysis module, for the latter case see Section 4.17.1 for example.

(14) Orbital overlap. For weak interactions involving orbital interaction, you can use Multiwfn to study orbital overlap, which is closely related to orbital interaction strength. The example Section in 4.100.15 illustrated how to calculate intermolecular orbital overlap integral. Section 4.0.2 exemplified how to visualize overlap degree of two NBO orbitals, high (low) overlap degree commonly implies large (small) second-order perturbation energy E(2) between the two NBOs.

(15) As demonstrated in *J. Mol. Model.*, **19**, 2035 (2013), interaction energy of halogen-bond complexes is well correlated with the properties of (3,-1) critcial point of Laplacian of electron density at  $\sigma$ -hole location. The topology analysis of Laplacian of electron density can be conveniently realized in main function 2. Section 4.2.2 showed how to perform topology analysis for LOL, however you can use the same method to analyze Laplacian of electron density.

There are also other possibly ways to study weak interactions, but they are not directly relevant to Multiwfn. These methods include: NBO E(2) and NBO deletion analyses (see the tutorials in NBO official website), rehybridization analysis (specific for H-bond, based on natural population analysis), variation of bond length and vibrational frequency, Mayer energy decomposition analysis (*Phys. Chem. Chem. Phys.*, **8**, 4630 (2006)), magnetically induced current (*Phys. Chem. Chem. Phys.*, **13**, 20500 (2011)), interacting quantum atoms (IQA, supported by AIMALL, see *J. Phys. Chem. A*, **117**, 8969 (2013) for example), SAPT analysis (supported by Molpro, PSI4 etc. see *WIREs Comput. Mol. Sci.*, **2**, 254 (2012)), ETS-NOCV (supported by ADF,

see *J. Chem. Theory Comput.*, **5**, 962 (2009)).

#### 4.A.6 Calculate odd electron density and local electron correlation function

##### Part 1: Odd electron density

Some papers calculate the so-called odd electron density (OED), its was originally defined in *Chem. Phys. Lett.*, **372**, 508 (2003), and employed in many papers, e.g. *Theor. Chem. Acc.*, **130**, 711 (2011) and *J. Phys. Chem. C*, **116**, 19729 (2012). Here I introduce how to plot it by using Multiwfn in combination with .wfn file produced by Gaussian.

Spatial natural orbitals are yielded by diagonalizing total density matrix and have occupation number within 0 and 2.0. The OED of the  $k$ th natural orbital is defined as

$$\rho_k^{\text{odd}}(\mathbf{r}) = \min(2 - n_k, n_k) \rho_k(\mathbf{r})$$

where  $\rho_k(\mathbf{r})$  and  $n_k$  are its electron density and occupation number, respectively. Thus for  $n_k \leq 1$ , the prefactor corresponds to occupation number, while for  $n_k \geq 1$ , the prefactor corresponds to the complement to achieve a closed shell. In other words, the  $\min(2-n_k, n_k)$  term can be regarded as the probability of the electron to be unpaired in this orbital.

The total OED is defined as the summation of OED for all natural orbitals:

$$\rho^{\text{odd}}(\mathbf{r}) = \sum_k \rho_k^{\text{odd}}(\mathbf{r})$$

Now we calculate OED for a closed-shell system OC-BH<sub>3</sub> at CCSD level (while at HF/DFT level, this quantity is obviously zero everywhere). The Gaussian input file can be found in *examples\COBH3\_CCSD.gjf*, note that *density out=wfn* keywords are used. The resulting file *examples\COBH3\_CCSD.wfn* contains all CCSD natural orbitals.

We first calculate total OED. Boot up Multiwfn and input

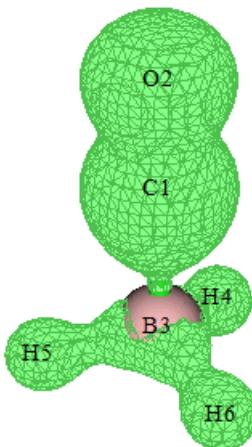
*examples\COBH3\_CCSD.wfn*

```
6
26 // Modify occupation number
0 // Select all orbitals
odd // Take min(2-nk, nk) as occupation number for all orbitals
q // Return
-1
```

Then we plot isosurface map of electron density as usual

```
5
1
2
-1
```

Then we set isovalue to 0.005, you will see the total OED, as shown below. Although the use of OED in above mentioned papers aims to study biradical character, *in my personal viewpoint, this function is also useful to reveal where electron correlation is significant*. As you can see in the below graph, electron correlation is very strong in the multiple-bonds region of CO.



Next, we plot OED for natural orbital 11. What we need to do first is cleaning the occupation number for all other orbitals. Close the GUI and input

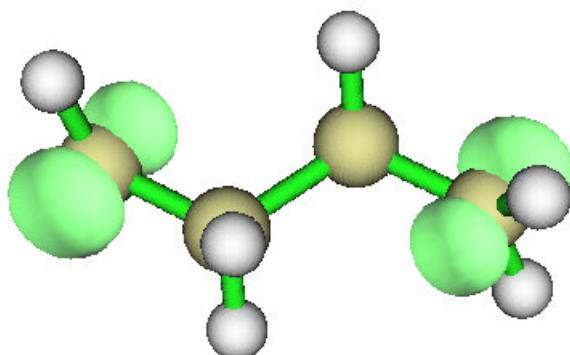
```

0
6
26
1-10
0 // Clean the occupation number for orbitals 1 to 10
12-57
0 // Clean the occupation number for orbitals 12 to 57

```

Then return to main menu and plot electron density as usual. That's all.

Below we plot total OED for a typical biradical system  $C_4H_8$  at M06-2X level. In this case, unrestricted open-shell calculation is needed and *guess=mix* keyword should be used to achieve symmetry-broken state. In addition, *pop=no out=wfn* must be specified so that spatial natural orbital will be generated by mixing alpha and beta density matrix, diagonalization and then be outputted to .wfn file. The natural orbitals obtained by such a UHF/UDFT calculation are sometimes referred to as unrestricted natural orbitals (UNO). The Gaussian input file for producing the .wfn file is *examples\c4h8-UNO.gjf*, and the resulting .wfn file is *examples\c4h8-UNO.wfn*. Please use this file to plot total OED like above example, the isosurface map with isovalue of 0.02 should look like below (its character is quite similar with spin density map)



## Part 2: Local electron correlation functions

The local electron correlation functions proposed in *Phys. Chem. Chem. Phys.*, **18**, 24015 (2016) and discussed in *J. Chem. Theory Comput.*, **13**, 2705 (2017) are very useful real space functions to reveal total, dynamic and nondynamic electron correlation in various molecular regions. The definition of these function can be found in entry 87, 88 and 89 of Section 2.7. As you can see, their forms are closely related to OED. Now let us plot local total electron correlation functions  $I_T$  for OC-BH<sub>3</sub>.

Set "iuserfunc" in settings.ini to 87, then boot up Multiwfn and input

*examples\COBH3\_CCSD.wfn*

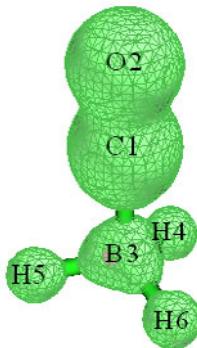
5

100 // User-defined function, now it corresponds to  $I_T$

2 // Medium quality grid

-1 // Visualize isosurface

Set isovalue to 0.013, then you will see



This graph is rather similar with the isosurface map of OED. Since  $I_T$  is a real space function specific for revealing electron correlation, our observation clearly demonstrates that OED is also capable of exhibit electron correlation.

Local electron correlation function has another two forms, namely  $I_D$  and  $I_{ND}$ , which aim for representing dynamic and nondynamic electron correlation, respectively. They can be plotted with the same way as shown above, but you need to set "iuserfunc" to 88 and 89, respectively.

Plotting individual contribution to local electron correlation functions is also possible, you can screen uninteresting natural orbitals by setting their occupation numbers to zero via suboption 26 of main function 6.

Using subfunction 4 of main function 100 you can integrate local electron correlation functions over the whole space, the result indicates the magnitude of electron correlation for the whole system. For example, we return to main menu and input

100

4 // Integrate a real space function over the whole space

100 // User-defind function

The result, which may be referred to as total electron correlation index, is 1.576. Repeat this calculation for dynamic and nondynamic electron correlation functions, you will find the resulting indices are 1.267 and 0.309, respectively. Evidently, dynamic correlation governs the total electron correlation effect for present system.

# 5 Skills

## 5.1 Make Multiwfn support more quantum chemistry programs

Although currently Multiwfn is able to directly accept Molden input file (.molden) as input file, only the file generated by a few programs is formally supported (see the related description in Section 2.5). If the Molden input file is generated by other programs then the analysis result may be incorrect. For these cases, you can use Molden2aim program written by W. Zou (<https://github.com/zorkzou/Molden2AIM>) to convert Molden input file to .wfn/.wfx/.47 file, or use this program to produce standardized Molden input file.

Using Molden2aim is easy. First move the Molden input file (e.g. ltwd.molden) into the directory where molden2aim.exe is placed, then properly modify its setting file m2a.ini, then boot up Molden2aim and follow its prompts to input commands, finally you will get ltwd\_new.molden (standardized Molden input file) and may be other files (.wfn, .wfx, etc.).

Since Molden2aim v2.0.5, orbital spin-types are explicitly written at the end of the converted wfn file (\$MOSPIN \$END field), this information is automatically loaded by Multiwfn.

Molden2aim can output GTFs with angular moment up to  $g$ . Although  $g$  GTFs is not originally defined in wfn format, these  $g$  GTFs can also be correctly identified and loaded into Multiwfn.

The "charge" field of the wfn file outputted by Molden2aim is the serial number of the element in periodic table rather than the effective nuclear charges, even if effective core potential (ECP) is used. This treatment is inconsistent with the wfn file outputted by Gaussian, in which "charge" is effective core charges when ECP is used (e.g. the "charge" of Au under Lanl2DZ is 19.0). So, if ECP is used and you want to calculate electrostatic potential, do not forget to modify "charge" field in the wfn file outputted by Molden2aim to effective nuclear charges.

## 5.2 Running Multiwfn in silent mode

Multiwfn aims for ease of use, so it is designed as an interactive program. Nevertheless Multiwfn can also run in silent mode, by which you do not need to press any keys during Multiwfn running. For example, you want to obtain the graph in example 4.4.1 silently, you need to write an inputstream file first, the content is (red texts are comments):

```
4
1
1
200, 200
```

```

2
0
0 ← Option 0: save graph to current directory

```

I suppose that the inputstream file is named as “4.4.1.txt”, I have already provided this file in “examples” directory. Now change “isilent” parameter in “settings.ini” from 0 to 1, this step tells Multiwfn to forbid any graph or GUI popping up automatically during running (otherwise you have to close the window by clicking mouse button). Then run this command in MS-DOS (to enter MS-DOS from Windows, click “Start”-“run” and type “cmd”): *Multiwfn hcn.wfn < 4.4.1.txt > medinfo.txt*, here I assume that Multiwfn.exe, 4.4.1.txt and hcn.wfn are in current directory. After a few seconds, you will find the expected graphic file appears in current directory, from medinfo.txt you can find all intermediate information outputted by Multiwfn (the same as in interactive mode).

What does the content in inputstream file mean? The answer is: the texts in each line of inputstream file are just what you need to input in interactive mode, you can redo example 4.4.1 to ensure it is true. It is easy to write a new inputstream file by following the prompts in interactive mode. The symbol “<” and “>” are known as redirection operator, they respectively tell Multiwfn that the contents in 4.4.1.txt are inputstream, while the outputstream should be stored into medinfo.txt. This redirection mechanism is not provided by Multiwfn but provided by operation system. Notice that the name of input file is missing in inputstream file, because it appears as an argument.

You may have noted that when the task is finished, some errors like below appear. They are not really errors, and hence you can safely ignore them.

```

forrtl: severe (24): end-of-file during read, unit -4, file CONIN$  

Image          PC          Routine         Line      Source  

Multiwfn.exe   00588F1A  Unknown        Unknown    Unknown  

Multiwfn.exe   00586438  Unknown        Unknown    Unknown  

Multiwfn.exe   00530B3A  Unknown        Unknown    Unknown  

.....

```

Another example, assume that you want to save detail compositions of orbital 1 to 3 of COCl2.fch, just create an inputstream file dubbed “orbana\_1\_3.in” with below content:

```

8 ← Orbital composition analysis
1 ← Mulliken method
1 ← Orbital 1
2 ← Orbital 2
3 ← Orbital 3

```

Then run the command: *Multiwfn COCl2.fch < orbana\_1\_3.in > orbana\_1\_3.txt*.

If you are a Linux or Mac OS user, you can also make use of "echo" command to avoid writting an inputstream file to run Multiwfn silently. The goal of the last example can be equivalently realized by running this command:

```
echo -e "8\n1\n1\n2\n3" / Multiwfn COCl2.fch > orbana_1_3.txt
```

Each “\n” means pressing ENTER button once.

Alternatively, you can add below lines into your script file:

```
Multiwfn COCl2.fch > orbana_1_3.txt << EOF
8
1
1
2
3
EOF
```

## 5.3 Running Multiwfn in batch mode (for Windows)

If you are familiar with writing shell-scripts and you have read last section, you must have already know how to use Multiwfn to process a batch of files, it is indeed very easy. Assume that you want to generate cube files of ELF for these files: ultravox.wfn, chinaski.fch, strawberry\_egg.wfn, you should compile a plain text file named “batchrun.bat” with below content:

```
Multiwfn ul travox.wfn < genELFcub.txt > nul
move ELF.cub ul travox.cub
Multiwfn chinaski.fch < genELFcub.txt > nul
move ELF.cub chinaski.cub
Multiwfn strawberry_egg.wfn < genELFcub.txt > nul
move ELF.cub strawberry_egg.cub
del nul
```

where "genELFcub.txt" is inputstream file for generating ELF cube file, its content is

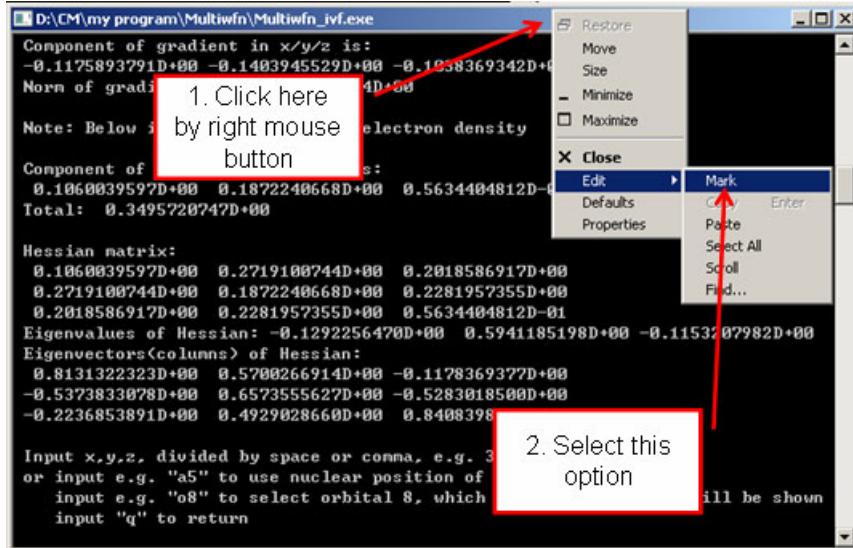
```
5
9
2
2 ← Option 2: Exporting cube file in current directory
```

If you cannot understand the meaning, read last section and consult example 4.5.1.

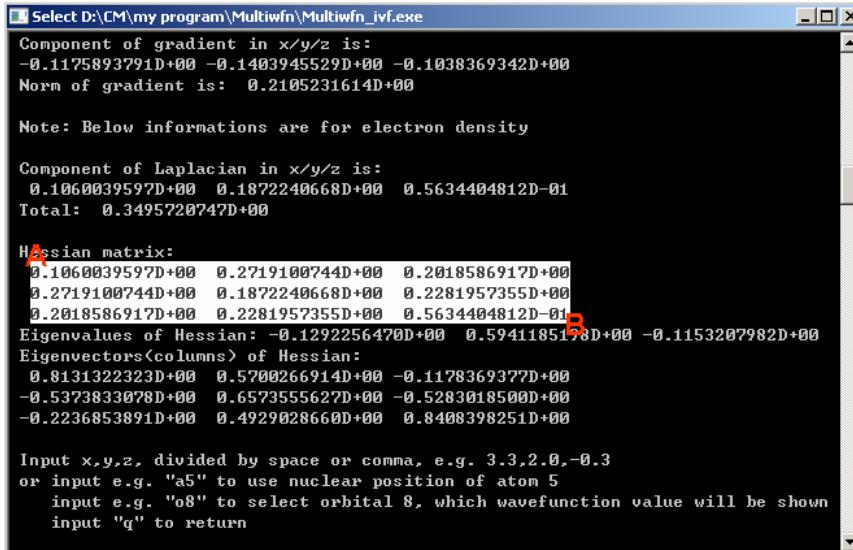
Now, double click the icon of "batchrun.bat" or input the command *batchrun* in MS-DOS, the work will start and then the three ELF cube files will be generated in current folder sequentially.

## 5.4 Copy outputs from command-line window to clipboard

Sometimes the outputs of Multiwfn on command-line window are needed to be stored permanently or transported to third-part softwares via plain text file. Here I describe how to copy these outputs to Windows clipboard, assuming that you want to copy Hessian matrix of electron density.



After you select "Mark", drag left mouse button from point A to point B



Then press ENTER button, the information highlighted by white rectangle will be stored to clipboard, you can paste them to anywhere, such as plain text file.

For Mac OS or Linux system running in graphical environment, you can also copy the output of Multiwfn from console to plain text file by similar manner.

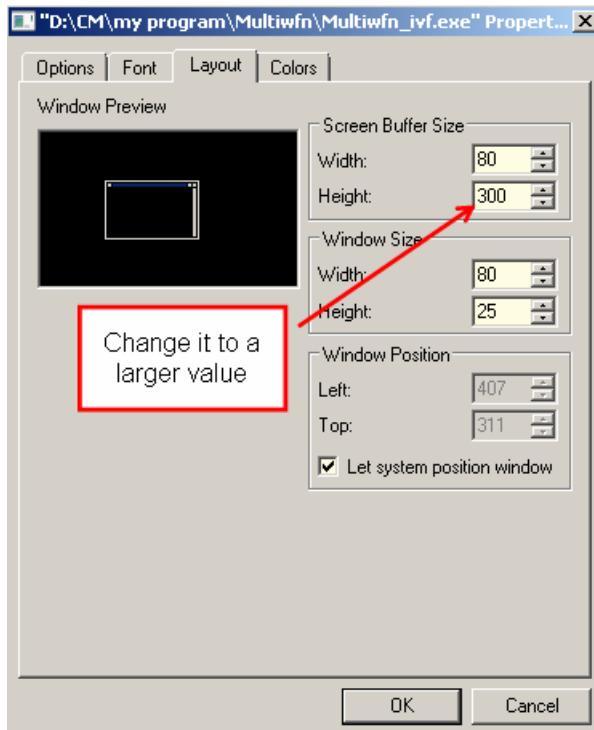
## 5.5 Make command-line window capable to record more outputs

Occasionally you may find command-line window cannot record entire outputs of Multiwfn. For example, you select option 6 in wavefunction modification module to get density matrix for a relative big wavefunction, however only the last part of the matrix can be found in the command-line window. The solution of the problem is to enlarge buffer size of the window, please follow below steps.

Boot up Multiwfn, click title of the window by right mouse button, click "Properties", select "Layout" page, you will find the default buffer size of the window is 300 (see the screenshot below), that means only up to 300 lines can be recorded in the window, which is obviously too small. Change the value to a larger value, for example 9999, and then click OK button. After that you will find the window capable to record much more outputs (If the complete output still cannot be recorded, enlarge buffer size again).

The buffer size setting is saved permanently in system, you needn't to set this value again at next time you boot up Multiwfn.

For Linux and Mac OS, you can also find similar option used to set buffer size of terminal.



## 5.6 Rapidly load a file into Multiwfn

Probably sometimes you feel inputting the path of input file is cumbersome, especially when the path is very long. Below I provide you some tricks, which make this step much more easier.

If you want to rapidly load a file into Multiwfn without inputting its path, you can boot up Multiwfn and then directly drag the icon of the file into the Multiwfn command-line window.

In Windows platform, an even more simple method is directly dragging the file onto the icon of "Multiwfn.exe", then the file will be automatically loaded into Multiwfn. Notice that in this situation, the "current folder" is the position of the input file.

If directly inputting letter *o*, the file last time loaded will be loaded again, whose path is recorded as *lastfile* variable in settings.ini file.

Assume that the file you last time loaded is C:\sob\lover\K-ON\Mio.wfn, and this time you want to load C:\sob\lover\K-ON\Azusa.wfn, you can simply input ?azusa.wfn, namely the path of the folder last time involved can be replace with a question mark.

# Appendix

## 1 Setting up environment variable for Gaussian in Windows

If the error “No executable for file 11.exe” occurs when Multiwfn is invoking Gaussian, that means the environment variable “GAUSS\_EXEDIR“ has not been set properly, therefore Gaussian does not know where to find 11.exe. Here I show you how to set it.

- (1) Windows XP users: Enter “control panel”-“System properties”-“Advanced”
- (2) Windows 7 users: Enter “control panel”-“System”-“Advanced system setting”-“Advanced”

Then click “Environment variables” button, then click “New” button (in “User variables” frame), input *GAUSS\_EXEDIR* in variable name, input the install directory of Gaussian in variable value (e.g. *d:\study\g09w\*, assuming that g09.exe is in this folder). Afterwards when Gaussian is invoking, Gaussian will search executable files of each link (such as 11.exe) in this folder.

## 2 The routines for evaluating real space functions

Below are the routines in function.f90 file. You can make use of them to construct new real space function by yourself. For more details please check the comments in the code of corresponding routine.

### **Calculate real space functions:**

function calcfuncall: A warpper for calculating any supported real space function at a given point

function userfunc: User defined real space function  
 function fmo: Orbital wavefunction value  
 function fdens: Electron density  
 function fsplndens: Spin or Alpha or Beta electron density  
 function fgrad: Gradient (x,y,z components or its norm) of density, or reduced density gradient (RDG)

function flapl: Laplacian of electron density (xx or yy or zz part or total)  
 function Lagkin: Lagrangian kinetic G(r), or its components  
 function Hamkin: Hamiltonian kinetic K(r), or its components  
 function signlambda2rho: Sign(lambda2(r))\*rho(r)  
 subroutine signlambda2rho\_RDG: Calculate Sign(lambda2(r))\*rho(r) and RDG at the same time  
 function signlambda2rho\_prodens: Sign(lambda2(r))\*rho(r) with promolecular approximation

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function RDGprodens: RDG with promolecular approximation  
subroutine signlambda2rho\_RDG\_prodens: Calculate Sign(lambda2(r))\*rho(r) and RDG at the same time with promolecular approximation  
function ELF\_LOL: ELF and LOL  
function avglocion: Average local ionization energy  
function loceleaff: Local electron affinity  
function linrespkernel: Approximate form of DFT linear response kernel for close-shell  
function pairfunc: Exchange-correlation density, correlation hole and correlation factor  
function srcfunc: Source function  
function infoentro: Shannon information entropy function or Shannon entropy density  
function totesp: Total ESP  
function nucesp: ESP from nuclear or atomic charges  
function eleesp: ESP from electrons  
subroutine planeesp: Calculate ESP in a plane  
subroutine espclib: Calculate grid data of ESP from electrons  
function twoorbnorm: Product of norm of two orbitals  
function beckewei: Generate Becke weighting function  
function densellip: Ellipticity of electron density and  $\eta$  index  
function xLSDA: Integrand of LSDA exchange functional  
function xBecke88: Integrand of Becke88 exchange functional  
function cLYP: Integrand of LYP corelation functional  
function DFTxcfunc: Various kinds of integrand of DFT exchange-correlation functionals  
function DFTxcpot: Various kinds of DFT exchange-correlation potentials  
function weizsacker: Integrand of Weizsacker functional (steric energy)  
function stericpot: Steric potential, which negative value is one-electron potential  
function stericcharge: Steric charge  
function stericforce: Magnitude of steric force  
function paulipot: Pauli potential  
function pauliforce: Magnitude of Pauli force  
function paulicharge: Pauli charge  
function Fisherinfo: Fisher information density  
function calcatmdens: Promolecular density calculated based on Lagrange interpolation of built-in atomic radial density  
function PAEM: Potential acting on one electron in a molecule  
function SEDD: Single exponential decay detector (SEDD)  
function DORI: Density Overlap Regions Indicator (DORI)  
function localcorr: Local electron correlation function

### Calculate derivatives of real space functions:

subroutine orbdrv: Calculate wavefunction value of a range of orbitals and their derivatives at given point, up to third-order  
subroutine EDFrho: Calculate contribution from EDFs (recorded in wfx file) to density and corresponding derivatives (up to third-order)

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subroutine gencalchessmat: A general routine used to calculate value, gradient and Hessian matrix at a given point for some real space functions

subroutine gendensgradab: Generate electron density and gradient norm for alpha and beta electrons at the same time

subroutine calchessmat\_dens: Calculate electron density, its gradient and Hessian matrix

subroutine calchessmat\_lapl: Calculate Laplacian of electron density, its gradient and Hessian matrix (Hessian is not available)

subroutine calchessmat\_ELF\_LOL: Calculate ELF/LOL, its gradient and Hessian matrix (Hessian is not available)

subroutine calchessmat\_prodens: Calculate electron density, its gradient and Hessian matrix with promolecular approximation

subroutine stericderv: Calculate the first-order derivative of steric potential

## 3 Detail of built-in atomic densities

Some analyses, such as Hirshfeld/ADCH population analyses and Hirshfeld orbital composition analysis request atomic densities. Though, as shown in Section 3.7.3, the atomic densities can be evaluated based on atomic .wfn files, the process is slightly complicated, namely the element .wfn files needed must be prepared and sphericalized first. In order to simplify these analysis tasks, a set of built-in atomic densities (available from H to Lr) was provided in Multiwfn and one can directly choose to use it.

These built-in atomic densities were evaluated at highly accurate computational level at atom ground-states, and have been sphericalized (density distribution of many atoms in their ground states are not spherically symmetric). Main group elements with index <=18 were calculated at B3LYP/cc-pVQZ level, those >18 were calculated at B3LYP/ANO-RCC level (except for Ca, UGBS is used since the ANO-RCC of Ca in EMSL website is wrong). Transition metals were calculated at HF/UGBS level. Lanthanides and Actinides were calculated at B3LYP/SARC-DKH level (except for U and Np, for which ROHF was used instead of B3LYP because DFT cannot reproduce their correct ground state configurations). For all elements heavier than Ar, DKH2 method was employed to take scalar relativistic effect into account. Unless otherwise specified, open-shell systems was treated by unrestricted open-shell formalism.

The atomic densities are recorded as radial points in "atmraddens.f90", the second kind of Gauss-Chebyshev method was used to generate the position of radial points, and the point distribution is identical for all elements. The atomic density at any point is evaluated in terms of Lagrange interpolation method based on the points.

If you want to replace built-in atomic density of an element with that calculated by yourself, after booting up Multiwfn and loading corresponding atom wavefunction file, select main function 98 ( a hidden function), then Multiwfn will calculate radial electron density and output the result to "sphavgval.txt" in current folder. You can directly copy the Fortran codes in this file into corrsponding field of atmradens.f90.

## 4 Details about supplying inner-core electron density for the wavefunctions involving pseudopotential

In Section 2.5, the characteristic and the meaning of electron density function (EDF) have been introduced. EDF information is used to represent the inner-core density replaced by pseudopotential, so that for the wavefunctions involving pseudopotential, the result of the wavefunction analyses that purely based on electron density can be almost exactly identical to full-electron wavefunction.

When the input file you used contains GTF information, and meantime some atoms utilized pseudopotential, Multiwfn automatically finds proper GTF information from built-in EDF library for these atoms. The built-in EDF library was developed by Wenli Zou and coworkers, it was originally released as a part of Molden2aim (<https://github.com/zorkzou/Molden2AIM>). The quality of this EDF library is quite good, and is better than the EDF field contained in the .wfx file produced by Gaussian program. This EDF library covers the entire periodic table, up to index of 120 currently. For most elements, it contains both EDF information for large and small core pseudopotentials. Some descriptions about this library posted by its developer can be found in <http://bbs.keinsci.com/forum.php?mod=viewthread&tid=5354>. If you do not want Multiwfn to read EDF information from this library automatically, set "isupplyEDF" in settings.ini to 0.

As mentioned in Section 2.5, the .wfx file produced by Gaussian directly carries EDF field when pseudopotential is used. When this kind of file is used as input, Multiwfn by default reads EDF information from EDF field of this .wfx file rather than from the built-in EDF library. If you do not want Multiwfn read EDF information from this file but from the built-in EDF library, you can change "readEDF" in settings.ini from 1 to 0.

Worhnotingly, Multiwfn also allows reading EDF information from atomic .wfx file produced by Gaussian rather than from the built-in EDF library of Multiwfn (This feature is rarely useful, since as mentioned above, the quality of the built-in EDF library in Multiwfn is better than the EDF library embedded in Gaussian). An example is provided as below:

"examples\Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.wfn" is a file corresponding to Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Lanl2 pseudopotential accompanied by Lanl2DZ basis-set is used for Pt and Cl, while 6-31G\* is used for other atoms. "examples\Pt\_lanl2.wfx" and "examples\Cl\_lanl2.wfx" are the Pt and Cl atomic .wfx files produced by G09, in which Lanl2 is also used, therefore their EDF fields represent the inner-core electron density of Pt and Cl replaced by Lanl2.

In order to borrow EDF information from the atomic .wfx files in the analysis of Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.wfn, first we need to set "isupplyEDF" parameter in settings.ini file to 1. Then boot up Multiwfn and input following commands

```
examples\Pt(NH3)2Cl2.wfn
Pt // Load EDF information for element Pt
examples\Pt_lanl2.wfx // Take EDF information of Pt from this file
Cl // Load EDF information for element Cl
examples\Cl_lanl2.wfx // Take EDF information of Cl from this file
q // We have finished, exit
```

Now we can perform wavefunction analysis as usual. But it is better to first carry out some

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tests to check if inner-core electron density has been properly represented, for example, we integrate electron density over the whole space

```
100 // 100 Other functions (Part1)
4 // Integrate a function in whole space
1 // Electron density
```

The result is 132.00, which is the expected total number of electron of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ . Assume that we didn't load the EDF information, then the result will be 52.00, which is just the number of valence electrons of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ .

Note that you can also directly input atomic indices instead of element name, for example, inputting 4,8-10,11 means selecting atoms 4,8,9,10,11 in present system. Of course, the atoms you selected each time must corresponds to the same element and the same pseudopotential.

It is users' responsibility to prepare the atomic .wfx files. Since there are too many kinds of pseudopotentials and elements, evidently I am uncapable of providing all of them for you.

## 5 Check sanity of wavefunction

The input files of Multiwfn generated by various quantum chemistry codes are not always standard. For example, .molden file generated by many programs are problematic in content or format. After you feeding them to Multiwfn and you want to make sure if the wavefunction has been correctly loaded, there are two useful ways to check sanity:

(1) Enter main function 100 and select subfunction 4, then choose electron density. If the integral of electron density over the whole space is very close to the actual number of electrons, then the wavefunction is ready for use.

(2) Enter main function 1000 (a hidden function) and select subfunction 100. This function will check satisfaction of normalization condition of all orbitals, and show you the maximum deviation to unity. If the maximum deviation is evidently larger than zero, then there must be some problems in the input file.