

# Multiwfn quick start

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Last update: 2019-Aug-20, corresponding to Multiwfn manual version 3.7(dev)

The Multiwfn manual is very detailedly written and well organized, however, it is relatively long. In order to make new user of Multiwfn quickly get started, here I provide a very short quick start document, which presents answer of a few frequently asked questions and basic guides on how to perform very common tasks.

## 1. FAQ

➤ **Q: What analysis can Multiwfn do? What is the use of Multiwfn?**

A: Please check "Overview" page of Multiwfn website or Chapter 1 of Multiwfn manual.

➤ **Q: Where can I obtain latest Multiwfn program and manual?**

A: The Multiwfn official website is <http://sobereva.com/multiwfn>, all resources related to Multiwfn can be acquired from this site. I highly suggest you frequently check this site to update your Multiwfn to the latest version, since development of Multiwfn is very active.

➤ **Q: How to cite Multiwfn in correct way?**

A: Check end of Chapter 1 of Multiwfn manual or "Download" page of Multiwfn website.

➤ **Q: What should I do when I encounter problems in using Multiwfn?**

A: Please always pay attention to all prompts on screen and do not forget to check corresponding section of Multiwfn manual. If you are unable to easily find solution, please do not hesitate to post message on Multiwfn forum, the English forum is <http://sobereva.com/wfnbbs>, the Chinese forum is <http://bbs.keinsci.com/wfn>. Commonly, the developer checks these two forums every day and always timely replies questions.

➤ **Q: What is the most smooth and quick way of learning Multiwfn?**

A: Reading Chapter 1, Sections 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 most important and frequently used functions rather than all functions of Multiwfn.

➤ **Q: How to install Multiwfn?**

A: Check Section 2.1.

➤ **Q: Which format of input file can be used?**

A: Check Section 2.3.

➤ **Q: How to generate input files for Multiwfn?**

A: Check beginning of Chapter 4. Almost all mainstream quantum chemistry codes can at least

generate one kind of input file that supported by Multiwfn for wavefunction analysis purpose.

➤ **Q: Why Multiwfn occasionally suddenly exits?**

A: Possible reasons:

(1) The format of input file is inappropriate for present task. Please carefully check the corresponding section of the manual on the requirement of input file.

(2) The input file is problematic or incomplete. Please regenerate it or open it using text editor to check for abnormalities.

(3) Your operation steps are incorrect or the command you inputted is wrong and thus cannot be recognized. Please always carefully check prompts on screen, or try to reproduce the corresponding examples in the manual before using Multiwfn to study your system.

(4) Insufficient of memory. If you are using Win32 version of Multiwfn, please change to the Win64 one. You can also try to increase "ompstacksize" in settings.ini. If you are using Linux version, please make sure you have properly configured your system according to Section 2.1.

(5) If your task relies on NBO output file and meantime diffuse functions are employed, remove diffuse functions and try again.

(6) Due to bug of Multiwfn. Please report it to developer via Multiwfn forum.

➤ **Q: Why Multiwfn crashes under Linux and show error "Segmentation fault"?**

A: Commonly this is because you didn't strictly follow Section 2.1.2 to configure your system. If you are really unable to solve this problem, please use Windows version. If your input file is problematic, you may also encounter this problem.

➤ **Q: How to copy output of Multiwfn from console window to text file?**

A: See Section 5.4.

➤ **Q: How to run Multiwfn using command line mode? How to use Multiwfn process a batch of input files?**

A: See Sections 5.2 and 5.3.

➤ **Q: The console window cannot record all printed information, the earlier output was flushed out**

A: Increase buffer size of the console window so that the window can record more lines of output, see Sections 5.5.

➤ **Q: I don't understand meaning of each column of the text file outputted by Multiwfn**

A: Please carefully check prompts on screen, when Multiwfn exports a file, the meaning of each column is always clearly shown.

➤ **Q: What is the unit of the data outputted by Multiwfn**

A: Unless otherwise specified, all units are in atomic unit (a.u.). When Multiwfn exports a text file, the unit is always explicitly shown on screen.

➤ **Q: I can't find the file(s) exported by Multiwfn**

A: If Multiwfn doesn't explicitly ask you to input the path of the file for exporting, the file is always generated in current folder. The meaning of "current folder" has clearly been mentioned in page 2 of the manual.

➤ **Q: Electrostatic potential analysis (ESP) is slow for large system**

A: I strongly suggest you let Multiwfn invoke cubegen utility in Gaussian package to significantly speed up ESP calculation. See Section 5.7.

➤ **Q: Multiwfn is failed to invoke Gaussian to perform calculation under Windows system with error "No executable for file l1.exe"**

A: See Appendix 1 of manual. You need to set up GAUSS\_EXEDIR environment variable in your system.

➤ **Q: How to load a new file without rebooting Multiwfn?**

A: Return to main menu, select option -11 (a hidden option).

➤ **Q: How to quit Multiwfn?**

A: Use Ctrl+C or directly close the window. If you want to exit gracefully, input  $q$  in the main function menu.

## 2. Using Multiwfn realizing common analyses

Below I will show you which manual section(s) should be read if you want to perform corresponding task. Only common tasks are covered. For brevity, such as "see Section x.x.x for introduction and Section y.y.y for example" will be abbreviated as "x.x.x (i); y.y.y (e)".

### ➤ **AIM analysis**

Topology analysis: 3.14 (i); 4.2 (e)

Plane map with critical points and bond paths: 3.5.5 (i); 4.4.6 (e)

Basin analysis: 3.20 (i); 4.17.1 and 4.17.5 (e)

### ➤ **ELF (electron localization function) and LOL (localized orbital locator) analysis**

Topology analysis: 3.14 (i); 4.2.2 (e)

Basin analysis: 3.20 (i); 4.17.2 and 4.17.7 (e)

Plotting as plane map: 4.4.2, 4.4.8, 4.4.9 (e), special case: 4.100.19 (e)

Plotting as isosurface map: 4.5.1, 4.5.3, 4.100.22 (e)

Spherically symmetric average ELF / LOL: 3.100.4 (i)

### ➤ **Visual analysis of weak interaction**

Non-covalent interaction (NCI) analysis: 3.23.1 (i,e); 4.20.1 (e).

Domain analysis within NCI isosurfaces: 3.200.14 (i); 4.200.14.1 (e)

Promolecular NCI analysis: 3.23.2 (i); 4.20.2 (e)

Averaged NCI analysis: 3.23.3 (i); 4.20.3 (e)

Independent gradient model (IGM) analysis: 3.23.5 (i); 4.20.10 (e)

Density overlap regions indicator (DORI) analysis: 3.23.4 (i); 4.20.5 (e)

Hirshfeld surface analysis: 3.15.5 (i); 4.12.5 and 4.12.6 (e)

### ➤ **Visualizing various kinds of orbitals as isosurface**

Isosurface map: 3.2 (i); 4.0 (e)

Plane map: 4.4.5 (e)

Exporting cube file for a batch of orbitals: 3.200.3 (i)

### ➤ **Evaluating various real space functions at a point**

3.3 (i); 4.1 (e)

### ➤ **Plotting various real space functions**

Curve map: 3.4 (i); 4.3 (e)

Plane map: 3.5 (i); 4.4 (e)

Isosurface map: 4.5 (e)

Radial distribution function: 3.200.5 (i); 4.200.5 (e)

### ➤ **Generate cube file of real space functions**

3.6 (i); 4.5 (e)

### ➤ **Atomic charge and population analysis**

Mulliken charges and population analysis: 3.9.3 (i); 4.7.0 (e)

Löwdin, SCPA: 3.9.4, 3.9.5 (i)

AIM charges: 3.9.12 (i); 4.17.1 (e)

ADCH (atomic dipole moment corrected Hirshfeld population): 3.9.9 (i); 4.7.2 (e)

CM5: 3.19.14 (i)

Hirshfeld: 3.9.1 (i); 4.7.1 (e)

Hirshfeld-I: 3.9.13 (i); 4.7.4 (e)

Electronegativity Equalization Method (EEM): 3.9.15 (i); 4.7.5 (e)

CHELPG: 3.9.10 (i); 4.7.1 (e)

RESP (Restrained ElectroStatic Potential): 3.9.16 (i); 4.7.7 (e)

➤ **Bond order analysis**

Laplacian bond order (LBO): 3.11.7 (i); 4.9.3 (e)

Mayer bond order: 3.11.1 (i); 4.9.1 (e)

Orbital occupancy-perturbed Mayer bond order 3.11.5 (i); 4.9.1 (e)

Multi-center bond order: 3.11.2 (i); 4.9.2 (e)

Wiberg bond order: 3.11.3 (i)

Wiberg bond order decomposition to atomic pair contributions: 3.11.8 (i); 4.9.4 (e)

Mulliken bond order analysis and its decomposition: 3.11.4 (i); 4.9.5 (e)

Fuzzy bond order: 3.11.6 (i), 4.9.1 (e)

Bond order alternation (BOA): 3.200.18 (i), 4.200.18 (e)

➤ **Density-of-state (DOS) and photoelectron spectrum (PES)**

Total, partial, overlap DOS (TDOS, PDOS, OPDOS): 3.12 (i); 4.10.1 (e)

Local DOS: 3.12.4 (i); 4.10.2(e)

Photoelectron spectrum: 3.12.4 (i); 4.10.4 (e)

➤ **Plotting IR, Raman, UV-Vis, ECD, VCD, ROA spectra**

3.13 (i); 4.11 (e)

➤ **Orbital composition analysis**

3.10 (i); 4.8 (e)

➤ **Orbital localization**

3.22 (i); 4.19 (e)

Oxidation state evaluation LOBA: 3.10.7 (i); 4.8.4 (e)

➤ **AdNDP (Adaptive natural density partitioning) analysis**

3.17 (i); 4.14 (e)

➤ **Charge decomposition analysis (CDA) and orbital interaction diagram**

3.19 (i); 4.16 (e)

➤ **Processing grid data**

Mathematical operation between grid data: 3.16.7 (i); 4.13.2 (e)

Screening specific regions: 3.16.9 and 3.16.10 (i); 4.13.4 (e)

Statistical analysis: 3.16.13 (i)

➤ **Electrostatic potential (ESP) analysis**

Various kinds of quantitative molecular surface analysis: 3.15 (i); 4.12.1 and 4.12.3 (e)

Plotting ESP colored vdW surface map: 4.A.13 (e)

Plotting plane map: 4.4.4 (e)

Basin analysis: 4.17.3 (e)

Predicting binding energy using ESP at nuclear position: 4.1.2 (i,e)

Plotting ESP minimum points with isosurface to reveal lone pairs: 4.17.4 (e)

Calculating area and average ESP value of  $\sigma$ -hole and  $\pi$ -hole: 4.12.10 (e)

Basin-like analysis on vdW surface for ESP: 4.12.11 (e)

#### ➤ **Electronic excitation analysis**

Comprehensive overview: 4.A.12

hole-electron analysis: 3.21.1 (i); 4.18.1 (e)

IFCT (InterFragment Charge Transfer) analysis, heat map of atom-atom charge transfer matrix:  
3.21.8 (i); 4.18.8 (e)

Transition density and transition dipole moment density analysis: 3.21.1 (i); 4.18.2.1 (e)

Heat map of transition density matrix (TDM) and transition dipole moment density matrix:  
3.21.2 (i); 4.18.2.2 and 4.18.2.3 (e)

Quantitative analysis for density difference grid data: 3.21.3 (i); 4.18.3 (e)

$\Delta r$  and  $\Lambda$  indices: 3.21.4, 3.21.14 (i); 4.18.4 (e)

Natural transition orbitals (NTOs): 3.21.6 (i); 4.18.6 (e)

Wavefunction analysis for an excited state: 4.18.13 (e)

Transition dipole moments between excited states, excited state dipole moment: 3.21.5 (i)

Generating transition density matrix between ground state and excited states, as well as  
between two excited states: 3.21.9 (i); 4.18.2.3 (e)

Generating natural orbitals for transition density matrix: 3.21.9 (i); 4.18.9 (i)

Decomposing transition dipole moment as MO contributions: 3.21.10 (i); 4.18.10 (e)

Decomposing transition dipole moment as fragment, atom or basis function contributions:  
3.21.11 (i); 4.18.11 (e)

TrEsp (transition charge from electrostatic potential) and excitonic coupling: 4.A.9 (i,e)

Mulliken atomic transition charges: 3.21.12 (i)

Evaluating NBO contributions to electron excitation: 3.200.13 (i); 4.200.13.3 (e)

Ghost-hunter index: 3.21.7 (i); 4.18.1 (e)

#### ➤ **Weak interaction analysis**

Comprehensive overview: 4.A.5

AIM topology study: 3.14 (i); 4.2 (e)

Various kind of visual studies: See "Visual analysis of weak interaction" in present document

Simple energy decomposition or EDA-FF energy decomposition: See "Energy decomposition  
analysis" in present document

Plane or isosurface map of electron density difference between interacting monomers: 4.5.5 (e)

Plotting electrostatic potential (ESP) colored van der Waals (vdW) surface map and penetration  
graph of vdW surface of monomers: 4.A.13 (e)

Studying minima and maxima of ESP on vdW surface: 3.15 (i); 4.12.1 (e)

Quantitative evaluation of mutual penetration of vdW surfaces: 4.A.5 (i)

CVB index: 3.100.1 (i,e)

LOLIPOP (LOL Integrated Pi Over Plane): 3.100.14 (i); 4.200.14 (e)

$\Delta\Delta V_n$  index: 4.1.2 (i,e)

#### ➤ **Predicting reactive site**

Overview: 4.A.4

ESP on vdW surface: 4.12.1 (e)

Average local ionization energy (ALIE) on vdW surface: 4.12.2 (e)

Fukui function and dual descriptor: 4.5.4 (e)

Condensed Fukui function and condensed dual descriptor: 4.7.3 (e)

Automatic calculation of all quantities involved in the conceptual density functional theory:  
3.100.16 (i); 4.100.16 (e)

Evaluating MO and NBO contributions to Fukui function: 3.200.13 (i); 4.200.13.1 and  
4.200.13.2 (e)

Orbital overlap distance function: 4.12.8 (e)

#### ➤ **Aromaticity analysis**

Comprehensive Overview: 4.A.3

Iso-chemical shielding surface (ICSS): 3.200.4 (i); 4.200.4 (e)

HOMA and Bird indices: 3.100.13 (i); 4.100.13 (e)

Multi-center bond order: 3.11.2 (i); 4.9.2 (e)

Shannon aromaticity index (SA) and properties at ring critical point (RCP): 3.14.6 (i); 4.2.1 (e)

PDI: 3.18.6 (i); 4.15.2 (e)

FLU, FLU- $\pi$ : 3.18.7 (i); 4.15.2 (e)

PLR: 3.18.9 (i); 4.15.2 (e)

ELF- $\sigma$ , ELF- $\pi$ : 4.4.9, 4.5.3, 4.100.22 (e)

Information-theoretic aromaticity index: 3.18.11 (i)

NICS<sub>ZZ</sub> for non-planar or tilted system: 3.100.24 (i)

#### ➤ **Electronic density difference (EDD) analysis**

Plane and isosurface EDD maps between two fragments: 4.5.5 (e)

Between excited state and ground state: 4.18.3 (e)

Between two excited states: 4.18.13 (e)

Deformation density: 4.4.7 (e)

Basin analysis: 4.17.4 (e)

Charge displacement curve: 3.16.14 (i) and 4.13.6 (e)

#### ➤ **Electronic spin distribution analysis**

Spin density curve map: 4.3.1 (e)

Overview of spin population calculation: 4.A.2

#### ➤ **Energy decomposition analysis**

Energy decomposition based on forcefield (EDA-FF): 3.24.1 (i); 4.21.1 (e)

Shubin Liu's energy decomposition (EDA-SBL): 3.24.2 (i); 4.21.2 (e)

Simple energy decomposition: 3.100.8 (i); 4.100.8 (e)

#### ➤ **Biorthogonalization analysis for unrestricted orbitals**

3.100.12 (i); 4.100.12 (e)

#### ➤ **(Hyper)polarizability study**

Parsing output file of "polar" task of Gaussian, obtaining various quantities related to (hyper)polarizability and hyper-Rayleigh scattering (HRS) experiment: 3.200.7 (i); 4.200.7 (e)

Calculating (hyper)polarizability using sum-over-states (SOS) method: 3.200.8 (i); 4.200.8 (e)  
(Hyper)polarizability density and atomic contribution to (hyper)polarizability: 4.A.7 (i,e)

➤ **Predicting properties of condensed phase**

3.15.1 (i); 4.12.7 (e)

➤ **Overlap analysis**

Intermolecular electron density overlap: 4.13.7 (e)

Intermolecular van der Waals surface penetration: 4.A.13 (e)

Overlap integral between Alpha and Beta orbitals of a system and estimating  $\langle S^2 \rangle$ : 3.100.5 (i)

Intrasystem orbital superposition and centroid distance: 3.100.11 (i)

Intermolecular orbital overlap integral: 3.100.15 (i); 4.100.15 (e)

Correspondence between orbitals in two wavefunctions, overlap integral and superposition between orbitals in single or two wavefunctions: 3.200.6 (i,e)

➤ **Geometry structure analysis**

Measuring diameter and length/width/height: 3.100.21 (i); 4.100.21 (e)

Visualizing molecular cavity and calculating its volume: 4.200.14.2 (e)

van der Waals volume (Monte Carlo method): 3.100.3 (i)

van der Waals volume (Marching Tetrahedron method): 4.12.1 (e)

Area of van der Waals surface of whole system or individual fragments: 4.12.9 (e)

Interatomic connectivity and atomic coordination number: 3.100.9 (e)

Average bond length and average coordinate number: 3.200.9 (i)

Bond length alternation (BLA): 3.200.18 (i), 4.200.18 (e)

Kinetic diameter: 4.12.12 (e)

➤ **Electronic correlation analysis**

Visual study of Fermi hole and Coulomb hole: 4.3.2 (e)

Localization index (LI) and delocalization index (DI): 3.18.5 (i); 4.15.1, 4.17.1 (e)

Odd electron density and local electron correlation function: 4.A.6 (i,e)

➤ **Overview of all methods supported by Multiwfn for studying chemical bonds**

4.A.11

➤ **Others**

File format conversion and yield input file of quantum chemistry codes: 3.100.2 (i)

Integrating a function over the whole space, examination of difference of a real space function between two wavefunction files: 3.100.4 (i,e)

Detecting  $\pi$  orbitals and setting their/others occupation numbers, evaluating  $\pi$  composition of a given set of orbitals: 3.100.22 (i); 4.100.22, 4.5.3, 4.4.9 (e)

Yoshizawa's electron transmission route analysis: 3.100.18 (i); 4.100.18 (e)

Calculating atomic and bond dipole moments in Hilbert space: 3.200.2 (i)

Outputting various kinds of integral between orbitals: 3.200.10 (i)

Outputting Coulomb and exchange integrals between two orbitals: 3.200.17 (i,e)

Calculating center, the first and second moments of a real space function: 3.200.11 (i,e)

Calculating energy index (EI) or bond polarity index (BPI): 3.200.12 (i); 4.200.12 (e)

Generating natural orbitals, natural spin orbitals and spin natural orbitals: 3.200.16 (i,e)



Generating Gaussian input file with initial guess combined from fragment wavefunctions:  
3.100.8 (i); 4.100.8 (e)  
Monitoring SCF convergence process of Gaussian: 3.100.6 (i)