Revision 6.36

AOMix (and its additional modules: ***AOMix-CDA, AOMix-L,*** and ***AOMix-S***) is a user-friendly, comprehensive package for the molecular orbital analysis with additional useful utilities (see Appendices I and II in this manual). *AOMix* calculates percentage contributions of different molecular fragments (atoms, ligands, groups of atomic orbitals / basis functions, groups of fragment molecular orbitals, etc.) to molecular orbitals from output files generated by *ADF, GAMESS (US), Gaussian, HyperChem*, *Jaguar*, *MOPAC, Q-Chem, Spartan, Turbomole, ZINDO* and *CNDO/INDO* programs and produces data tables (in the ASCII text format) with relevant MO information, condensed Fukui functions, etc. In addition, *AOMix-S* generates total, partial and overlap population density-of-states (DOS) plots and can be used for MO composition analysis in systems with many fragments. *AOMix-CDA* calculates the MO compositions in the basis of fragment molecular orbitals (FOs), occupation numbers for FOs and atomic orbitals (AOs), and, if the number of fragments is greater than 1, the amounts of electron donation / back-donation between molecular fragments (charge decomposition analysis, CDA), electronic polarizations of fragments, generates plot data for MO interaction diagrams, and calculates Green function matrix elements for electronic coupling between donor and acceptor through the bridge. In addition, *AOMix-CDA* can be used for Morokuma's energy decomposition analysis (EDA) and to generate a guess wave function of multi-fragment molecular systems from the wave functions of fragments. *AOMix-L* calculates total and free valence indices of fragments, 2-center (Wiberg, Löwdin, and Mayer) and 3- and 4-center bond orders between molecular fragments (which can be defined as atoms, groups of atoms, or groups of atomic orbitals) and performs the Löwdin population analysis. For Mayer bond orders, *AOMix-L* prints α- and β-spin orbital and symmetry contributions. *AOMix-L* can be also used for recovery of the initial guess (as the converged wave function) and the analysis of spin-unrestricted MO calculations: the program projects β-spin molecular orbitals on to α-spin molecular orbitals and prints the overlap matrix $\left\langle \psi_i^\alpha \middle| \psi_j^\beta \right\rangle$.

The *AOMix* package helps to **analyze the nature of the chemical bonding** in molecular systems and to **monitor changes in the electron density distribution upon the electron excitation**. Let's say, there is a band in an absorption spectrum of a molecule or an ion at 400 nm which is assigned to a HOMO→LUMO+2 electron excitation. What does it tell about properties of this molecule / ion, what do we know about the nature of the corresponding excited state? What will happen with this molecule / ion after the photoexcitation? *AOMix* helps to answer these questions using the molecular orbital decomposition analysis and various density-of-states (DOS) plots.

The main use of DOS plots is to provide a pictorial representation of MO populations. The orbital character is determined by means of the Mulliken population analysis (MPA) or another available population analysis procedure (such as SCPA) per molecular orbital. The DOS plots, therefore, provide the same information as given by the main *AOMix* output file – a population analysis per orbital – but they enable an easy graphical representation and are particularly useful when there are many one-electron levels in a given molecular system. You can obtain a simple view of the character of the molecular orbitals in a certain energy range. One can also find out in which molecular orbitals certain basis functions or fragment orbitals give large contributions, and whether such contributions are bonding, nonbonding or anti-bonding with respect to particular bonds of fragment pairs.

The following options are available for DOS computations:

- total Density of States (TDOS);
- partial Density of States (PDOS, showing contributions of molecular fragments to TDOS);
- overlap population Density Of States (OPDOS) between molecular fragments, OPDOS plots are also known in the literature as Crystal Orbital Overlap Population (COOP) diagrams.

Typographical Conventions in This Manual:

The *Italics* font is used for program names and variables.
The ***Bold Italics*** font is used for file names.
The **`Bold Courier New`** font is used for program input and output examples.
The **Elephant** font is used for the *AOMix* keywords.
The **Bold Verdana** font is used for keywords of the other program packages (such as *Gaussian 03*, etc.).

Software Requirements:

Supported operating systems:	**MS Windows NT/ 2000 / XP**. NO COMPLICATED INSTALLATION IS REQUIRED! JUST DOWNLOAD THE SOFTWARE TO YOUR COMPUTER and RUN THE INITIALIZATION SCRIPT.
Other requirements:	CPU: Pentium-II or higher, an ethernet card (Only necessary for a computer with a single-workstation license).

AOMix processes output files from the following programs:

ADF (Scientific Computing & Modelling NV). Only calculations *with no core functions* (do not confuse core functions with core orbitals, please refer to the *ADF* user manual for details).

CNDO/INDO (Dr. J. R. Reimers, U. of Sydney, Australia)

GAMESS-US (Gordon group at Iowa State University)

Gaussian 98, Gaussian 03 (Gaussian, Inc.)

HyperChem (HyperCube, Inc.)

Jaguar 3.x-6.x (Schrodinger, Inc.)

MOPAC (Dr. J. J. P. Stewart, Fujitsu Limited)

Q-Chem 2.x-3.x (Q-Chem, Inc.)

Spartan (Wavefunction, Inc.)

**** Turbomole v. 5*** (Quantum chemistry group, University of Karlsruhe)

ZINDO (M.C.Zerner, Quantum Theory Project, U. of Florida, USA;
ZINDO is available in *Cerius*^{2} (Accelrys Inc.) and *CAChe* (Fujitsu Inc.)

* Processing of these output files is achieved by using *AOMix-prep.exe* only.

Other computational chemistry packages can be added to the above list. Contact the *AOMix* author about it.

Available options for *AOMix* and its modules

Software	**Calculation type**	***AOMix***	***AOMix-prep***	***AOMix-S***	***AOMix-CDA***	***AOMix-L***
ADF	DFT	+		+	+	+
GAMESS (US)	HF, DFT	+		+	+	+
Gaussian 98, Gaussian 03	HF, DFT	+		+	+	+
	ZINDO	+		+	+	+
HyperChem	HF, DFT	+ O		+ O	O	O
	Semiempirical	+		+	+	+
Jaguar 3.x-6.x	HF, DFT	+		+	+	+
MOPAC	Semiempirical	+		+	+	+
Q-Chem 2.x	HF, DFT	+		+ Q	Q	Q
Q-Chem 3.x	HF, DFT	+		+	+	+
Spartan	HF, DFT	+ O		+ O	O	O
	Semiempirical	+		+	+	+
Turbomole 5	HF, DFT		+	+		+
ZINDO	Semiempirical	+		+	+	+
CNDO/INDO	Semiempirical	+		+	+	+

+ = SCPA, MPA and MMPA are available.

+ O = SCPA is available, MPA and MMPA are not available.

+ Q = SCPA is available; MPA and MMPA are also available if the overlap matrix has been added to a *Q-Chem 2.x* output file by running a special *Q-Chem* output converter (contact Professor C.-P. Hsu at *cherri@sinica.edu.tw* to request a copy of the converter).

Q = available if the overlap matrix has been added to a *Q-Chem 2.x* output file by running a special *Q-Chem* output converter (contact Professor C.-P. Hsu at *cherri@sinica.edu.tw* to request a copy of the converter).

Procedures for population analysis in *AOMix*:

1. **Mulliken population analysis (MPA)**[1-4]
2. **modified Mulliken population analysis (MMPA)**[5-8] (in *AOMix-S.exe*)
3. **c^2 population analysis (SCPA)**[9]
4. **Löwdin population analysis (LPA)**[10] **and other types based on the $S^a\ P\ S^{1-a}$ formula** (in *AOMix-L.exe*). User can set his/her own value of the parameter $\boldsymbol{a}$ (a = 0.5 corresponds to Löwdin population analysis, a = 1 corresponds to MPA).
5. **the MO analysis in terms of the contributions from fragment molecular orbitals** and **charge decomposition analysis (CDA)** (using *AOMix-CDA.exe*).
   CDA has been devised to analyze molecular interactions in systems which can be described as donor-acceptor complexes. The electronic changes associated with the formation of a molecule consisting of two or more fragments are partitioned in terms of the Dewar-Chatt-Duncanson model.[11,12] For *ab initio* and DFT wave functions, *AOMix-CDA* uses the CDA method of Frenking and co-workers[13,14] and the extended CDA (ECDA)[15,16] which includes evaluation of charge transfer and polarization contributions.
6. **Calculation of the two-center (Wiberg,**[17] **Löwdin,**[18,19] **and Mayer**[20-24]**) bond orders B_{AB}** (in *AOMix-L.exe*).
7. **Calculation of the three- and four-center bond order indices,**[25-30] **B_{ABC}** and **B_{ABCD}** (in *AOMix-L.exe*).

Methods to Derive Atomic Orbital Contributions to Molecular Orbitals

Electronic structure calculations yield the electronic energy and the wave function of a molecular system in a particular electronic state. The wave function itself is usually too complicated to provide a simple physical picture of the system. One needs to define simplified notions and characteristics of the wave function in order to gain insight into the electronic structure of molecules and to predict chemical reactivity and other properties.

Within the LCAO-MO formalism, the wave function for the i^{th} eigenstate of the molecule/ion can be written as

$$\psi_i = \sum_{a=1}^{NBF} \mathbf{c}_{ai}\chi_a \qquad (3.1.1)$$

for an atom localized basis set χ_a.

If the MOs are obtained with semiempirical zero differential overlap (ZDO) methods, then the overlap between any two different basis functions,

$$\boldsymbol{S}_{ab} = < \chi_a \mid \chi_b >, \tag{3.1.2}$$

is neglected, and the contribution of the atomic orbital (AO) χ_a to the i^{th} MO is equal to the square of the corresponding LCAO coefficient, $(\boldsymbol{c}_{ai})^2$, and the electron population of atom A equals to

$$\sum_i n_i \sum_{a\in A} \mathbf{c}_{ai}{}^2 \tag{3.1.3}$$

where the index a runs over all AOs localized on atom A, n_i are MO occupation numbers, and the index i runs over all MOs.

This is no longer the case if the overlap integrals (3.1.2) are non-zero, which is generally the case. To analyze wave functions with non-zero overlap it's necessary to include the overlap populations, $2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab}$, in the calculations. Several schemes were proposed in the literature to deal with the overlap populations. These methods are described below.

Mulliken Population Analysis

The most popular and widely used procedure is Mulliken population analysis (MPA).[1-4] In MPA, the overlap population is split equally between two atoms, so the net contribution of χ_a to the i^{th} MO is equal to

$$\sum_b \mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab} \tag{3.1.4}$$

and the gross atomic population of atom A is

$$GP_A = \sum_i n_i \sum_{a\in A} \sum_k \mathbf{c}_{ai}\mathbf{c}_{ki}\mathbf{S}_{ak} \ , \tag{3.1.5}$$

where the index a runs over all AOs localized on the atom A, k runs over all AOs of the molecule, $n_i = 2, 1, 0$ are MO occupation numbers, and i runs over all MOs.

MPA can be utilized for the analysis of the MO compositions in terms of the contributing fragments. % Contribution of fragment A to the i-th MO is given by:

$$\%_{A,i} = 100 * \sum_{a \in A} \sum_{k} \mathbf{c}_{ai} \mathbf{c}_{ki} \mathbf{S}_{ak} \tag{3.1.6}$$

The above expression can be re-written in the following form:

$$\%_{A,i} = 100 \left(\sum_{a \in A} \sum_{a' \in A} \mathbf{c}_{ai} \mathbf{c}_{a'i} \mathbf{S}_{aa'} + \sum_{a \in A} \sum_{b \notin A} \mathbf{c}_{ai} \mathbf{c}_{bi} \mathbf{S}_{ab} \right) \tag{3.1.7}$$

The first sum (so-called *net fragment populations*) contains only contributions from fragment A and the second sum contains contributions from the overlap populations. *AOMix.exe* and *AOMix-S.exe* can be used to calculated the MO compositions (gross fragment populations) and the overlap populations between fragments; in addition, *AOMix-S.exe* will also print the net populations (the first sum in Eqn. 3.1.7) if the **NETPOP=ON** keyword is present in *aomixpar.txt*.

There are deficiencies in MPA:

1. MPA orbital populations can have non-physical negative values or be in excess of two. The fragment contributions can exceed 100% or be less than 0% when analyzing the MO compositions.
2. MPA-derived populations are sensitive to a basis set, particularly as the basis set is enlarged to get higher accuracy and includes diffuse functions (see Table 1).

The reason for these two problems is the imbalance of the overlap populations and the net atomic populations. This imbalance is due primarily to the arbitrary equal distribution of the overlap population between atoms involved.

When $-\sum_{b \neq a} \mathbf{c}_{ai} \mathbf{c}_{bi} \mathbf{S}_{ab}$ is greater than $\boldsymbol{c}_{ai}^2$, the contribution of the a^{th} AO to the i^{th} MO becomes negative. Clearly, this is likely to happen when the coefficient $\boldsymbol{c}_{ai}$ is small but the overlap integral $\boldsymbol{S}_{ab}$ and the coefficient $\boldsymbol{c}_{bi}$ are large. This is a typical situation for high-energy unoccupied MOs from calculations that use an extended or *unbalanced* basis set. In this case, it is not reasonable to split the overlap populations equally; rather it would be better to assign a smaller portion of $2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab}$ to χ_a and the greater portion to χ_b.

Modified Mulliken Population Analysis

One approach to address some of the MPA deficiencies is to divide the overlap populations in a way that better reflects the non-equivalent sharing of electrons between non-equivalent atoms. Stout and Politzer[5] suggested that the overlap populations are to be split between atoms *A* and *B* based on the ratio of the corresponding LCAO-MO coefficients $\boldsymbol{c}_{ai}$ and $\boldsymbol{c}_{bi}$:

$$\frac{\mathbf{c}_{ai}^2}{\mathbf{c}_{ai}^2+\mathbf{c}_{bi}^2} \text{ for atom } A, \tag{3.1.8}$$

$$\frac{\mathbf{c}_{bi}^2}{\mathbf{c}_{ai}^2+\mathbf{c}_{bi}^2} \text{ for atom } B. \tag{3.1.9}$$

This method is known as the modified Mulliken population analysis (MMPA) and is available for use in *AOMix-S.exe*. In MMPA, the contribution of χ_a to the i^{th} MO is equal to

$$\mathbf{c}_{ai}{}^2+\sum_{b\neq a}2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab}\frac{\mathbf{c}_{ai}^2}{\mathbf{c}_{ai}^2+\mathbf{c}_{bi}^2}\,. \tag{3.1.10}$$

Even though this method should divide the overlap population between atoms less arbitrarily, Eqn. 3.1.10 itself does not guarantee that orbital populations derived will not have non-physical negative values or be in excess of two.

The major drawback of MMPA is that the orbital compositions and electron populations obtained with MMPA (Equation 3.1.10) are invariant **neither** to unitary transformations among degenerate molecular orbitals **nor** to unitary transformations of basis orbitals[7] and, thus, MMPA is not particularly useful. Nevertheless, it is available in *AOMix-S.exe* and can be applied by using the **MMPA** keyword in the *AOMix* parameter file (*aomixpar.txt*).

SCPA

An alternative way to partition electron density in molecules was proposed by Ros and Schuit (SCPA).[9] In this method, the overlap populations are not considered and the contribution of χ_a to the i^{th} MO is assumed to be equal to:

$$\frac{\mathbf{c}_{ai}^2}{\sum_k \mathbf{c}_{ki}^2}, \tag{3.1.11}$$

where *k* runs over all AOs.

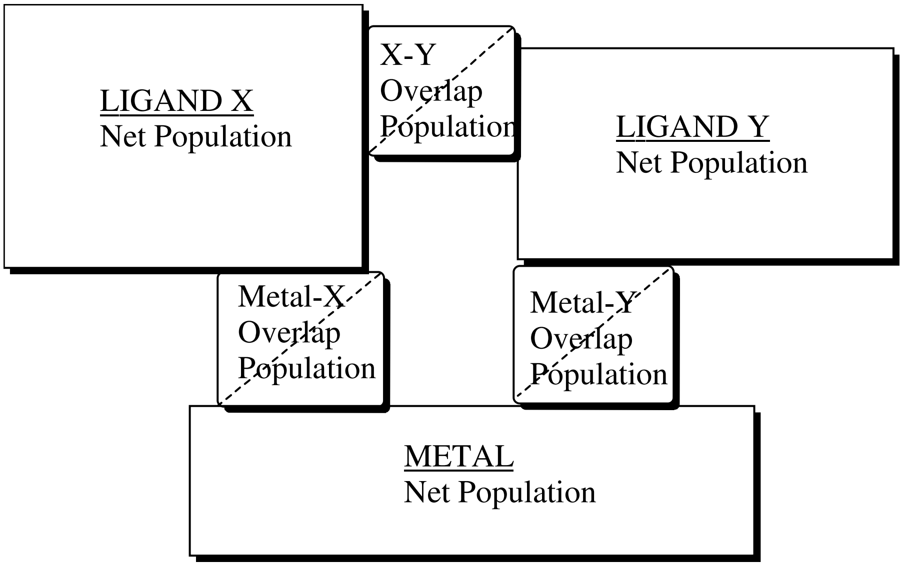
This method does not suffer from the same problems as MPA and MMPA, because Eqn. 3.1.11 guarantees that orbital populations derived will be only positive and will not be in excess of two. However, SCPA still suffers from a problem of basis set dependence.

It has been incorrectly stated in some papers that the MMPA equation (Eqn. 3.1.10) can be, *after some rearrangement*, transformed to the SCPA equation (Eqn. 3.1.11). In a general case, Equation 3.1.10 cannot be reduced to Equation 3.1.11 except in one special case: SCPA is only equivalent to MMPA when the molecular orbitals of the system are represented as linear combinations of just two atomic orbitals with non-zero overlap:

$$\psi_i = \mathbf{c}_{ai}\chi_a + \mathbf{c}_{bi}\chi_b \tag{3.1.12}$$

In a general case of many-electron many-orbital systems, where the majority of overlap integrals $\boldsymbol{S}_{ab}$ are not equal to zero, SCPA and MMPA are not equivalent and provide different numerical answers for MO compositions.[8] Nonetheless, MO compositions computed by all three methods are usually consistent and do not differ too much. This is because the overlap populations between fragments are much lower than the net populations (Scheme 1), at least for a majority of occupied molecular orbitals.

Appreciable differences between MPA, MMPA, and SCPA results may occur when molecular orbitals are either *strongly* bonding or antibonding (MOs with large overlap populations).



Scheme 1. Electron population analysis for transition metal complexes. The gross electron population of the molecular fragment is equal to a sum of the net population and the appropriate overlap populations.

Löwdin Population Analysis

Using *AOMix-L.exe,* a user can employ Löwdin population analysis (LPA)[10] and other related methods based on the $S^a\ P\ S^{1-a}$ formula. In the Löwdin approach, nonorthogonal AOs are transformed to an orthogonal set. The transformed orbitals χ_b' are given by:

$$\chi_b' = \sum_a (\mathbf{S}^{-1/2})_{ab} \chi_a$$

In LPA, the *α*-, *β*- and gross electron populations associated with fragment *A* are:

$$GP_A^{\alpha} = \sum_{a \in A} (\mathbf{S}^{1/2}\mathbf{P}^{\alpha}\mathbf{S}^{1/2})_{aa} ,$$

$$GP_A^{\beta} = \sum_{a \in A} (\mathbf{S}^{1/2}\mathbf{P}^{\beta}\mathbf{S}^{1/2})_{aa} \text{, and}$$

$$GP_A = GP_A^{\alpha} + GP_A^{\beta} .$$

The spin density is given by:

$$SP_A = GP_A^{\alpha} - GP_A^{\beta}$$

The *AOMix-L* program will print the α-, β- and gross electron (Mulliken and Löwdin) populations and spin densities for each fragment, α-, β- and gross electron (Mulliken and Löwdin) populations and spin densities of each atomic orbital:

```
======================== GROSS POPULATIONS OF ATOMS ======================
                   --- MULLIKEN ---                       --- LOWDIN ---
    ATOM    ------------------------------    ------------------------------
   # Symb   ALPHA    BETA     TOTAL  SPINDENS  ALPHA    BETA     TOTAL SPINDENS
   1  Cu:  14.682  14.211  28.893  0.47150  14.624  14.125  28.749  0.49982
   2  N :   3.512   3.512   7.023  0.00017   3.549   3.550   7.099 -0.00041
   3  N :   3.552   3.553   7.105 -0.00073   3.497   3.498   6.995 -0.00045
   4  N :   3.513   3.443   6.956  0.07057   3.563   3.505   7.068  0.05763
   5  N :   3.542   3.543   7.085 -0.00085   3.490   3.490   6.981 -0.00010
   6  N :   3.513   3.443   6.956  0.07057   3.563   3.505   7.068  0.05763
   7  N :   3.542   3.543   7.085 -0.00085   3.490   3.490   6.981 -0.00010
   8  C :   3.107   3.107   6.214 -0.00018   3.018   3.018   6.037  0.00006
   9  C :   3.001   3.001   6.002 -0.00009   3.074   3.074   6.148 -0.00007
```

```
 ======================== GROSS ATOMIC ORBITAL POPULATIONS ================
                   --- MULLIKEN ---                       --- LOWDIN ---
 AO#   FR#    ------------------------------    ------------------------------
              ALPHA    BETA     TOTAL SPINDENS   ALPHA    BETA     TOTAL SPINDENS
   1    1:    1.000   1.000   2.000  0.00000   0.998   0.998   1.997  0.00000
   2    1:    1.000   1.000   2.000  0.00001   0.999   0.999   1.999  0.00000
   3    1:    0.613   0.611   1.224  0.00169   0.558   0.557   1.115  0.00065
   4    1:    0.380   0.381   0.761 -0.00122   0.419   0.420   0.839 -0.00081
   5    1:    0.397   0.404   0.801 -0.00659   0.159   0.161   0.320 -0.00254
   6    1:   -0.024  -0.024  -0.048 -0.00040   0.062   0.063   0.126 -0.00105
```

...

LPA-derived atomic charges are rather sensitive to the basis set (see Table 1). A good point of LPA is that it does not give negative populations or orbital populations greater than 2. WARNING: if a **6D/10F basis set** (a basis set with 6 Cartesian d functions (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, d_{yz}) or/and 10 Cartesian f functions) are used in calculations, **LPA exhibit a rotational dependence, can predict non-equal populations for equivalent atoms, and thus, in this situation, should not be used** for the analysis.[31]

Table 1. The charge of the carbon atom in the CO_2 molecule at the B3LYP level of theory.

	Basis Set [a]					
	6-31G*	**6-31+G***	**6-311G***	**6-311+G***	**6-311+G(3df)**	**TZVP**
MPA	0.63	0.66	0.50	0.46	1.03	0.55
LPA	0.20	0.35	-0.06	0.09	-0.46	0.24
NPA	1.04	1.04	1.00	0.99	1.02	0.95

a) each basis set was set to use the 5D polarization functions on C and O. The structure of CO_2 was optimized at the B3LYP/6-311G* level ($R_{C\text{-}O}$=1.1605 Å).

In the above calculations, LPA-derived charge of the carbon atom in CO_2 displays largest variation from -0.46 to 0.36 a.u.; NPA[32-34]-derived charges show very little variation.

Overlap Populations and Chemical Bonding

The $2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab}$ terms, where $a \in$ atom A and $b \in$ atom B, are the overlap populations between the two atoms with atomic orbitals χ_a and χ_b respectively of the i^{th} MO. The total overlap population (TOP) between atoms A and B in a molecule is calculated by adding together overlap populations for orbitals centered on these two atoms:

$$TOP_{AB} = \sum_i n_i \sum_{a\in A}\sum_{b\in B} 2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab} \qquad (3.2.1)$$

where $\mathbf{c}_{ai}$ is the LCAO-MO coefficient of χ_a on atom A, $\mathbf{c}_{bi}$ is the coefficient of χ_b on atom B, both in the i^{th} MO, and $\mathbf{S}_{ab}$ is the overlap integral for these two AOs.

The overlap populations (OP) concept can be extended to the analysis of the bonding between the central atom and the ligands in transition metal complexes or other large molecules. In *AOMix.exe* and *AOMix-S.exe*, Equation 3.2.1 is applied to user-defined fragments (which can be individual atoms, groups of atoms, or an atomic orbital or groups of orbitals):

$$OP_{AB,i} = \sum_{a\in A}\sum_{b\in B} 2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab} \qquad (3.2.2)$$

$$TOP_{AB} = \sum_i n_i OP_{AB,i} = \sum_i n_i \sum_{a \in A} \sum_{b \in B} 2\mathbf{c}_{ai}\mathbf{c}_{bi}\mathbf{S}_{ab} \, . \qquad (3.2.3)$$

The TOP_{AB} and $OP_{AB,i}$ values are printed in the *AOMix* output file (*AOMix-MP.txt*). For example, in the $[Ru(NH_3)_4(quinone)]^{2+}$ complex, one gets:

```
OVERLAP POPULATIONS  2*cai*cbi*Sab, where a belongs to fragment A and b
belongs to fragment B.

               Overlap Populations between Fragments
 MO #          OP(1&2)       OP(1&3)       OP(2&3)
----------------------------------------------------
 TOP           0.404         0.472        -0.044
----------------------------------------------------
 58  LUMO+2   -0.465        -0.542        -0.059
 57  LUMO+1   -0.144        -1.0          -0.09
 56  LUMO     -0.045        -0.041        -0.007
--- occupied - virtual orbital gap ---
 55  HOMO     -0.112        -0.053         0.001
 54  HOMO-1   -0.067        -0.053         0.007
 53  HOMO-2   -0.026        -0.062         0.004
```

(Fragment 1 is the central atom (Ru), fragment 2 is the quinone ligand, and fragment 3 is the four NH_3 ligands). In this example, the second column contains the overlap populations between the central atom and the quinone ligand. The 3rd column contains the overlap populations between Ru and the ammonia ligands. The 4th column contains the overlap populations between the quinone ligand and the four ammonia ligands. **Positive OP_{AB} values represent a bonding interaction, large negative OP_{AB} values correspond to an anti-bonding interaction, and $OP_{AB} \approx 0$ indicates no bonding between *A* and *B*.**[35-38]

As it can be seen from the table above, the three highest occupied MOs (HOMO-0,1,2) remain mostly non-bonding with respect to metal-ligand interactions ("t_{2g}" (Ru) orbitals), while LUMO+1 and LUMO+2 is anti-bonding with respect to the Ru-ligand interactions.

AO contributions ($|2^*\mathbf{c}_{ai}{}^*\mathbf{c}_{bi}{}^*\mathbf{S}_{ab}|>0.01$) to overlap populations can be printed to *AOMix-S* output files by using the **OP-CONTRIBUTIONS** keyword. For example,

```
Alpha MO    8, OP contributions > 0.01:
    4   19 Ca=  -0.4093 Cb=   0.5523 Sab= 0.1150  2*Ca*Cb*Sab=  -0.052
    4   23 Ca=  -0.4093 Cb=   0.6021 Sab= 0.1709  2*Ca*Cb*Sab=  -0.084
```

```
    8   19 Ca=  -0.4348 Cb=   0.5523 Sab= 0.3178  2*Ca*Cb*Sab=  -0.153
    8   23 Ca=  -0.4348 Cb=   0.6021 Sab= 0.5781  2*Ca*Cb*Sab=  -0.303
```

Bond Orders

In the *AOMix-L* program, four types of bond order indices are available for the analysis of bonding between molecular fragments:

1) “generalized” Wiberg indices calculated in the canonical MO basis,[20]

2) Wiberg indices calculated in the Löwdin basis,[18,19]

3) Mayer indices (calculated in the canonical MO basis),[21-24] and

4) 3- and 4-center bond order indices (calculated in the canonical MO basis).[25,26]

AOMix is very flexible about how a user can define fragments: it is possible to obtain bond orders between atoms, groups of atoms, groups of orbitals, etc. The latter option is especially useful when you are interested to perform symmetry decomposition of bond orders (see below).

Generalized Wiberg bond order indices B_{AB}^{W} are[20]

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

and the **Mayer bond orders B_{AB}** are[21-24]

$$B_{AB} = \sum_{a\in A}\sum_{b\in B} \left[(\mathbf{PS})_{ba} (\mathbf{PS})_{ab} + (\mathbf{P}^{s}\mathbf{S})_{ba} (\mathbf{P}^{s}\mathbf{S})_{ab} \right],$$

where **P** and $\mathbf{P}^{s}$ are total density and spin-density matrices, respectively. The above equation for the Mayer bond orders can be re-written using the Mayer bond orders for α- and β-spin orbitals:

$$B_{AB}^{\alpha} = 2\sum_{a\in A}\sum_{b\in B} (\mathbf{P}^{\alpha}\mathbf{S})_{ba} (\mathbf{P}^{\alpha}\mathbf{S})_{ab} \quad \text{and}$$

$$B_{AB}^{\beta} = 2\sum_{a\in X}\sum_{b\in Y} (\mathbf{P}^{\beta}\mathbf{S})_{ba} (\mathbf{P}^{\beta}\mathbf{S})_{ab} ,$$

Thus, the total Mayer bond orders are:

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

For the closed-shell spin-singlet state calculations, $\boldsymbol{P}^{\alpha} = \boldsymbol{P}^{\beta}$ and, as a result:

$\boldsymbol{B_{AB}}^{\alpha} = \boldsymbol{B_{AB}}^{\beta}$ and $\boldsymbol{B_{AB}} = \boldsymbol{B_{AB}}^{\boldsymbol{W}}$.

In a general case with $\boldsymbol{P}^{\alpha} \neq \boldsymbol{P}^{\beta}$, the generalized Wiberg and Mayer bond orders are not equal.

It is also possible to define components of bond orders, by performing the summation only for orbitals of the given symmetry type.[39,40] In this manner, the bond order may be broken down into the contributions from the different symmetry/orbital character contributions:

$$\boldsymbol{B_{AB}} = \sum_{\Gamma_i} B_{AB}(\Gamma_i)$$

If molecular symmetry is present, *AOMix-L* attempts to resolve the bond order contributions ($\boldsymbol{B_{AB}}^{\alpha}$ and $\boldsymbol{B_{AB}}^{\beta}$) for each irreducible presentation. For example, for a molecule with C_{2v} symmetry, *AOMix-L* prints:

- $\boldsymbol{B_{AB}}^{\alpha}$ for α-spin orbitals with a_1 symmetry, $\boldsymbol{B_{AB}}^{\alpha}(a_1)$;
- $\boldsymbol{B_{AB}}^{\alpha}$ for α-spin orbitals with a_2 symmetry, $\boldsymbol{B_{AB}}^{\alpha}(a_2)$;
- $\boldsymbol{B_{AB}}^{\alpha}$ for α-spin orbitals with b_1 symmetry, $\boldsymbol{B_{AB}}^{\alpha}(b_1)$;
- $\boldsymbol{B_{AB}}^{\alpha}$ for α-spin orbitals with b_2 symmetry, $\boldsymbol{B_{AB}}^{\alpha}(b_2)$;
- and $\boldsymbol{B_{AB}}^{\alpha} = \boldsymbol{B_{AB}}^{\alpha}(a_1) + \boldsymbol{B_{AB}}^{\alpha}(a_2) + \boldsymbol{B_{AB}}^{\alpha}(b_1) + \boldsymbol{B_{AB}}^{\alpha}(b_2)$.

For example, here is the symmetry bond-order components for the Cu-S bond (atoms 1 and 28, respectively) in the Cu(L)-SC_6F_5 complex (C_s symmetry with two irreducible representations *a'* and *a"*):[39,40]

```
================= Symmetry Contributions to Bond Orders ===================
---- Resolved contributions to 2(PA*S)(PA*S) that are larger than 0.01 ----
 - FR1 - FR2 - a'    a"
...
   1Cu   28S   0.35  0.03
...

---- Resolved contributions to 2(PB*S)(PB*S) that are larger than 0.01 ----
- FR1 - FR2 - a'    a"
...
  1Cu   28S   0.36  0.33
...
```

Thus, the results from the *AOMix-L.exe* calculations can deliver local information on the chemical bonding between molecular fragments and the symmetry decomposition with respect to Γ_i makes it possible to resolve the σ- , π-, and δ- contributions.

Table 2. Mayer bond orders for selected small molecules (at the B3LYP/TZVP level)

Single bonds:	$\mathbf{H_2}$ 1.00, $\mathbf{Na_2}$ 1.00, $\mathbf{K_2}$ 0.99, $\mathbf{F_2}$ 0.90, $\mathbf{Cl_2}$ 0.97, $\mathbf{Br_2}$ 1.00
Aromatic C-C bonds:	$\mathbf{C_6H_6}$ 1.42
Double bonds:	H_2**C-C**H_2 1.97, $\mathbf{O_2}$ (spin triplet ground state) 1.74,
Triple bonds:	H**C-C**H 3.12, $\mathbf{N_2}$ 2.689, $\mathbf{P_2}$ 2.90

Bond order indices can be used for describing and analyzing intermediate structures in reaction paths. Several reports have been published, in which bond orders were utilized for the interpretation of reaction pathways by monitoring the variation of bond orders along a reaction path or internuclear distance, so-called *bond order profiles*.[15,41,42] These studies indicate that

1. the breaking of existing chemical bonds is synchronized with the formation of new chemical bonds and/or strengthening of remaining ones (the *bond order conservation rule*)[43,44];
2. the position of the transition state is localized in the vicinity of the inflection point on the bond order profile;
3. the inflection point on the bond order profile (see Figure 1) occurs if there is a change in the ground state wave function.[41]

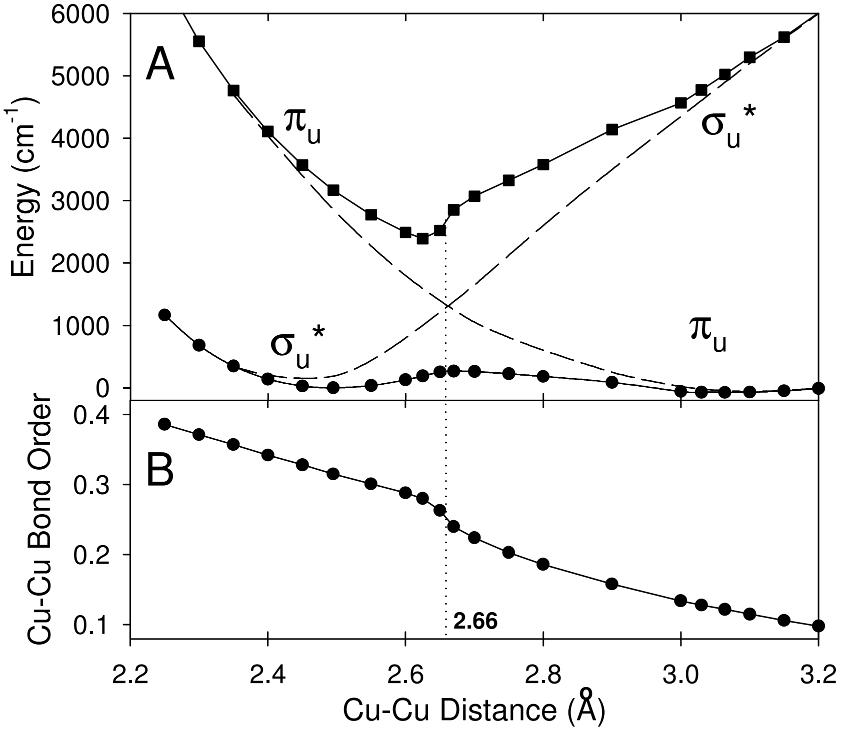


Figure 1 (adopted from Fig. 3 in Ref.[41]). (A) The ground state and the first excited-state potential energy surfaces of the Cu_A cluster (the N_{His}-$Cu(S_{Cys})_2Cu$-N_{His} cluster) and (B) Mayer bond order $\boldsymbol{B_{AB}}$ between the two Cu atoms of Cu_A as a function of the Cu-Cu distance.

Most single chemical bonds can be considered as being formed by a pair of electrons occupying a two-center molecular orbital. Multiple bonds (double or triple) are formed by two or three pairs of electrons occupying two or three molecular orbitals, respectively.

There are systems in which three-center two-electron bonds are proposed. The **3-center bond orders $\boldsymbol{B_{ABC}}$** for closed-shell species are[25-29]

$$B_{ABC} = \sum_{a\in A}\sum_{b\in B}\sum_{c\in C}\left[(\mathbf{PS})_{ab}(\mathbf{PS})_{bc}(\mathbf{PS})_{ca}\right].$$

For open-shell species,[30]

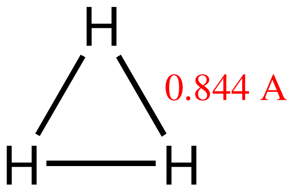
$$B_{ABC} = B^{\alpha}_{ABC} + B^{\beta}_{ABC}\text{ , where}$$

$$B_{ABC}^{\alpha} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \left[(\mathbf{P}^{\alpha}\mathbf{S})_{ab} (\mathbf{P}^{\alpha}\mathbf{S})_{bc} (\mathbf{P}^{\alpha}\mathbf{S})_{ca} \right] \text{ and}$$

$$B_{ABC}^{\beta} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \left[(\mathbf{P}^{\beta}\mathbf{S})_{ab} (\mathbf{P}^{\beta}\mathbf{S})_{bc} (\mathbf{P}^{\beta}\mathbf{S})_{ca} \right] .$$

These indices can be used to identify the 3-center orbital interactions in molecules. The bond order indices of 3-center bonds are positive with the maximum theoretically-possible value of $\frac{8}{27} \approx 0.296$. *AOMix-L.exe* will print α- and β-spin components of $\boldsymbol{B_{ABC}}$ for open-shell species.

An example of **a 3-center 2-electron bond** is the cyclic H_3^+ ion:



where the 3-center bond order index I_{123} is 0.296 (at the HF/6-31G level):

```
  A    B    C    3-CENTER bond order index (value > 0.01)
---- ---- ----  ----------------------------------------
  1H   2H   3H   B(ABC)= 0.296
```

Diborane (B_2H_6) and the $C_2H_4...H^+$ and $C_2H_4...H_3O^+$ complexes are also systems with two-electron 3-center chemical bonds (also known in the literature as). In B_2H_6, the B_{BHB} index is 0.24 at the HF/6-31G* level.[25] In the $C_2H_4...H_3O^+$ complex with the $\pi_{\text{ethylene}} \rightarrow \sigma_H$ interaction the B_{CHC} index is 0.224 at the B3LYP/TZVP level. For systems with no 3-center bonds, the 3-center B_{ABC} indices have values near zero. The 3-center bond order index can be used to identify agostic interactions.[45,46]

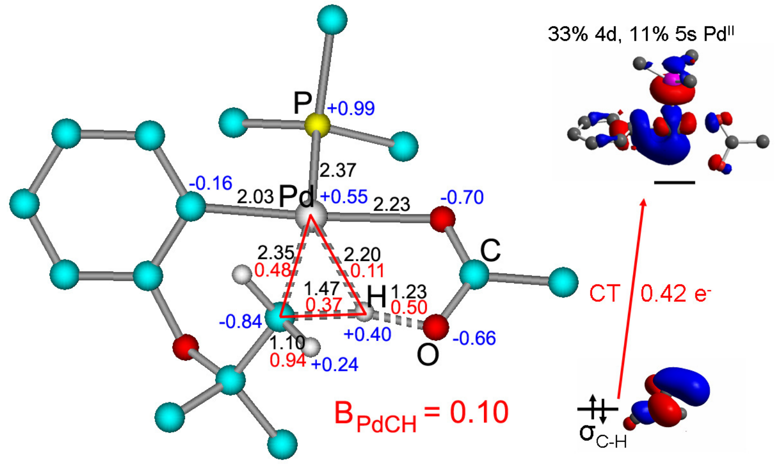


Figure 2 (adopted from Fig. 1 in Ref.[46]). Calculated TS for concerted palladation-deprotonation. Select H atoms have been removed for clarity. Relevant two- and three-center bond orders (red), distances (Å) (black), and NPA-derived atomic charges (blue) are shown. The 3-center covalent interaction and charge transferred (CT) from the C-H bond to the metal-based acceptor orbital are shown at right.

In addition to 3-center bond indices, the **4-center bond orders** $\boldsymbol{B_{ABCD}}$ [25,27,28]

$$B_{ABCD} = \sum_{a\in A}\sum_{b\in B}\sum_{c\in C}\sum_{d\in D}\left[(\mathbf{PS})_{ab}(\mathbf{PS})_{bc}(\mathbf{PS})_{cd}(\mathbf{PS})_{da}\right] \quad \text{(printed for closed-shell species)}$$

and α- and β-spin components of $\boldsymbol{I_{ABCD}}$ (printed for open-shell species)

$$B^{\alpha}_{ABCD} = \sum_{a\in A}\sum_{b\in B}\sum_{c\in C}\sum_{d\in D}\left[(\mathbf{P}^{\alpha}\mathbf{S})_{ab}(\mathbf{P}^{\alpha}\mathbf{S})_{bc}(\mathbf{P}^{\alpha}\mathbf{S})_{cd}(\mathbf{P}^{\alpha}\mathbf{S})_{da}\right] \text{ and}$$

$$B^{\beta}_{ABCD} = \sum_{a\in A}\sum_{b\in B}\sum_{c\in C}\sum_{d\in D}\left[(\mathbf{P}^{\beta}\mathbf{S})_{ab}(\mathbf{P}^{\beta}\mathbf{S})_{bc}(\mathbf{P}^{\beta}\mathbf{S})_{cd}(\mathbf{P}^{\beta}\mathbf{S})_{da}\right],$$

can be evaluated by using *AOMix-L.exe* to identify the 4-center interactions in molecules.

Total and free valence indices of atoms (or fragments)

In addition to bond orders and fragment and orbital populations, *AOMix-L* calculates the **total and free valences of fragments**. The **total valence of atom A (fragment A)** is defined as[20]

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

Its **free valence** is the difference between the total valence V_A and the sum of the bond orders formed by it:

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

From the above equation, it is clear that the free valence index F_A vanishes for all closed-shell systems ($\boldsymbol{P^S} = 0$).

As an example, atomic total and free valence indices are shown below for the NH_3BF_3 molecule:

```
Atom ========= Total and Free Valences =========
                V        F
   1  N :     3.355    0.000
   2  H :     0.942    0.000
   3  H :     0.942    0.000
   4  H :     0.942    0.000
   5  B :     3.527    0.000
   6  F :     0.904    0.000
   7  F :     0.904    0.000
   8  F :     0.904    0.000
```

Condensed Fukui Functions in Molecules

Fukui functions[47-51] are the common descriptors of site reactivity. They are defined as the derivative of the electron density with respect to the total number of electrons N in the system, at the constant external potential $\upsilon(r)$:

$$f(\vec{r}) = \left[\frac{\partial\rho(\vec{r})}{\partial N}\right]_{\upsilon(r)}$$

Since chemists are mostly concerned with properties associated with atoms and/or molecular fragments (functional groups, etc.), rather than properties associated with points in space, *condensed Fukui functions* were define. In a finite-difference approximation, they can be expressed by the following equations:

$$f_k^+ = \rho_k(N+1) - \rho_k(N) \qquad \text{(condensed Fukui function for a nucleophilic attack),}$$

$$f_k^- = \rho_k(N) - \rho_k(N-1) \qquad \text{(condensed Fukui function for an electrophilic attack)}$$

$$f_k^{\cdot} = [\rho_k(N+1) - \rho_k(N-1)]/2 \qquad \text{(condensed Fukui function for a radical attack),}$$

where *k* are sites (atoms / molecular fragments) for nucleophilic, electrophilic and radical agents, and ρ_k are their gross electron populations. A high value of f_k implies a high reactivity of that site *k*. Besides, the type of condensed Fukui function whose value is highest at a particular site, predicts the type of attack that predominates at that site.

It is possible to evaluate the condensed Fukui functions using *AOMix* from single-point calculations directly, without resorting to additional calculations involving the systems with *N*-1 and *N*+1 electrons (as an example, see Ref.[52]):

$$f_k^+ = \sum_{a \in k} \left[\mathbf{c}_{ai}^{\ 2} + \mathbf{c}_{ai} \sum_{b \neq a} \mathbf{c}_{bi} \mathbf{S}_{ab} \right], \text{ where } i = \text{LUMO;}$$

$$f_k^- = \sum_{a \in k} \left[\mathbf{c}_{ai}^{\ 2} + \mathbf{c}_{ai} \sum_{b \neq a} \mathbf{c}_{bi} \mathbf{S}_{ab} \right], \text{ where } i = \text{HOMO.}$$

Because the above two expressions represent **the fragment contributions** (in the MPA framework) **to the LUMO and the HOMO respectively**, **the condensed Fukui functions are calculated automatically when compositions of molecular orbitals are evaluated**. This formulation is suitable if the two frontier orbital description (the HOMO and the LUMO) is sufficient for describing the reactivity of a particular molecular system. This description, however, is not suitable for systems with high density-of-states near the HOMO-LUMO gap (such as transition metal systems).[53]

It is easy to see that the condensed Fukui functions must be non-negative (owing that all fragment contributions to MOs must be non-negative). Note also that the condensed Fukui functions (just like the fragment contributions to MOs) are normalized:

$$\sum_{k}^{NF} f_k = 1$$

and

$$f_k^{\cdot} = [f_k^+ - f_k^-]/2\,.$$

As an example, let's consider naphthalene ($C_{10}H_8$). Figure 3 shows the compositions of the HOMO and the LUMO of the molecule:

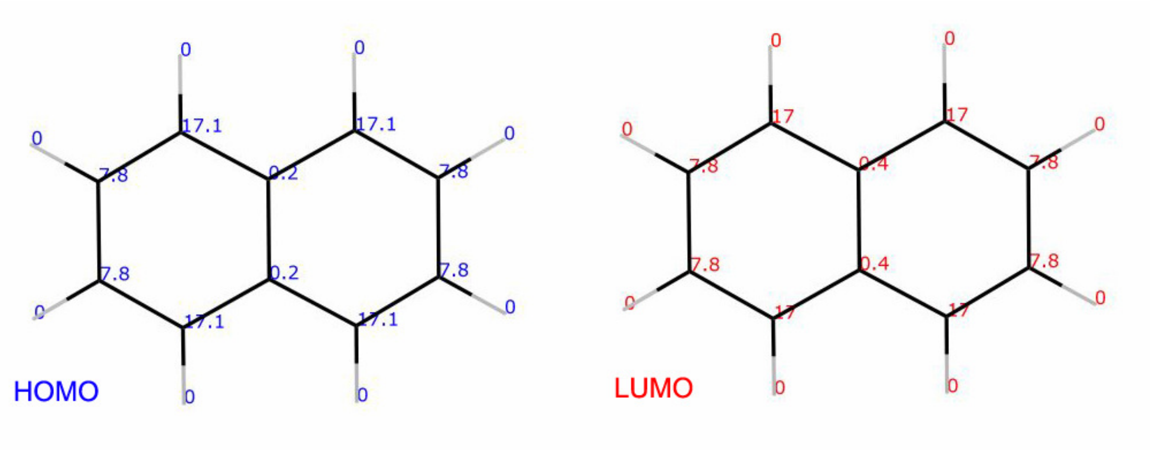


Figure 3. The MPA-derived composition of the HOMO and the LUMO of naphthalene (at the B3LYP/6-31G* level). The HOMO composition (shown in blue) represents the condensed Fukui function for an electrophilic attack (f_k^-) and the LUMO composition (shown in red) represents the condensed Fukui function for a nucleophilic attack (f_k^+).

For the HOMO, the contributions of the carbon atoms at the α and β positions are 17.1% and 7.8%, respectively. For the LUMO, the contributions of the carbon atoms at the α and β positions are 17.0% and 7.8%, respectively. These contributions indicate that electrophilic, nucleophilic, and radical (since $f_k^{\cdot} = [f_k^+ - f_k^-]/2$) attacks at the α carbon atom of naphthalene should be more effective than those at the β carbon atom.

You can also refer to a recent paper of Makedonas et al.[52] as an example of the analysis of the reactivity of [Metal(diimine)(dithiolato)] complexes using Fukui functions and *AOMix*.

Overlap Matrix between α- and β-Spin Molecular Orbitals

In a spin-unrestricted wave function, the α- and β-spin molecular orbitals are not necessarily orthogonal to one another (only within each set, either α-MOs or β-MOs, are all of the molecular orbitals mutually orthogonal to one another). Thus, there are cases of interest where it is relevant to evaluate the overlap integrals between α- and β-spin MOs.

If *AOMix-L.exe* is instructed (using the **PROJECTION** keyword) to print the full or partial MO overlap matrix $\left\langle \psi_i^\alpha \middle| \psi_j^\beta \right\rangle$ for a spin-unrestricted wave function Ψ_U, the expectation value of S^2 is computed by the *AOMix-L* program:

$$\left\langle \Psi_U \,|\, S^2 \,|\, \Psi_U \right\rangle = \frac{n_\alpha - n_\beta}{2}\left(\frac{n_\alpha - n_\beta}{2} + 1\right) + n_\beta - \sum_{i,j}^{occupied} \left\langle \psi_i^\alpha \,|\, \psi_j^\beta \right\rangle^2 ,$$

where n_α is the number of α-spin electrons and n_β is the number of β-spin electrons.

Total, Partial, and Overlap Population Density-of-States Plots

If the number of fragments in a calculation is less than 14, *AOMix-S.exe* generates total (TDOS), partial (PDOS), and overlap population (OPDOS) density-of-states plots.[36,54] The main use of the DOS plots is to provide a pictorial representation of MO compositions and their contributions to chemical bonding through the OPDOS plots which are also referred in the literature as Crystal Orbital Overlap Population (COOP) diagrams.

The total density of states (TDOS) at energy *E* is written as

$$TDOS(E) = \sum_i \delta(E - \varepsilon_i),$$

where the summation index ***i*** goes over all one-electron energy levels. Thus, the integral of *TDOS*(*E*) over an energy interval (E_1 to E_2) gives the number of one-electron states in that energy interval.

In DOS calculations with *AOMix-S.exe*, the δ-function can be substituted by Lorentzians, Gaussians, or pseudo-Voigt functions *F*:

$$TDOS(E) = \sum_i F(E - \varepsilon_i)$$

In order to find out how much a given fragment *A* (an orbital, an atom, a group of orbitals, or a groups of atoms) contributes to one-electron levels at certain energies, one may weigh a one-electron level with the fragment character, $C_{A,i}$. These fragment characters are determined by means of MPA or SCPA. Thus, for the partial density of states, one gets:

$$PDOS_A(E) = \sum_i C_{A,i} F(E - \varepsilon_i)$$

A sum of $PDOS_A(E)$ for all fragments gives *TDOS(E)*:

$$TDOS(E) = \sum_A PDOS_A(E).$$

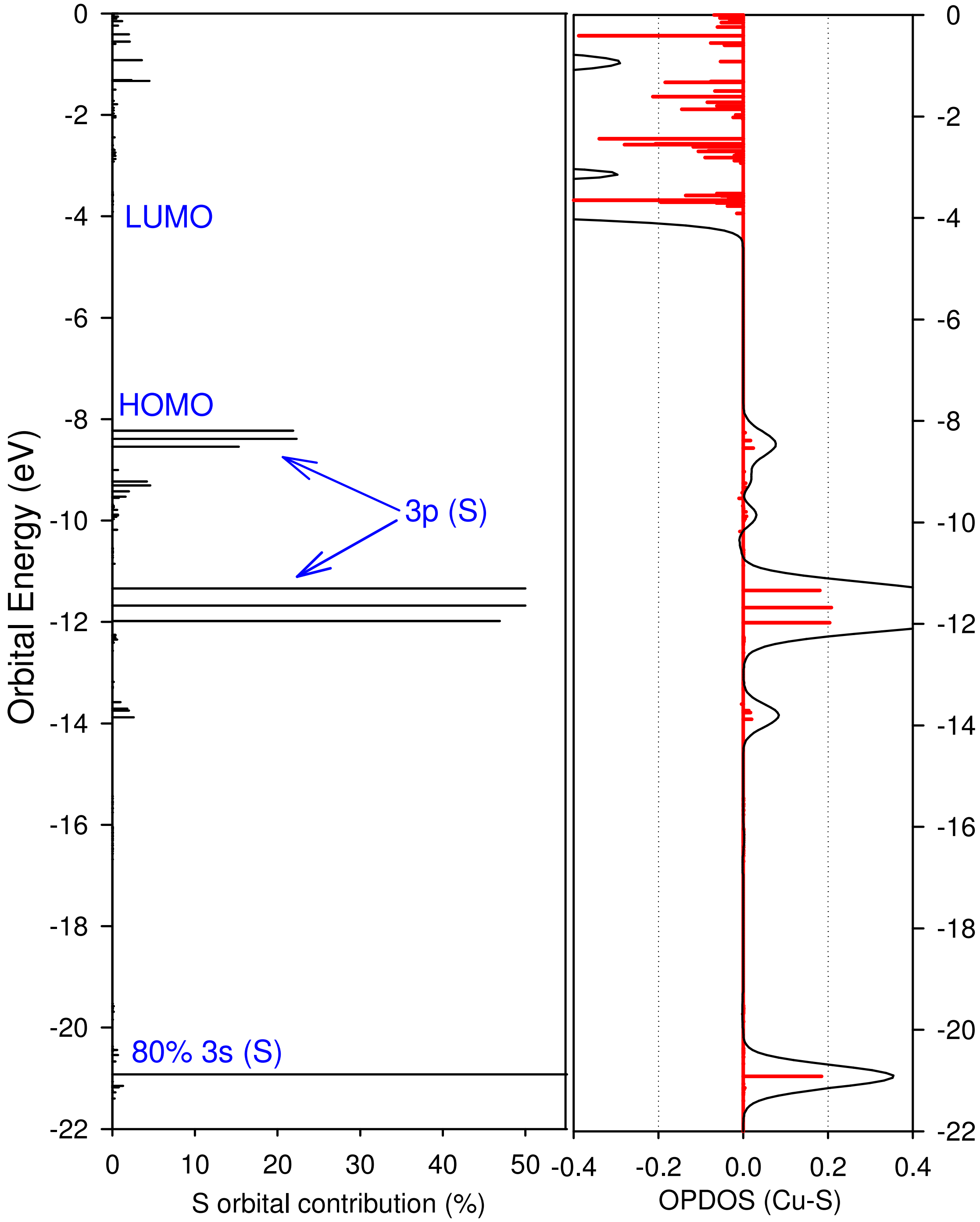
The overlap population density-of-states for fragments *A* and *B*, is

$$OPDOS_{AB}(E) = \sum_i OP_{AB,i} F(E - \varepsilon_i)$$

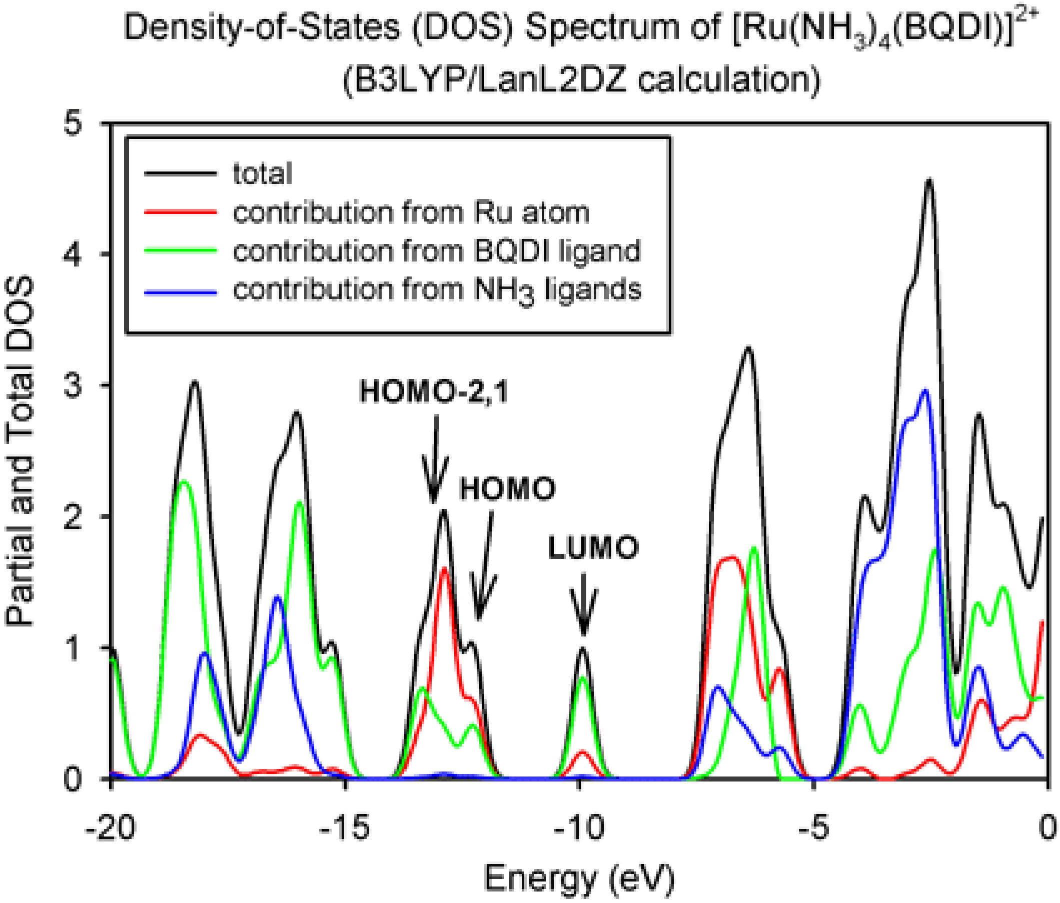
The integration of the $OPDOS_{AB}(E)$ function over all populated levels gives the total overlap population TOP_{AB} between fragments *A* and *B*:

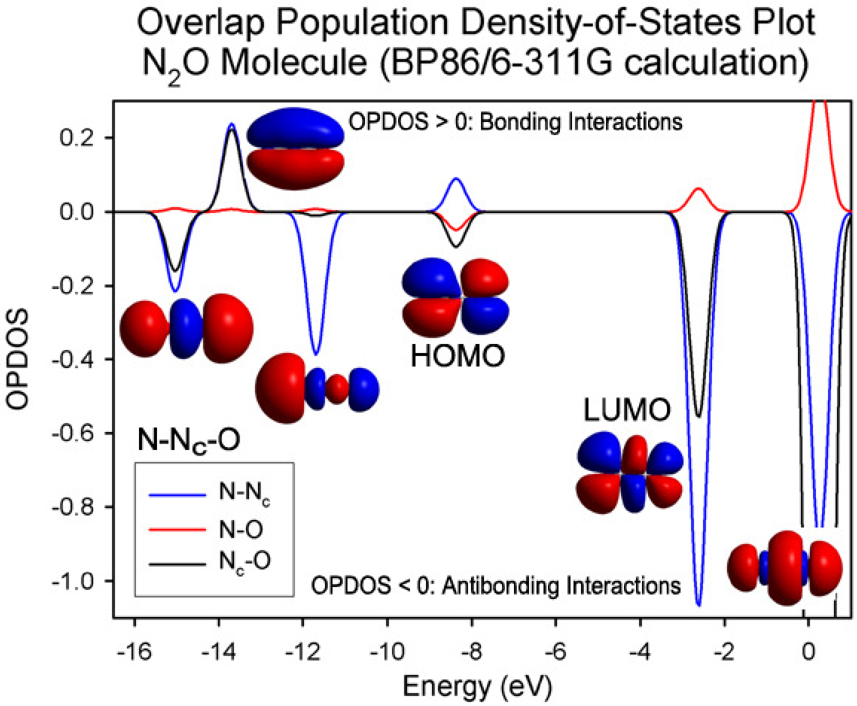
$$TOP_{AB} = \int_{-\infty}^{E_F} OPDOS_{AB}(E) dE.$$

Positive $OPDOS_{AB}(E)$ regions represent energy regions where *A*-*B* bonding levels are located and negative $OPDOS_{AB}(E)$ regions represent energy regions where *A*-*B* anti-bonding level are located. Thus, the *OPDOS* functions enable one to ascertain the bonding characteristics of electronic levels in a given energy range with respect to any pair of molecular fragments. Since calculations of the *OPDOS* functions require the overlap populations $OP_{AB,i}$, the OPDOS plots are only calculated for non-ZDO calculations with MPA as a method for electron population analysis.



In the above example, two DOS plots are shown. The PDOS plot (on the left) indicates the sulfur atom character in the molecular orbitals of the complex containing the tetrahedral Cu_4S^{2+} cluster. The OPDOS(Cu-S) plot (on the right) indicates which molecular orbitals are bonding, non-bonding, or anti-bonding with respect to Cu-S bonds. The OPDOS data are presented in two formats: a line plot (red) and a continuous Gaussian-band shape plot (black). In some cases, it is convenient to use line plots to show DOS data. In other cases, it is more helpful to present DOS data in a continuous format such as shown below:





More examples of the TDOS and PDOS plots are given in Refs.[15,55,56] ; examples of the OPDOS plots are given in Refs.[15,55,57,58]

The *AOMix-S* program writes continuous TDOS/PDOS plot data to *AOMix-S-X-DOS-line.txt* and continuous TDOS/PDOS plot data to *AOMix-S-X-DOS.txt*, where X is the population scheme used (MPA, MMPA, SCPA). The data structure of these TDOS/PDOS plot files is: the first column is energy (eV), the second column – the PDOS for the first fragment, the third column - the PDOS for the second fragment, etc. For continuous DOS data files, the last column is the TDOS (the sum of PDOSs for all fragments). **All PDOS and TDOS values in continuous plots are scaled by 1/2.** For a spin-unrestricted calculation, *AOMix-S.exe* prints PDOS/TDOS data for α-spin molecular orbitals first and, then, the corresponding values for β-spin molecular orbitals:

Column 1:	orbital energy (units: eV)
Column 2:	PDOS$_1$: contribution of Fragment 1 to TDOS (α-spin orbitals)
…	
Column NF+1:	PDOS$_{NF}$: contribution of Fragment *NF* to TDOS (α-spin orbitals)

<u>Column NF+2</u>:	**TDOS (α-spin orbitals)**
<u>Column NF+3</u>:	$PDOS_1$: contribution of Fragment 1 to TDOS (β-spin orbitals)
…	
<u>Column 2 NF + 2</u>:	$PDOS_{NF}$: contribution of Fragment N to TDOS (β-spin orbitals)
<u>Column 2 NF + 3</u>:	**TDOS (β-spin orbitals)**

By default, *AOMix-S.exe* calculates continuous DOS data in a $(\varepsilon_{HOMO} - 10\ eV) \rightarrow (\varepsilon_{LUMO} + 10\ eV)$ energy region using **Gaussian** functions with half-widths of 0.5 eV. If you want to specify an energy range explicitly, un-comment the **ENERGYRANGE** keyword and enter the desired lower and upper energy values (eV) for DOS calculations (see the example below). In addition, the **Lorentzian model** and the **pseudo-Voigt model** (a convolution using both the Gaussian and Lorentzian functions with the weighting factors *w* and 1-*w*, respectively) are available. You can change the continuous DOS convolution settings by modifying the **corresponding parameters** in the *aomixpar.txt* file:

```
###############################################################

###      Density-of-States (DOS) convolution parameters     ###
###                for the AOMix-S program                  ###
###############################################################
# 1st DOS parameter: Peak Shape.
#     Possible values: 0 -Gaussian; 1 -Lorentzian; 2 -pseudo-Voigt
# 2nd parameter: Print Window. Default value: 10.0 eV
# 3rd parameter: Width at Half-Height. Default value: 0.5 eV
# 4th parameter: Data sampling step. Default value: 0.05 eV
# 5th parameter: the gaussian-weighting coefficient in the pseudo-
#     Voigt function. Default value: 0.50. This parameter only
#     applies if the peak shape parameter is 2 (pseudo-Voigt).
DOS
0 10.0 0.5 0.05 0.50
# 1st parameter must be an integer, parameters 2-5 must be real numbers

#ENERGYRANGE
-20.0 10.0
```

AOMix-S.exe writes the OPDOS data to the following files: *AOMix-S-MPA-OPDOS.txt* (continuous plot) and *AOMix-S-MPA-OPDOS-line.txt* (line plot) and. The data structure of these files is the same as the order of overlap populations in *AOMix-S* output files:

NF	**Order of columns in OPDOS data files (*AOMix-S-MPA-OPDOS.txt* and *AOMix-S-MPA-OPDOS-line.txt*)**
2	Energy(eV), $OPDOS_{12}(\alpha)$ (and $OPDOS_{12}(\beta)$ if this is a spin-unrestricted calculation)
3	Energy(eV), $OPDOS_{12}(\alpha)$, $OPDOS_{13}(\alpha)$, $OPDOS_{23}(\alpha)$ (and $OPDOS_{12}(\beta)$, $OPDOS_{13}(\beta)$, $OPDOS_{23}(\beta)$ if this is a spin-unrestricted calculation)
4	Energy(eV), $OPDOS_{12}(\alpha)$, $OPDOS_{13}(\alpha)$, $OPDOS_{14}(\alpha)$, $OPDOS_{23}(\alpha)$, $OPDOS_{24}(\alpha)$, $OPDOS_{34}(\alpha)$ (and $OPDOS_{12}(\beta)$, $OPDOS_{13}(\beta)$, $OPDOS_{14}(\beta)$, $OPDOS_{23}(\beta)$, $OPDOS_{24}(\beta)$, $OPDOS_{34}(\beta)$, if this is a spin-unrestricted calculation)
…	…

3.4 Charge Transfer Character of Electronic Transitions

Typically, one interprets features in electronic spectra of transition metal complexes as metal-centered (MC), metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), ligand-to-ligand charge transfer (LLCT), metal-to-metal charge transfer (MMCT), intraligand or ligand-centered (LC) transitions, etc. However, such descriptions are only appropriate in the weak metal-ligand coupling limit, where "pure" excited states are most rigorously defined. When the metal-ligand coupling is high, the MOs are of mixed metal-ligand character, and descriptions of electronic excitations such as "pure" MC, MLCT, LMCT, LLCT, or LC become very approximate.

For characterization of the electronic transitions as partial CT transitions, the following definition of the CT character can be used:[59]

$$CT_l(M) = 100\ (\ P_g(M) - P_l(M)\ ), \qquad (3.4.1)$$

where $P_g(M)$ and $P_l(M)$ are electronic densities on the metal in the electronic ground state and the l-th excited state, respectively. Positive $CT_l(M)$ values correspond to MLCT transitions, negative $CT_l(M)$ values – to LMCT transitions.

This definition (Eqn. 3.4.1) can be re-written using the AO contributions to the MOs. For the HOMO-x→LUMO+y excitation, the metal CT character is:

$$CT(M) = \%(M)_{HOMO-x} - \%(M)_{LUMO+y} . \qquad (3.4.2)$$

For example, here are the frontier MOs of the $[Ru(terpy)_2]^{2+}$ complex from B3LYP/LanL2DZ calculations:

```
MO Number   Eigenvalue, eV                Contribution, %
                      Symmetry Fragment:  Ru          terpy
---------------------------------------------------------------
132  LUMO+2   -7.66        a2             0           100
131  LUMO+1   -7.79        e              8           92
130  LUMO     -7.79        e              8           92
-- occupied - unoccupied orbital gap -- 3.41eV
129  HOMO     -11.2        b1             70          30
128  HOMO-1   -11.31       e              72          28
127  HOMO-2   -11.31       e              72          28
```

The one-electron excitations have the following MLCT characters:

```
HOMO→LUMO+0,1                  70 - 8 = 62%
HOMO→LUMO+2                    70 - 0 = 70%
HOMO-1,2→LUMO+0,1              72 - 8 = 64%
HOMO-1,2→LUMO+2                72 - 0 = 72%.
```

If the excited state is formed by more than one one-electron excitation, then the metal CT character of this excited state is expressed as a sum of CT characters of each participating excitation, $i \rightarrow j$:

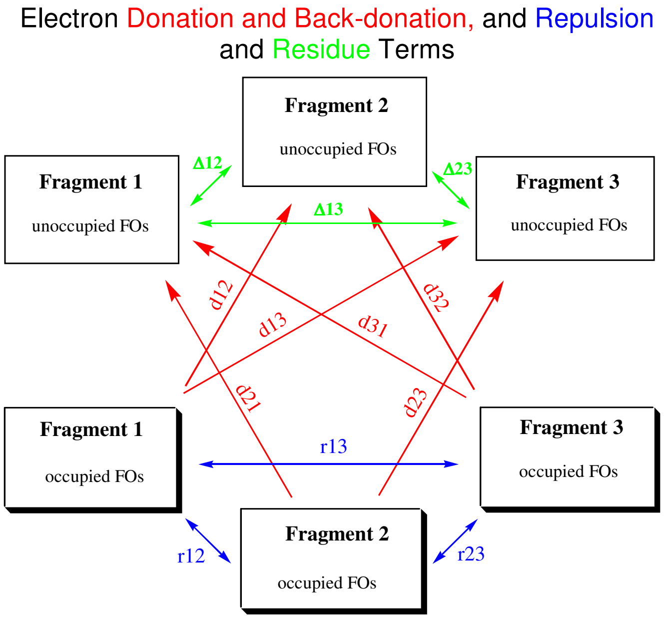
$$CT_l(M) = \sum_{i,a} [C_l(i \rightarrow j)]^2 \left(\%(M)_i - \%(M)_j \right), \qquad (3.4.3)$$

where $C_l(i \rightarrow j)$ are the appropriate coefficients of the l-th eigenvector of the CI matrix.

So, one can very effectively use the MO compositions in terms of fragment orbital contributions to probe the nature of electronic transitions.

Charge Decomposition Analysis (CDA)

The CDA method of Frenking and co-workers[13,14] is one of the two methods that are currently implemented in the *AOMix-CDA* program and can be used to evaluate fragment-to-fragment donation and back-donation in molecular systems. In CDA, it is also possible to calculate so-called repulsion and residue terms, r_{ij} and Δ_{ij}, respectively (Scheme 2).



Scheme 2. Charge decomposition analysis for a molecular system with three fragments.

In the CDA method,[13] the terms **donation** and **back-donation** do not mean only charge transfer interactions, they rather correspond to an overall reorganization of electronic density (including both charge transfer and electronic polarization).

Thus, **the difference between the amount of donation and back-donation between fragments is not equal to the net charge transfer between fragments**.[15] Stronger electronic polarization of fragments will produce a greater deviation between the difference between the amount of donation and back-donation and the net charge transfer. Thus, in cases with large electronic polarization of fragments, it is recommended to use ECDA (see the *AOMix-CDA* section in this manual) where fragment polarization contributions are taken into account and separated from charge transfer interactions.

Along the same line, the repulsion values in CDA (Scheme 2) correspond to the repulsion after polarization (i.e. electron density rearrangement), not the repulsion between pristine fragments.

Energy decomposition analysis

AOMix-CDA (coupled with Gaussian 98/03 calculations) can be used for Morokuma's energy decomposition analysis (EDA).[60]

(this section of the *AOMix* manual will be added soon)

Evaluation of Electronic Coupling between Donor and Acceptor in Donor-Bridge-Acceptor Systems using *AOMix-CDA*

(this section of the *AOMix* manual will be added soon)

Working with *AOMix*:

Execution environment of the *AOMix* software is controlled by the parameter file (*aomixpar.txt*). This file will be created when you run *AOMix.exe* for the first time. You can modify the execution parameters to tune the program to your particular tasks. See the AOMix keyword descriptions in this manual.

To start the *AOMix* program, execute ***AOMix.exe*.** If you are using "**non-Latin**" MS Windows version (such as Chinese, Japanese, or Korean), execute the **US** command in the Windows command prompt before you start *AOMix.exe*.

AOMix.exe reads the molecular orbital information directly from output files of the common quantum chemistry software packages and produces ASCII text files which contains molecular orbital energies, symmetries, percentages of contributions from fragments of the molecule (atoms, groups of atoms, groups of orbitals, etc.), overlap populations (HF and DFT wave functions), DOS plot data, etc.

The default scheme for the population analysis of HF/DFT calculations is MPA (if the overlap matrix is printed in an output file). You can select SCPA as an alternative method by adding the **SCPA** keyword to *aomixpar.txt*.

Unless you want to treat all atomic orbitals or all atoms as individual fragments (for *AOMix-S* and *AOMix-L* calculations), you have to specify fragments. You can do so by identifying which atoms or atomic orbitals / basis functions should be included in a particular fragment. The option to specify fragments as a list of atomic orbitals gives you the greatest flexibility, thus, it is available for processing output files from all software packages. Using this ORBITAL option, you can separate *s, p, d, f* orbital contributions by appropriately defined fragments for *AOMix* calculations. For convenience, you can also specify fragments as a list of atoms. However, this option is not available for all software packages (see the Table below).

QC Program	**Option to specify molecular fragments as a list of**		
	ORBITALS	**ATOMS**	Both **ORBITALS** and **ATOMS**
ADF	available	-	-
GAMESS (US)	available	available	available
Gaussian 98 / 03 ab initio	available	available	available
Gaussian 98 / 03 ZINDO	available	-	-
HyperChem	available	available	available
Jaguar 3.x	available	-	-
Jaguar 4.x-6.x	available	available	available
MOPAC	available	available	available
Reimers' CNDO/INDO	available	-	-
Q-Chem 2.x	available	-	-
Q-Chem 3.x	available	-	-
Spartan	available	-	-
Turbomole	available[a]	-	-
ZINDO	available	available	available

a) available by using *AOMix-prep*.exe to prepare *AOMix-L,S* input files.

EXAMPLE OF THE LCAO-MO OUTPUT FROM *Gaussian 98/03*:

```
...
191 13  C  1S         0.00110   0.00000   0.01488   0.00262  -0.01567
192        2S        -0.00290   0.00000  -0.03439  -0.00783   0.03699
193        3S        -0.00845   0.00000  -0.06530  -0.00508   0.08224
194        4PX        0.00000  -0.03074   0.00000   0.00000   0.00000
195        4PY       -0.01065   0.00000   0.01379  -0.21671  -0.01171
196        4PZ       -0.01577   0.00000   0.13845  -0.03374  -0.28372
197        5PX        0.00000  -0.00129   0.00000   0.00000   0.00000
198        5PY        0.00241   0.00000   0.03258  -0.03023  -0.04244
199        5PZ        0.00146   0.00000   0.00053  -0.00159  -0.01050
200        6D 0       0.00096   0.00000  -0.00478   0.01128   0.00719
201        6D+1       0.00000  -0.00295   0.00000   0.00000   0.00000
202        6D-1       0.00017   0.00000  -0.01295   0.00131   0.02599
203        6D+2       0.00011   0.00000  -0.00075   0.00406   0.00041
204        6D-2       0.00000   0.00284   0.00000   0.00000   0.00000
205 14  H  1S         0.05999   0.02475  -0.00957  -0.01148  -0.00726
206        2S         0.00010   0.00412  -0.00272  -0.01142  -0.00497
207 15  H  1S         0.05999   0.02475   0.00957  -0.01148   0.00726
208        2S         0.00010   0.00412   0.00272  -0.01142   0.00497
...
```

Atomic orbitals 191-204 are on atom 13 (carbon), atomic orbitals 205-206 are on atom 14 (hydrogen), and atomic orbitals 207-208 are on atom 15 (hydrogen). Note that if the number of orbitals is greater than 999, the *Gaussian* output will look like this:

```
997 117 O  1S        -0.00153   0.01285  -0.00334   0.00332  -0.01444
998        2S        -0.00157  -0.07079   0.05159  -0.01941   0.06777
999        2PX       -0.00900  -0.00035   0.05751   0.00858  -0.05029
```

```
 ***         2PY          -0.03250   0.08764  -0.00535  -0.00048   0.00408
 ***         2PZ           0.02568  -0.14132  -0.03181  -0.04061   0.12659
 ***         3S            0.01522   0.08717  -0.20222   0.07398   0.11025
 ***         3PX           0.01543  -0.04160  -0.11174  -0.01109   0.05886
 ***         3PY           0.04850  -0.12485  -0.01519  -0.00101   0.07823
 ***         3PZ          -0.03569   0.22263   0.08798   0.04233  -0.17658
 ***         4D 0         -0.00001   0.01147  -0.00853   0.01036  -0.00491
 ***         4D+1         -0.00125   0.00983  -0.00432   0.00508   0.00158
 ***         4D-1          0.00000  -0.00847   0.02461  -0.01637   0.00552
 ***         4D+2         -0.00135   0.00209  -0.01908   0.00488  -0.00852
 ***         4D-2          0.00344  -0.00388  -0.00551  -0.00235  -0.01688
 *** 118 H   1S           -0.01024  -0.02248   0.06354  -0.02228   0.06322
 ***         2S            0.05947  -0.15626  -0.06432   0.00795   0.00288
 *** 119 H   1S           -0.00169  -0.12149  -0.08394   0.06407  -0.02118
 ***         2S           -0.02293   0.27698   0.06610  -0.15275  -0.27837
```

AOMix.exe will process such output with no problem: the *AOMix* program does not use orbital numbers printed in the first column by *Gaussian*.

EXAMPLE OF THE LCAO-MO OUTPUT FROM *HyperChem*:

```
  S  C   1     -0.36236    0.26975   -0.39441    0.17211    0.30592    0.08809
 Px  C   1     -0.13668    0.08866    0.06608   -0.18388   -0.01395   -0.29675
 Py  C   1     -0.07705   -0.15871   -0.10536    0.24226   -0.21133   -0.13282
 Pz  C   1     -0.00000    0.00000    0.00000   -0.00000    0.00000   -0.00000
  S  C   2     -0.36094   -0.20123   -0.43173    0.17441   -0.30181    0.09679
 Px  C   2     -0.13627   -0.09761    0.04994   -0.18252    0.00357   -0.29442
 Py  C   2      0.07715   -0.17237    0.07771   -0.23894   -0.20795    0.13844
 Pz  C   2     -0.00000    0.00000    0.00000    0.00000    0.00000   -0.00000
  S  C   3     -0.36904   -0.48305   -0.04042   -0.35945   -0.00208    0.04514
 Px  C   3     -0.00029   -0.01904    0.22765   -0.00235    0.36219   -0.00604
 Py  C   3      0.15833   -0.00765   -0.00073   -0.16561    0.00344    0.31819
 Pz  C   3     -0.00000    0.00000    0.00000    0.00000    0.00000   -0.00000
...
```

Atomic orbitals 1-4 are on atom 1 (carbon), atomic orbitals 5-8 are on atom 2 (carbon), and atomic orbitals 9-12 are on atom 3 (carbon). Note that, unlike the majority of the other programs, *HyperChem* and *MOPAC* DO NOT PRINT ATOMIC ORBITAL NUMBERS in the LCAO-MO output, only ATOM NUMBERS. Thus, if you want to analyze MOs in terms of contributions from specific atomic orbitals, you have to find their "list" numbers in the LCAO-MO output by counting orbitals manually.

Unless you want to treat all atomic orbitals or all atoms as individual fragments (for *AOMix-S* and *AOMix-L* calculations), you have to create an auxiliary ASCII file to specify molecular fragments. *AOMix.exe* will read the fragment information from this file. This auxiliary file must be created using the following format:

Line 1: NF `(1, 2, 3, etc.)`

Line 2*: `orbitals/atoms in the 1`st `fragment followed by -1 or -2`

Line 3: **the name of the 1st fragment or a blank line**

Line 4*: **orbitals/atoms in the 2nd fragment followed by -1 or -2**

Line 5: **the name of the 2nd fragment or a blank line**

etc.

* The atom/orbital list statements are **not restricted to one line** for a fragment. You can use as many lines as necessary to list all relevant atoms/orbitals. Fragment names are limited to one line per fragment. If you do not want to assign any name to a fragment, the name line should be blank.

DON'T USE <TAB>s AS DELIMITERS IN FRAGMENT LIST FILES! The program may not see them as valid delimiters and this may lead to unpredictable program execution. Use only blank space characters and commas as delimiters.

Fragments can be specified using the following formats. The first format is to have a list of numbers (N_1, N_2, N_3, etc.):

$N_1\ N_2\ N_3\ N_4\ N_5\ \ldots\ N_n\ -X$

The numbers can be in an arbitrary order.

The second format is to specify a range (from N_1 to N_2) to be included in a fragment:

$0\ N_1\ N_2\ -X$

If ***X*** is **1,** then this is a list of atomic orbitals. If ***X* is 2**, then this is a list of atoms.

The above formats can be used together. For instance, the following instructions tell *AOMix.exe* to group atomic orbitals 1, 5, 10-50, 60, 62 and 70-80 into the first fragment and orbitals 2, 3, 4, 6-9 and 63-69 into the second fragment:

```
2
1 5 0 10 50 60 62 0 70 80 -1
First fragment
2 3 4 0 6 9 0 63 69 -1
Second fragment
```

Note that there should be **no duplication in fragments**: two different fragments cannot contain the same basis functions. *AOMix.exe* automatically checks for duplications and will exit with an error message, if it detects a duplication.

Don not worry if your partitioning is not complete. If you do not include all atoms or orbitals in fragments, *AOMix.exe* will find omitted orbitals/atoms and will include them as an additional fragment (named “Leftovers”).

HOW TO DEFINE FRAGMENTS (the format of fragment list files)

EXAMPLE 1. A list of **atomic orbitals** (3 fragments):

```
3
0 1 22 -1
Ru atom
0 23 40 0 77 130 0 155 162 -1
Quinine
0 41 76 0 131 154 -1
NH3 ligands
```

These instructions tell *AOMix.exe* to group atomic orbitals 1-22 into the 1st fragment (the Ru atom), atomic orbitals 23-40, 77-130, and 155-162 into the 2nd fragment (the quinine ligand), and atomic orbitals 41-76 and 131-154 into the 3rd fragment (the NH_3 ligands).

EXAMPLE 2. A list of **atoms** (3 fragments):

```
3
1 -2
Ru atom
2 3 0 8 13 0 26 29 -2
Quinine
0 4 7 0 14 25 -2
NH3 ligands
```

These instructions tell *AOMix.exe* to treat atom 1 as the 1st fragment (the Ru atom), group atoms 2, 3, 8-13 and 26-29 into the 2nd fragment (quinone), and group atoms 4-7 and 14-25 into the 3rd fragment (the NH_3 ligands).

EXAMPLE 3. A list of **atoms and atomic orbitals** (4 fragments):

```
4
0 1 12 -1
s,p orbitals of Ru atom
0 13 22 -1
d orbitals of Ru atom
2 3 0 8 13 0 26 29 -2
Quinine
0 4 7 0 14 25 -2
NH3 ligands
```

These instructions tell *AOMix.exe* to group atomic orbitals 1-12 into the 1st fragment (*s,p* orbitals of Ru atom), atomic orbitals 13-22 into the 2nd fragment (*d* orbitals of Ru atom), atoms 2, 3, 8-13 and 26-29 into the 3rd fragment (quinone), and atoms 4-7 and 14-25 into the 4th fragment (the NH_3 ligands).

For correct execution of the program, ensure that your output files contain all necessary data. To make sure that this is the case, use the following settings:

Use only **SINGLE-POINT CALCULATION OUTPUT FILES** for *AOMix* processing. **Don't use geometry optimization job files.**

ADF calculations with **no core functions**[b]	use the **symmetry nosym** keyword;[a] your *ADF* output file should contain energies and coefficients of all molecular orbitals; the **TITLE** field must be present in your output file because it is used as an identifier for the results section.
HyperChem calculations	use **QuantumPrintLevel = 1**
GAMESS (US) calculations	use **RUNTYP=ENERGY** and **NPRINT=3** in the `$CONTRL` input section
Gaussian 98 / Gaussian 03	
- for *ab initio* / DFT calculations	use a single point job with the keywords **POP=FULL**, **SCF=TIGHT** and **IOp(3/33=1)**
- for ZINDO calculations	use a single point job with **IOp(5/33=2)**
Jaguar 3.x-6.x calculations	use the keywords **ipvirt=-1, ip102=8**, **ip18=2**, and **numd=6** in the **&gen** input section If you are using more than 1 CPU to run your Jaguar calculations, make sure that the output files do not contain any lines with the **WARNING OPEN_M2IO_FILES** messages. If they do, just delete those lines.
MOPAC calculations	use the keywords **VECTORS, EIGEN** and **ALLVEC**
Q-Chem 2.x calculations	use the keywords **PRINT_ORBITALS 99999** and the **converter utility** to add the overlap matrix to an output file
Q-Chem 3.x calculations	use the keywords **PRINT_ORBITALS 99999** and **IPRINT 200**
Spartan calculations	For processing, use output files (instead of .spartan

	files)
Turbomole calculations	**$scfmo file=mos** [c)] **$last step dscf** **$intsdebug cao** **$scforbitalorder on**
ZINDO calculations	use the keyword **MOS** in the **`$OUTPUT`** input section

[a)] The **nosym** keyword is only necessary for symmetric molecules. b) Do not confuse the core functions and core orbitals, please refer to the *ADF* user manual for details. c) Use *Turbomole* default format (4D20.14) for the MO output.

It is known that in all types of orbital-based population analysis schemes the numerical values of calculated electron populations and related indices (bond orders, MO compositions, etc.) generally depend on the quality of the basis set used. For this reason, it is always prudent to analyze the basis set dependence (especially when using Pople-type basis sets with diffuse functions such as 6-311++G) of any calculated parameter.

Working with *AOMix-L* and *AOMix-S*:

If the overlap matrix is included in an output file of a QC package (*ADF, GAMESS, Gaussian, Jaguar, Q-Chem*), the default scheme for population analysis of HF/DFT calculations is MPA in *AOMix-S.exe* and both MPA and LPA in *AOMix-L.exe*. In *AOMix-S.exe*, you can select SCPA or MMPA as alternative methods for the population analysis by adding the **SCPA** / **MMPA** keywords to the *AOMix* execution parameter file (*aomixpar.txt*). You can utilize several keywords (see the *AOMix* keyword table in this manual) to control the printing level for *AOMix-L.exe* / *AOMix-S.exe* output files. For example, if you do not need to perform LPA in *AOMix-L* calculations, you can use the **LPA=OFF** keyword (or **LOWDIN=OFF**). This will reduce the CPU time required for the calculation.

1. Uncomment (remove #) the **LARGE** keyword in the *AOMix* parameter file (*aomixpar.txt*). Note that the **LARGE** keyword will be ignored by *AOMix.exe* if the **CDA** keyword is uncommented in the parameter file. If you prepare input files for *AOMix-L,S* calculations, make sure that the **CDA** keyword is absent or commented (# **CDA**).
2. If you are using “**non-Latin**” MS Windows version, execute the **US** command in the Windows command prompt before you start *AOMix.exe*.

3. Start the *AOMix.exe* program (or *AOMix-prep.exe* for *Turbomole* files (for Turbomoles, files with the default names will be required: *DSCF* for the overlap matrix, *mos* for the closed-shell MO output, *alpha* and *beta* for the open-shell MO output) and run it with your output file from *Gaussian 03* or from the other *AOMix*-supported package. You should see the message:

   ```
   Preparing the AOMix-L,S input files -  ON
   ```

   Then, *AOMix* will create several files (*AOMix.c, AOMix.ind, AOMix.e, etc.*) which will be used in Step 3. The fragment list file **is not required** if you ant to treat **all basis functions** or **all atoms** as **individual fragments**. Otherwise, the same format rules are in place (see the format description of *AOMix* fragment list files in this manual).
4. Run *AOMix-L.exe* and/or *AOMix-S.exe* in the same directory where the *AOMix* files from Step 2 are located. If you include the **AOMIX-S TO-FOLLOW** keyword in the *AOMix* parameter file (*aomixpar.txt*), *AOMix-S*.exe calculations will run automatically after the *AOMix-L.exe* execution and, at the end of the program run, *AOMix* temporary files will be deleted.

Here is an example of the *AOMix-S* MO composition output:

```
    Beta MO:     111      112      113      114      115      116      117      118      119      120
              HOMO-7   HOMO-6   HOMO-5   HOMO-4   HOMO-3   HOMO-2   HOMO-1     HOMO     LUMO   LUMO+1
 Energy(eV):   -7.53    -7.47    -7.32    -7.30    -7.19    -7.14    -6.87    -6.63    -4.24    -1.01
===========================================================================================================
ATOM#   1Cu:   17.42     0.07    18.59     2.82     3.25    35.58     0.37    24.14    48.57     1.47
 Net pop.(%)   18.05     0.06    17.21     2.94     3.07    37.70     0.31    22.40    54.73     1.71
 s orbitals:    0.15     0.00     2.56     0.00     0.00     1.90     0.00     0.00     0.00     0.00
 p orbitals:    1.71     0.01     4.20     0.25     0.49     2.55     0.09     3.46     1.06     0.29
 d orbitals:   15.55     0.05    11.82     2.56     2.77    31.13     0.27    20.68    47.51     1.18
-----------------------------------------------------------------------------------------------------------
ATOM#   2N :    4.39     0.06    -0.16     0.21    22.97    16.42     8.29     2.72     0.02     0.02
 Net pop.(%)    5.69     0.05     0.53     0.14    23.49    25.11     9.46     3.25     0.01     0.01
 s orbitals:    1.22     0.00    -0.01     0.00     0.00     4.27     0.00     0.00     0.00     0.00
 p orbitals:    3.15     0.06    -0.16     0.12    22.89    12.13     8.20     2.71     0.02     0.02
 d orbitals:    0.02     0.00     0.00     0.09     0.08     0.02     0.09     0.01     0.00     0.00
-----------------------------------------------------------------------------------------------------------
ATOM#   3N :    1.42     0.06     0.30     8.49     6.47     0.77    12.21     0.04    -0.01     0.01
...
```

In this table, the gross and net populations are printed for each fragment, it is followed by s,p,d orbital contributions. In the above example, the net and gross populations in the LUMO for the Cu atom (fragment 1) are 48.6 and 54.7%, respectively. The net population of the Cu atom comes from the d and p orbitals (their contributions to the LUMO are 47.5% and 1.1% respectively).

At the end of the *AOMix-S.exe* output for all non-closed-shell-singlet calculations, the contributions to the spin density are printed:

```
 ATOM    ============== SPIN DENSITY ==============
          gross   -- s --   -- p --   -- d --   -- f -- etc.
  1Cu     0.471   -0.006    -0.025     0.503
```

```
   2N     0.000    0.000    0.000    0.000
   3N    -0.001    0.000   -0.001    0.000
   4N     0.071    0.019    0.052    0.000
   5N    -0.001    0.001   -0.002    0.000
   6N     0.071    0.019    0.052    0.000
   7N    -0.001    0.001   -0.002    0.000
```

In the above example, for the 1Cu atom (fragment 1), the spin density (0.471) comes almost entirely from the difference (0.503) in the d orbital occupation and slightly altered by spin polarization of the s and p orbitals (their contributions to the atom spin density are -0.006 and -0.025, respectively).

(***AOMix-S.exe***)

Note 1 Automatic breakdown into atomic spdf contributions is limited to the cases with 5D/7F basis sets (basis sets with 5 d functions and 7 f functions) and *HyperChem* and *Gaussian 03* output files. If you basis set has 6 Cartesian d functions and 10 Cartesian f functions, *AOMix-S.exe* will skip the spdf analysis.

Note 2 Overlap populations and DOS plot data are generated only if NF ≤ 13 (this is done to limit the size of *AOMix-S* output files).

Note 3 Atomic orbital contributions to overlap populations can be printed to *AOMix-S* output files by using the **OP-CONTRIBUTIONS** keyword.

Note 4 For *Gaussian* calculations, *AOMix-S.exe* will generate two scripts (*AOMix-S-cube-win.bat* for MS Windows and *AOMix-S-cube.bat* for Linux/UNIX) for cube file generation. These *AOMix* scripts will be very helpful to *Gaussian* users to generate cube files for visual analysis of molecular orbitals, spin density and electrostatic potential. The example of the UNIX script (*AOMix-S-cube.bat*) is shown below:

```
touch temp.fchk
rm temp.fchk
formchk temp.chk
cubegen 0 potential temp.fchk C9H17CuN4S2-ESP.cub 0 h
cubegen 0 spin temp.fchk C9H17CuN4S2-spin.cub 0 h
cubegen 0 MO=78 temp.fchk C9H17CuN4S2-A-78-HOMO-2.cub 0 h
cubegen 0 MO=79 temp.fchk C9H17CuN4S2-A-79-HOMO-1.cub 0 h
cubegen 0 MO=80 temp.fchk C9H17CuN4S2-A-80-HOMO-0.cub 0 h
cubegen 0 MO=81 temp.fchk C9H17CuN4S2-A-81-LUMO+0.cub 0 h
cubegen 0 MO=82 temp.fchk C9H17CuN4S2-A-82-LUMO+1.cub 0 h
cubegen 0 MO=83 temp.fchk C9H17CuN4S2-A-83-LUMO+2.cub 0 h
cubegen 0 MO=374 temp.fchk C9H17CuN4S2-B-77-HOMO-2.cub 0 h
cubegen 0 MO=375 temp.fchk C9H17CuN4S2-B-78-HOMO-1.cub 0 h
cubegen 0 MO=376 temp.fchk C9H17CuN4S2-B-79-HOMO-0.cub 0 h
cubegen 0 MO=377 temp.fchk C9H17CuN4S2-B-80-LUMO+0.cub 0 h
cubegen 0 MO=378 temp.fchk C9H17CuN4S2-B-81-LUMO+1.cub 0 h
cubegen 0 MO=379 temp.fchk C9H17CuN4S2-B-82-LUMO+2.cub 0 h
```

In the above script, *AOMix-S.exe* instructs the *cubegen* program (from the *Gaussian* package) to create cube files for electrostatic potential, spin density (for open-shell species), and 6 frontier orbitals (α- and β-spin HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2) from a spin-unrestricted calculation in which *temp.chk* was a *Gaussian* checkpoint file. For convenience, cube files names (for example, `C9H17CuN4S2-B-82-LUMO+2.cub`) include **molecular formula**, **spin (A= α-spin MO, B= β-spin MO)**, and **MO number**.

By default, the generate script will include five HOMOs and five LUMOs. If you want the script to include more orbitals, use **CUBE=10** (then the script will include 10 HOMOs and 10 LUMOs), **CUBE=20** (then the script will include 20 HOMOs and 20 LUMOs) or the **CUBE=ALL** keyword (then the script will include all molecular orbitals).

(***AOMix-L.exe***)

Note 1 *AOMix-L* will only run when molecular fragments are defined as

- a list of atoms or orbitals, or
- each atom is a fragment.

AOMix-L cannot be used for calculations when each atomic orbital is defined as a fragment (NF = the number of basis functions).

Note 2 If 6D/10F basis sets (basis sets with 6 Cartesian d functions and 10 Cartesian f functions) are used in calculations, LPA exhibit a rotational dependence, can predict non-equal populations for equivalent atoms, and thus, in this situation, should not be used.[31]

Note 3 4-center bond order indices are printed if the **4-CENTER=ON** keyword is present in the *aomixpar.txt* file.

Note 4 for spin-unrestricted calculations, the program projects β-spin MOs on to α-spin MOs and prints the overlap matrix $\left\langle \phi_i^{\alpha} \middle| \phi_j^{\beta} \right\rangle$ (the so-called mutual overlap matrix) for 8 highest occupied and 8 lowest unoccupied MOs (the default settings). A user can select to print the full mutual overlap matrix (by using the **PROJECTION=FULL** keyword in the *aomixpar.txt* file), to print a portion of the mutual overlap matrix that includes only the occupied MOs (the **PROJECTION=OCCUPIED** keyword), or to skip this step (**PROJECTION=OFF**).

Note 5 A user can select to print eigenvalues and eigenvectors of the overlap matrix and the $\mathbf{S}^{1/2}$ and $\mathbf{S}^{-1/2}$ matrices by using the **S-EIGV=ON** and **LOWDIN=ON** keywords in the *aomixpar.txt* file.

Visualization of *AOMix-L/S*-calculated properties using *UCSF Chimera*

UCSF Chimera[61] (http://www.cgl.ucsf.edu/chimera) is a very advanced, extensible graphical package for visualization of structures and properties of both simple and very complex molecular structures.

If *AOMix-L.exe* and *AOMix-S.exe* are executed with each atom defined as a fragment, the programs will generate *Chimera*-readable atomic attribute files (*AOMix-L-atom-chimera.txt* and *AOMix-S-MPA-atom-chimera.txt*) and pseudobond attribute files (*AOMix-L-atom-chimera2.txt*). Those contain the following data:

***AOMix-L* output**

(*AOMix-L-atom-chimera.txt*): 1-center attributes such as MPA- and LPA-derived spin densities, total and free valences of atoms

(*AOMix-L-atom-chimera2.txt*): 2-center (pseudobond) attributes such as Mayer bond orders

***AOMix-S* output**

(*AOMix-S-MPA-atom-chimera.txt*): atomic contributions to the frontier orbitals (10 HOMOs and 10 LUMOs) which also represent the condensed Fukui functions.

If *AOMix-L.exe* and *AOMix-S.exe* are executed with user-defined fragments and ***NF*** is the number of fragments, the two programs will generate attribute files *AOMix-L-fr**NF**-chimera.txt*, *AOMix-L-fr**NF**-chimera2.txt* and *AOMix-S-MPA-fr**NF**-chimera.txt*. These files contain the same data as *AOMix-L-atom-chimera*, *AOMix-L-atom-chimera2* and *AOMix-S-atom-chimera*. However, one can only use *AOMix-L-fr**NF**-chimera.txt*, *AOMix-L-fr**NF**-chimera2.txt* and *AOMix-S-MPA-fr**NF**-chimera.txt* with *UCSF Chimera* if user-defined fragments are individual atoms.

Importing 1-center attribute data:

Define Attribute Render by Attribute To import *AOMix*-calculated ATOMIC (1-center) attribute data to your *UCSF Chimera* session, open the structure file for your molecule. Then use the Define Attribute tool (Tools→Structure Analysis→Define Attribute) to import the data from *AOMix-L-atom-chimera.txt* or *AOMix-S-MPA-atom-chimera.txt*; then, you should employ the Actions→Label→other... command to show a desired attribute (such as the HOMO composition (Figure 2) or MPA-derived atomic spin densities) as atomic labels. In addition, you can use the Render By Attribute tool to color atoms or change their sizes based on the attribute.

Importing 2-center attribute data:

In *UCSF Chimera*, 2-center interactions between pairs of atoms are referred to as pseudobonds (PB). Pseudobonds are lines drawn between atoms to signify connections other than standard bonds. The PseudoBond Reader (Tools→Depiction→PseudoBond Reader) allows *Chimera* users to create pseudobonds connecting arbitrary pairs of atoms. Apply the PseudoBond Reader to visualize Mayer bond orders from *AOMix-L-atom-chimera2.txt*. Bond order depiction (e.g. line style and color) can be controlled with PseudoBond Panel (under the Tools→General controls). See the FAQ page (http://www.sg-chem.net/NP/faq.php) for more details.

By default, bond orders are depicted in blue color and only those that are higher than 0.1 (the default threshold value) are written to *AOMix-L-atom-chimera2.txt*. You can change the default values by using the **PSEUDOBONDS** keyword in the *aomixpar.txt* file:

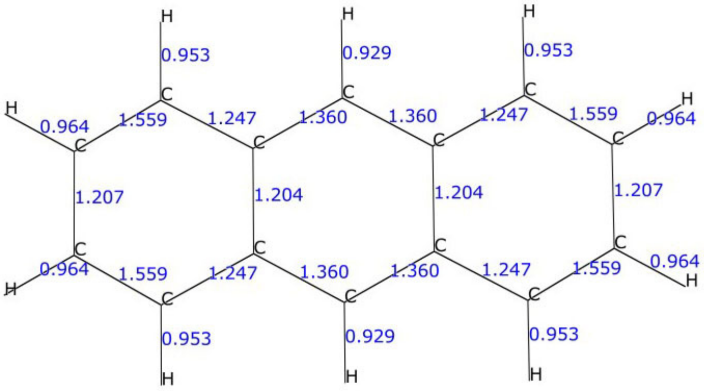
PSEUDOBONDS= 2 0.3 red

The above line will instruct *AOMix-L.exe* to assign red color to bond orders and print them to *AOMix-L-atom-chimera2.txt* using the X.XX output format with the 0.3 threshold value (all bond order indices with values less than 0.3 will be omitted). The default keyword values correspond to:

PSEUDOBONDS= 3 0.1 blue

Thus, *AOMix-L.exe* will assign blue color to bond orders and print them to *AOMix-L-atom-chimera2.txt* using the X.X output format with the 0.1 threshold value (all bond order indices with values less than 0.1 will be omitted).

The figure below shows the Mayer bond orders in anthracene at the B3LYP/TZVP level of theory:



You can edit *AOMix*-created atom/bond attribute files using any text editor (such as *Notepad*) before importing them to *UCSF Chimera* to fit your needs.

Working with *AOMix-CDA.exe*:

AOMix-CDA can be most helpful for the analysis for chemical bonding in molecules. However, a user must understand how to select appropriate fragments to describe the chemical bonding in a given system. There are many books (for example, Ref.[51,62]) describing this topic in considerable detail. You can find additional information in the papers quoted in this manual. *AOMix-CDA* can be used to generate a guess wave function of multi-fragment molecular systems from the wave functions of fragments.[63] See APPENDIX II for details.

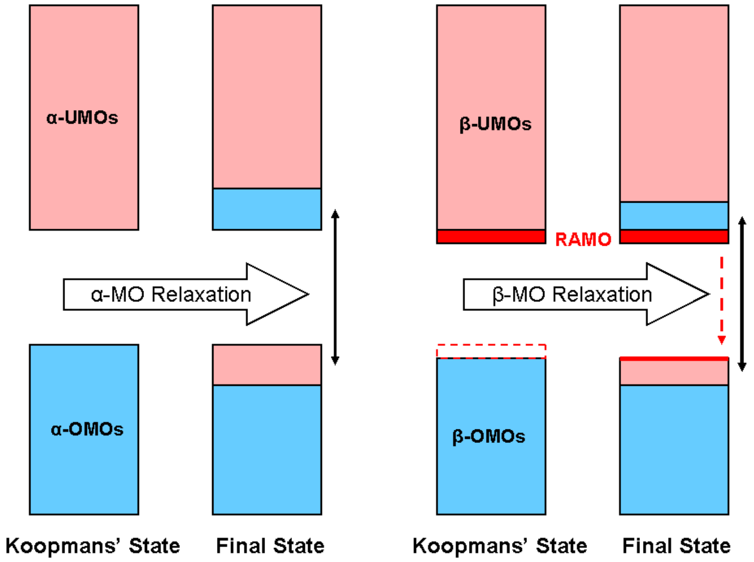
The MOs of a molecular system can be expanded as linear combinations of the MOs of fragments, ϕ_a^{FO} (the LCFO-MO expansion):

$$\psi_i^{MO} = \sum_k^{NF} \sum_a \mathbf{c}_{ai} \psi_{a,k}^{FO} ,$$

where *NF* is a number of fragments. In *AOMix-CDA*, a possible number of fragments varies from 1 to 99. For calculations with *NF*=1, *AOMix-CDA* calculates the MO compositions of a molecule in terms of the MOs of the same molecule in some other, reference state (defined in a *fragm1.log* calculation). Thus, this option can be used to find the MO compositions of cation A^+ in terms of the MOs of a neutral molecule A:

$$\psi_i^{A+} = \sum_a \mathbf{c}_{ai} \psi_a^{A} ,$$

or the Koopmans' state[16] :



Scheme 3 Analysis of the electronic relaxation process after the ionization from the β-spin HOMO (dashed red area) using the contributions from the occupied MOs (OMOs, shown in blue), the RAMO (shown in red) and the other unoccupied MOs (UMO, shown in pink) of the Koopmans' state as the basis. The population of the unoccupied RAMO when going from the Koopmans' state to the final state is presented by a red dashed arrow (adopted from Ref.[16]).

Alternatively, you can analyze MO compositions of molecule A* (in an excited state) in terms of the MOs of a molecule A in the ground state; or to compare MO descriptions obtained using different levels of theory (such as HF and DFT). For details, please see Ref.[16]

For systems with the number of fragments greater than 1, *AOMix-CDA* will use CDA[13,14] and ECDA.[15,16] The latter allows separate evaluation of charge transfer and polarization contributions (see below). In addition, the *AOMix-CDA* program (version 2.2 and up) allows the analysis of electronic coupling between donor and acceptor through the bridge.

AOMix-CDA.exe can process Hartree-Fock (HF), correlated, and DFT wave functions from *ADF, GAMESS, Gaussian, Jaguar*, and *Q-Chem* calculations and semiempirical ZDO wave functions from *Gaussian ZINDO, HyperChem, Spartan, ZINDO*, and *CNDO/INDO* calculations. Fragment list files (which you need to run regular *AOMix* calculations) are not needed for *AOMix-CDA* calculations because the fragments are defined by the *fragmX.log* files (see below).

The *AOMix-CDA* program can be used for both spin-restricted and spin-unrestricted calculations. In addition, it can process "*mixed type*" calculations such as, for example, a whole molecule is treated at the spin-unrestricted level while one or all of molecular fragments are treated at the spin-restricted level. The requirements for *AOMix-CDA* calculations are:

Number of basis functions in the molecule = ∑ *number of basis functions of all molecular fragments*
Number of α-spin electrons in the molecule = ∑ *number of α-spin electrons of all molecular fragments**
Number of β-spin electrons in the molecule = ∑ *number of β-spin electrons of all molecular fragments**
Number of canonical orbitals = *number of basis functions***.

*) These requirements does not apply for calculations with one fragment; the α- and β-spin electron conservation is not a limitation to study orbital interactions between open-shell radicals. See the OPEN-SHELL CDA CALCULATIONS section below.

) If this is not the case, then your QC package has removed nearly linearly dependent functions from the basis set, which generally stabilizes the SCF and post-SCF calculations. *AOMix-CDA* requires that *Number of canonical orbitals* = NBF and will use the full NBF×NBF array. You can force *Gaussian 98/03* to turn off the projection of basis functions to obey the (*Number of canonical orbitals* = NBF) condition by adding the **`IOp(3/32=2)` keyword to the route. A similar option is present in the other QC packages.

The necessary and highly recommended keywords for preparing output files of QC software packages for *AOMix-CDA* calculations:

QC package *Type of calculation*	Calculation keywords in Step 1 (a whole molecule)	Calculation keywords in Step 2 (molecular fragments)
ADF with **no core functions**[b]	use the **symmetry nosym** keyword and basis sets with no core functions; the **TITLE** field must be present in your output file.	same as for a whole molecule calculation
GAMESS (US) ab initio / DFT	Use **RUNTYP=ENERGY** and **NPRINT=3** in the **$CONTRL** input section	same as for a whole molecule calculation
Gaussian 98 / 03 ab initio / DFT	**POP=FULL IOp(3/33=1) NoSymm[a] SCF=Tight**	**POP=FULL IOp(3/33=1) NoSymm SCF=Tight**
Gaussian 98 / 03 **ZINDO** keyword	**IOp(5/33=2) NoSymm[a]**	**IOp(5/33=2) NoSymm**
Jaguar 3.x-6.x ab initio / DFT	**isymm=0, ipvirt=-1, ip102=8, ip18=2, numd=6 , iacc=2** in the **&gen** input section If you are using more than 1 CPU to run your Jaguar calculations, make sure that the output files do not contain any lines with the **WARNING OPEN_M2IO_FILES** messages. If they do, just delete those lines.	same as for a whole molecule calculation
HyperChem ZDO calculations	**QuantumPrintLevel = 1**	same as for a whole molecule calculation
MOPAC ZDO calculations	use the keywords **VECTORS, EIGEN** and **ALLVEC**	same as for a whole molecule calculation
Q-Chem 2.x calculations	use the keywords **PRINT_ORBITALS 99999** and the **converter utility** to add the overlap matrix to an output file	same as for a whole molecule calculation

Q-Chem 3.x calculations	use the keywords **PRINT_ORBITALS 99999** and **IPRINT 200**	same as for a whole molecule calculation
ZINDO ZDO calculations	use the keyword **MOS** in the `$OUTPUT` input section	same as for a whole molecule calculation

a) The **NoSymm** keyword is only necessary if the specified molecular geometry is not **in the standard orientation** (defined in a particular QC package, for example *Gaussian 03*). b) Do not confuse the core functions and core orbitals, please refer to the *ADF* user manual for details.

If you have never done *AOMix-CDA* calculations before, it can useful to run one or two sample *AOMix-CDA* calculations first. The *AOMix-CDA* input and output examples are provided for the *ADF*, *GAMESS, Gaussian,* and *HyperChem* packages and can be downloaded from http://www.sg-chem.net/download/

<u>FIVE STEPS FOR AOMIX-CDA CALCULATIONS</u> (Steps 1 and 2 are performed using a QC package; see APPENDIX II if you want to use *AOMix-CDA.exe* to construct the wave function of a molecular systems from the wave functions of the fragments)

1. Calculate MOs of an entire molecule.

An output file is a regular output file for *AOMix* calculations.

The atom sequence is critical and should not be changed in fragment calculations. As a result, the geometry specification of an entire molecule must follow this order:

```
(fragment 1)      atom1  x1  y1  z1
                  atom2  x2  y2  z2
                  atom3  x3  y3  z3
(fragment 2)      atom4  x4  y4  z4
                  atom5  x5  y5  z5
(fragment 3)      atom6  x6  y6  z6
                  atom7  x7  y7  z7
                  …
Etc.
```

In this example, atoms 1-3 belong to Fragment 1, atoms 4-5 form to Fragment 2, and all remaining atoms form Fragment 3.

2. Calculate MOs of molecular fragments using atomic coordinates in Step 1.

Output files for molecular fragments are outputs of single-point calculations. They must contain the LCAO-MO and overlap matrices. A fragment can be a single molecule (a single ligand) or a group of molecules (a group of ligands).

IMPORTANT! The atom order* and xyz atomic coordinates in fragments must match those in an entire molecule! If a default setting in your QC package is to rearrange atoms* or/and reorient a molecule when it starts a calculation, you should disable such software features using appropriate keywords (such as **NoSymm** in *Gaussian 98* and *Gaussian 03*)**.** *The atom order requirement does not apply to *HyperChem* calculations where the program puts all hydrogen atoms at the end of the molecule specification: *AOMix* deals automatically with H-atom reordering in *HyperChem*.

Fragment file names are pre-defined as described below. For correct *AOMix* and *AOMix-CDA* execution, output files from your electronic structure package (*ADF, Gaussian, GAMESS,* etc. ***except Turbomole***) must be named as follows:

	Output File Name
Whole molecule	Any name with the **.log** / **.out** extension except *fragm#.log**
Fragment #1	*fragm1.log*
Fragment #2 (if present)	*fragm2.log*
Fragment #3 (if present)	*fragm3.log*
…	…
Fragment #99 (if present)	*fragm99.log*
…	**…**

* *fragm1.log – fragm9999.log* names are reserved for fragment output files.

This name scheme is implemented to make it easier to run *AOMix-CDA* calculations with a large number of fragments. For a molecule with two fragments, three outputs files should be prepared for processing: *molecule.log*, *fragm1.log*, and *fragm2.log*; for a molecule with 3 fragments, 4 outputs files should be prepared for processing: *molecule.log*, *fragm1.log*, *fragm2.log*, and *fragm3.log*; etc.

When you want to obtain the MO composition for a molecule using another molecule as a reference, 2 outputs files should be prepared for processing: *molecule.log* and *fragm1.log* (a reference molecule).

Output files from *Turbomole* must be named as follows (this is the proposed name scheme. If you think you can suggest a better/more convenient scheme, please contact the author):

	Output File Names*
Whole molecule	***DSCF, mos***
Fragment #1	***DSCF1, mos1***
Fragment #2 (if present)	***DSCF2, mos2***
Fragment #3 (if present)	***DSCF3, mos3***
…	**…**

* In the case of spin unrestricted *Turbomole* calculations, the *alpha#* and *beta#* files are required instead of mos# files.

Let's take the BH_3CO complex as an example and define BH_3 and CO as two fragments. Then, the input structures for the single-point calculations must be given as shown below:

[CDA EXAMPLE 1] the BH_3CO complex; the *Gaussian 03* input file:

```
#P HF/6-31G(d) NoSymm Pop=Full IOp(3/33=1) SCF=Tight

BH3-CO
0 1
  B       0.90571       0.71072       1.31687
  H       0.83756       1.90583       1.19882
  H       2.00975       0.24811       1.19883
  H       0.25148       0.24811       2.21397
  C       0.13818       0.16800      -0.01251
  O      -0.38420      -0.20138      -0.91730
```

The results of the calculation are written to the output file *BH3CO.log*

1st fragment, BH_3; the *Gaussian 03* input file:

```
#P HF/6-31G(d) NoSymm Pop=Full IOp(3/33=1) SCF=Tight

Fragment 1, BH3

0 1
  B       0.90571       0.71072       1.31687
  H       0.83756       1.90583       1.19882
  H       2.00975       0.24811       1.19883
  H       0.25148       0.24811       2.21397
```

The results of the calculation are written to the output file *fragm1.log*

2nd fragment, CO; the *Gaussian 03* input file:

```
#P HF/6-31G(d) NoSymm Pop=Full IOp(3/33=1) SCF=Tight

Fragment 2, CO

0 1
  C       0.13818       0.16800      -0.01251
  O      -0.38420      -0.20138      -0.91730
```

The results of the calculation are written to the output file *fragm2.log*

Since the atomic coordinates in the above calculations do not correspond to the standard input orientation in *Gaussian*, the **NoSymm** keyword in the *Gaussian* input files is needed.

3. Uncomment (remove #) the **CDA** keyword in the *AOMix* parameter file (*aomixpar.txt*). If you are using "**non-Latin**" MS Windows version, execute the **US** command in the Windows command prompt.

4. Start the *AOMix.exe* program and run it using single-point output files you prepared in Steps 1 and 2 (for the current example calculation, select the *BH3CO.log* file as an output file for the whole molecule; make sure that the output files for the molecular fragments (*fragm1.log* and *fragm2.log*) are present in the *AOMix* directory)

First, you should see the message:

```
Preparing the AOMix-CDA input files -  ON
```

Then, *AOMix.exe* will create several files:

aomix.c, aomix.e, aomix.g, aomix.ao, (and *aomix.o* if it's an MPA calculation),
aomix.c1, aomix.e1, (and *aomix.o1* if it's a non-ZDO calculation),
aomix.c2, *aomix.e2*, (and *aomix.o2* if it's a non-ZDO calculation), etc.

which will be used in the next step.

At the end of the *AOMix.exe* run, you should see the message:

```
Normal Termination
```

5. Start the *AOMix-CDA.exe* program in the same directory where the *AOMix* files from Step 4 are located. The *AOMix-CDA* program runs several checks before starting the main calculation:

   1. the program verifies the wave function of the whole molecule;
   2. the program verifies the wave functions of the fragments; and
   3. the program verifies the overlap matrix of the molecule and its fragments.

If any of these checks fails, make sure that you setup your calculations in Step 1 and 2 (see above) correctly. After the main calculation, *AOMix-CDA.exe* runs a final check: it compares and prints fragment populations calculated in the AO and FO basis sets. These populations should be identical. Here is an example:

```
FRAGMENT POPULATIONS calculated in the AO and FO basis sets (the final test)
 --------------------------------------------------------------------------
        ALPHA ORBITALS     BETA ORBITALS        TOTAL       ALPHA-BETA(SPIN)
 Fragm  -- AO ---- FO -  -- AO ---- FO -  -- AO ---- FO -  -- AO ---- FO -
   1:    4.115    4.115    4.115    4.115    8.230    8.230    0.000    0.000
   2:    6.885    6.885    6.885    6.885   13.770   13.770    0.000    0.000
```

If fragment populations calculated in the AO and FO basis sets are different, *AOMix-CDA.exe* will print a warning message.

At the end of the *AOMix-CDA.exe* run, you should see the message:

```
Normal Termination of AOMix-CDA
```

***AOMix-CDA* Output**

Donation, back-donation, repulsion and residue terms (that are printed in the *AOMix-CDA.txt* file) are computed using the CDA scheme.[13]

```
 Electron donation between fragments (<0.001e for any omitted MO)
 ================================================================

 --- ALPHA ORBITALS ---
                  1->2   2->1
 HOMO  -9 (#  2)  0.000  0.001
 HOMO  -7 (#  4) -0.001 -0.013
 HOMO  -6 (#  5) -0.003  0.041
 HOMO  -5 (#  6) -0.020  0.038
 HOMO  -2 (#  9)  0.027  0.171
 HOMO  -1 (# 10)  0.044 -0.001
 HOMO   0 (# 11)  0.044 -0.001
 -----------------------------
 Total over OMOs  0.091  0.236
 =============================
 TotalALPHA+BETA  0.181  0.471

 Repulsion and residue (Delta) terms between fragments
 =====================================================

 --- ALPHA ORBITALS ---
                  1<->2  Delta
 HOMO  -9 (#  2)  0.000  0.000
 HOMO  -7 (#  4) -0.003  0.000
 HOMO  -6 (#  5)  0.116  0.001
 HOMO  -5 (#  6)  0.107  0.000
 HOMO  -2 (#  9) -0.370 -0.001
 HOMO  -1 (# 10) -0.019  0.001
 HOMO   0 (# 11) -0.019  0.001
 -----------------------------
 Total over OMOs -0.167  0.002
=============================
 TotalALPHA+BETA -0.335  0.002

 FRAGMENT POPULATIONS calculated in the AO and FO basis sets (the final test)
 ----------------------------------------------------------------------------
         ALPHA ORBITALS     BETA ORBITALS        TOTAL       ALPHA-BETA(SPIN)
 Fragm  -- AO ---- FO -   -- AO ---- FO -   -- AO ---- FO -   -- AO ---- FO -
  1:    4.115    4.115    4.115    4.115    8.230    8.230    0.000    0.000
  2:    6.885    6.885    6.885    6.885   13.770   13.770    0.000    0.000
```

Initially, one would expect that **the difference between the amount of donation and back-donation between fragments should be equal to the net charge transfer between fragments**. However, **in the CDA,[13] this is not the case**.[15] For the above example (the BH_3CO molecule),

CT(2→1) -**CT(1→2)** = 0.471 – 0.181 = **0.29 e$^-$**,

which is only *fairly close* to the net charge transfer (**0.23 e$^-$**). For many complexes, the situation is much worse: the difference between the calculated amounts of donation and back-donation is very different from the net charge donation between fragments. This is because the terms *donation* and *back-donation* in the CDA method[13] do not include only charge transfer interactions but rather an overall reorganization of electronic density (including both charge transfer between fragments and electronic polarization of fragments).

MO compositions in terms of fragment orbital contributions (LCFO-MO coefficients) are written to *AOMix-MO-FO-alpha.txt* and *AOMix-MO-FO-beta.txt* for *α*- and *β*-spin orbitals respectively. These files will also include the FO overlap matrix if a user has instructed *AOMix-CDA* to print this matrix.

Here is part of the "LONG FORM" of *AOMix-MO-FO-alpha.txt* output for the H_3B-CO complex (BH_3 is fragment 1 and CO is fragment 2). It contains the MO compositions in terms of percentage contributions of fragment orbitals:

```
   MO:       1       2       3       4       5       6       7       8
         HOMO-7  HOMO-6  HOMO-5  HOMO-4  HOMO-3  HOMO-2  HOMO-1    HOMO
 E(eV): -44.37  -26.31  -21.04  -18.59  -18.59  -14.11  -11.07  -11.07
============================ Fragment  1 ======================
 Total:   0.34   39.18   36.03    1.30    1.30   43.41   95.45   95.45
SumOFO:   0.19   35.82   36.03    1.24    1.24   26.42   95.35   95.35
SumUFO:   0.15    3.36    0.00    0.06    0.06   16.99    0.10    0.10
 FO# OC ----------------------------------------------------------------
   1 1:   0.19+  35.82+  36.03-   0.00    0.00   26.42+   0.00    0.00
   2 1:   0.00    0.00    0.00    0.03    1.22+   0.00   95.13-   0.23+
   3 1:   0.00    0.00    0.00    1.22+   0.03    0.00    0.23+  95.13+
   4 0:   0.13+   3.04+   0.00    0.00    0.00   15.98-   0.00    0.00
   5 0:   0.03    0.33-   0.00    0.00    0.00    1.02+   0.00    0.00
============================ Fragment  2 ======================
 Total:  99.66   60.82   63.97   98.70   98.70   56.59    4.55    4.55
SumOFO:  99.66   60.58   63.68   98.62   98.62   56.53    1.33    1.33
SumUFO:   0.00    0.23    0.29    0.08    0.08    0.05    3.21    3.21
 FO# OC ----------------------------------------------------------------
   1 1:  99.62+   0.24-   0.03    0.00    0.00    0.00    0.00    0.00
   2 1:   0.03   50.34+  47.52+   0.00    0.00    0.01    0.00    0.00
   3 1:   0.00    0.00    0.00   98.61-   0.01    0.00    0.05    1.28+
   4 1:   0.00    0.00    0.00    0.01   98.61+   0.00    1.28+   0.05
   5 1:   0.01   10.00-  16.13+   0.00    0.00   56.52+   0.00    0.00
   6 0:   0.00    0.00    0.00    0.00    0.08    0.00    3.21-   0.00
   7 0:   0.00    0.00    0.00    0.08    0.00    0.00    0.00    3.21+
   8 0:   0.00    0.23-   0.29+   0.00    0.00    0.05    0.00    0.00
```

The signs (+,-) after the FO contributions in the above Table indicate the signs (wave function phase factors) of the LCFO-MO coefficients, $\mathbf{c}_{ai}$:

$$\psi_i^{MO} = \sum_k^{NF} \sum_a \mathbf{c}_{ai} \psi_{a,k}^{FO}$$

From the above table, for example, it can be seen that the HOMO of BH_3CO is composed of

95.1% HOFO (BH_3) + 3.2% LUFO+1 (CO) + 1.3% HOFO-2 (CO)

and HOMO-2 of BH_3CO is composed of

26.4% HOFO-2 (BH_3) + 16.0% LUFO (BH_3) + 56.5% HOFO (CO).

The LCFO-MO coefficients, $\mathbf{c}_{ai}$, can be also printed to *AOMix-CDA* output files by adding the **LCFO** keyword to the *aomixpar.txt* file:

```
THE LCFO-MO MATRIX:

   MO:      1      2      3      4      5      6      7      8
        HOMO-7 HOMO-6 HOMO-5 HOMO-4 HOMO-3 HOMO-2 HOMO-1   HOMO
 E(eV): -44.37 -26.31 -21.04 -18.59 -18.59 -14.11 -11.07 -11.07
 ============================ Fragment  1 ======================
   1 1:  0.043  0.598 -0.600  0.000  0.000  0.514  0.000  0.000
   2 1:  0.000  0.000  0.000 -0.016  0.110  0.000 -0.975  0.048
   3 1:  0.000  0.000  0.000  0.110  0.016  0.000  0.048  0.975
   4 0:  0.035  0.174  0.002  0.000  0.000 -0.400  0.000  0.000
   5 0: -0.017 -0.057 -0.005  0.000  0.000  0.101  0.000  0.000
   6 0:  0.000  0.000  0.000  0.024  0.004  0.000  0.001  0.031
   7 0:  0.000  0.000  0.000 -0.004  0.024  0.000 -0.031  0.001
 ============================ Fragment  2 ======================
   1 1:  0.998 -0.049  0.018  0.000  0.000  0.002  0.000  0.000
   2 1:  0.018  0.710  0.689  0.000  0.000  0.009  0.000  0.000
   3 1:  0.000  0.000  0.000 -0.993  0.011  0.000  0.023  0.113
   4 1:  0.000  0.000  0.000  0.011  0.993  0.000  0.113 -0.023
   5 1: -0.011 -0.316  0.402  0.000  0.000  0.752  0.000  0.000
   6 0:  0.000  0.000  0.000 -0.006  0.028  0.000 -0.179 -0.001
   7 0:  0.000  0.000  0.000  0.028  0.006  0.000 -0.001  0.179
   8 0:  0.001 -0.048  0.054  0.000  0.000  0.023  0.000  0.000
```

<u>**Note.**</u> In order to produce concise output files, *AOMix-CDA* prints LCFO-MO coefficients in the LONG FORM only if they are no less than the threshold value (the default value is **0.1%**; a user can increase it to 1% by using the **FORMAT.P** = **0** keyword or decrease it to 0.01% by using the **FORMAT.P** = **2** keyword in the *AOMix* parameter file). So, if some LCFO-MO coefficients "went missing" in the LONG FORM of your *AOMix-CDA* output, this is not a software bug.

After the LONG FORM, *AOMix-CDA.exe* prints the % compositions of all occupied and unoccupied molecular orbitals in terms of occupied and unoccupied fragment orbitals:

```
 MO compositions in terms of fragment molecular orbitals,
 charge transfer (CT) and electronic polarization (PL) terms:
 ==============================================================
    Fragment       1       2
 --------------------------------------------------------------
      FO contributions (%) to   all occupied molecular orbitals
 Occupied   FO    390.4   680.5
 Unoccupied FO     21.1     8.0
 Sum %            411.5   688.5
 --------------------------------------------------------------
      FO contributions (%) to all unoccupied molecular orbitals
```

```
Occupied   FO      9.6     19.5
Unoccupied FO   1678.9   2292.0
Sum %           1688.5   2311.5
---------------------------------------------------------------
      PL(1) - PL(2):     1.6
CT(2->1) - CT(1->2):    11.5; net charge transfer = 0.23 e-
```

If symmetry is present, *AOMix-CDA.exe* prints a summary for each set of molecular orbitals of given irreducible representation.

AOMix-CDA.exe also prints contributions of each fragment molecular orbital to all occupied molecular orbitals (OMOs) and unoccupied molecular orbitals (UMOs).

For example:

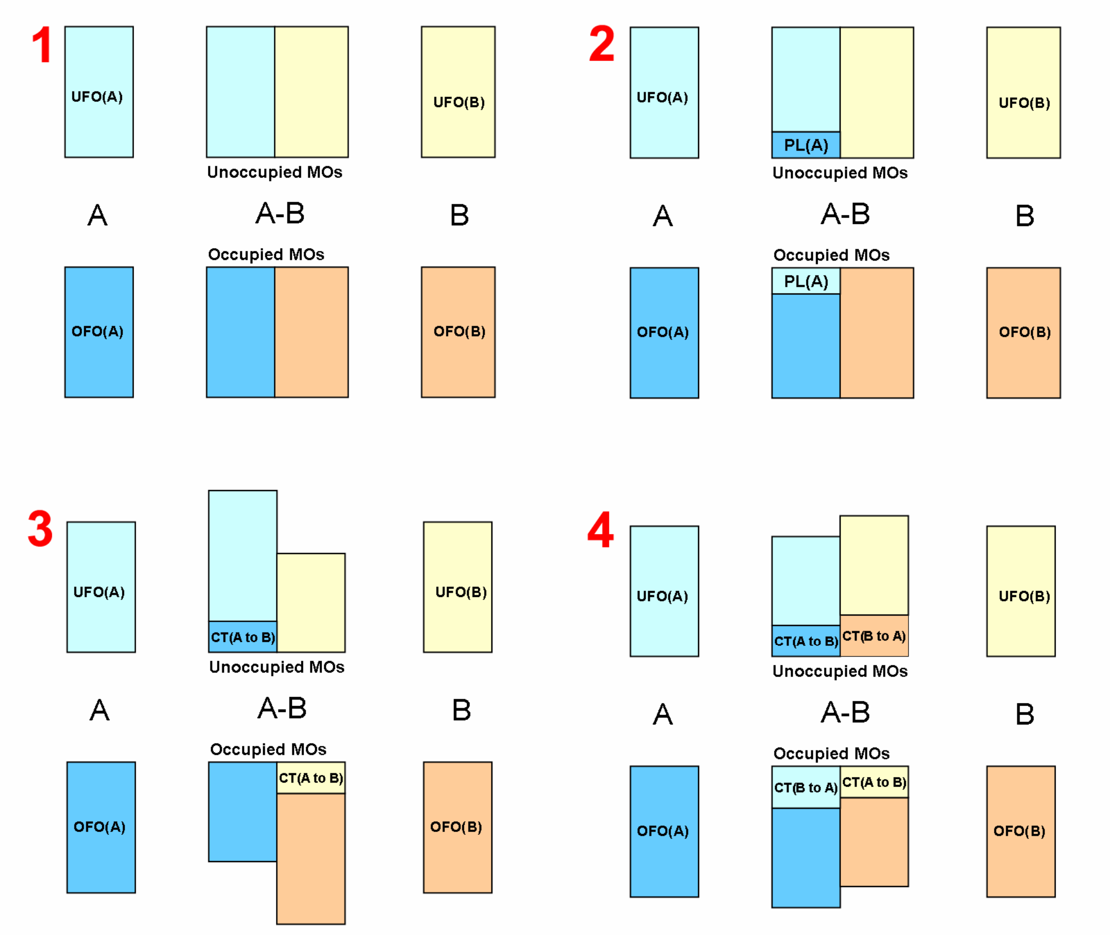
```
FR#   ORB# OCCUP  SUM-over-OMOs  SUM-over-UMOs
...
  2     8    1      99.908         0.091
  2     9    1      91.108         8.902
  2    10    1     100.000         0.000
  2    11    1     100.000         0.000
  2    12    0       5.779        94.222
  2    13    0       5.787        94.213
  2    14    0       0.171        99.828
...
```

Here, the 1st column is the fragment number, the 2nd column is the fragment molecular orbital number, the 3rd column indicates the initial FO occupancy (1 for occupied FOs and 0 for unoccupied FOs), and the last two columns show the contributions to all occupied molecular orbitals and unoccupied molecular orbitals, respectively. **FO contributions (%) to all occupied MOs** (printed in the 4th column: `SUM-over-OMOs`) are equal to **FO occupations in the complex**:

FO occupation in the complex = FO contribution to all OMOs / 100%

So, in the above example, the α-spin LUMO (orbital #12) of fragment 2 contributed 5.78% to the the α-spin occupied molecular orbitals of the complex (or, putting it another way, the α-spin LUMO of fragment 2 has the 0.058 occupancy in the complex); the α-spin HOMO-2 (orbital #9) of fragment 2 contributed 8.90% to the the α-spin unoccupied molecular orbitals of the complex and has the 0.911 occupancy in the complex.

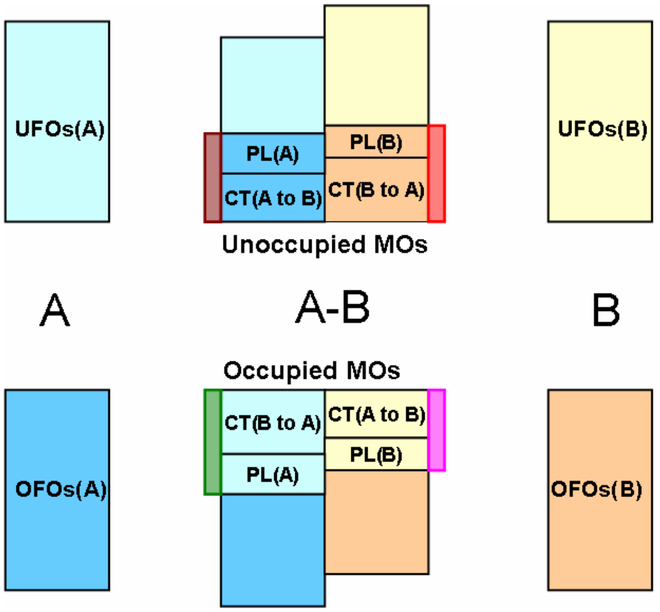
This information and the MO-FO matrix are very helpful for analyzing **polarization** and **charge-transfer** interactions between fragments:



Scheme 4. Compositions of occupied and unoccupied molecular orbitals of A-B in terms of occupied and unoccupied molecular orbitals of fragments A and B (adopted from Ref.[15]):

1. **No charge transfer** between fragments A and B and **no electronic polarization** of fragments (this case corresponds to a molecule with no covalent interaction between fragments);
2. **Polarization of fragment A, PL(A), in presence of fragment B (this mixes the OFOs and UFOs of fragment** A)**,** no charge transfer between A and B and no polarization of fragment B;
3. **Charge transfer from fragment A to fragment B, CT(A→B) (mixing the OFOs of fragment A with the UFOs of fragment B)**, no polarization of A and B; and
4. **Charge transfer from fragment A to fragment B, CT(A→B) (mixing the OFOs of fragment A with the UFOs of fragment B), larger charge transfer from fragment B to fragment A, CT(B→A) (mixing the OFOs of fragment B with the UFOs of fragment A),** and no polarization of A and B.

In a general case, there is some electronic polarization of both fragments, **PL(A)** and **PL(B)**, charge donation from A to B, **CT(A→B)**, and charge donation from B to A, **CT(B→A)**:



PL(A) + **CT(A to B)** = **%OFO(A) in unoccupied MOs** (A-B)
PL(A) + **CT(B to A)** = **%UFO(A) in occupied MOs** (A-B)
PL(B) + **CT(B to A)** = **%OFO(B) in unoccupied MOs** (A-B)
PL(B) + **CT(A to B)** = **%UFO(B) in occupied MOs** (A-B)

Scheme 5. Compositions of occupied and unoccupied molecular orbitals (OMOs and UMOs) of the A-B complex in terms of occupied and unoccupied molecular orbitals of fragments A and B (OFOs and UFOs). The FO contributions are color-coded to help in reading this scheme (adopted from Ref.[15]).

By analyzing the MO compositions in terms of occupied and unoccupied fragment molecular orbitals, it is possible to separate electronic polarization and charge transfer (donation) interactions.

If, for example (the BH_3CO adduct), one has:

```
MO compositions in terms of fragment molecular orbitals,
charge transfer (CT) and electronic polarization (PL) terms:
==============================================================
   Fragment       1       2
--------------------------------------------------------------
     FO contributions (%) to   all occupied molecular orbitals
Occupied   FO   390.4   680.5
Unoccupied FO    21.1     8.0
Sum %           411.5   688.5
--------------------------------------------------------------
     FO contributions (%) to all unoccupied molecular orbitals
Occupied   FO     9.6    19.5
Unoccupied FO  1678.9  2292.0
Sum %          1688.5  2311.5
--------------------------------------------------------------
      PL(1) - PL(2):     1.6
CT(2->1) - CT(1->2):    11.5; net charge transfer = 0.23 e-
```

then the difference in electronic polarization contributions, **PL(1)** - **PL(2),** is 1.6 orbital% and the difference in charge transfer contributions, **CT(1→2)** - **CT(2→1)**, is 11.5 orbital% (which, in a case of doubly-occupied orbitals, corresponds to a net charge transfer of 2*0.115=0.23 e^-).

This extended *CDA* analysis is especially helpful in connection with the energy decomposition analysis (EDA) of Kitaura-Morokuma[60] and Ziegler[64], where the interaction energy between molecular fragments is divided in the following components:

1. **ES, the classical electrostatic interaction** of the occupied FO of fragment A with those of another fragment B; **this interaction does not result in any orbital mixing between different FOs**;
2. **EX**, **the exchange interaction**, the interaction between OFO of fragments A and B that causes the “exchange” repulsion;
3. **PL, the electronic polarization**, **mixes the OFOs and UFOs within each fragment** (“intra-fragment excitations”); PL interactions can be further split into two types: **initial polarization** and **induced polarization.** The initial polarization is the polarization before CT and the induced polarization is the polarization after CT;
4. **CT, the charge transfer (covalent bond) interaction**, which causes electron delocalization between fragments by **mixing the OFOs of fragment A with the UFOs of fragment B** (charge donation from fragment A to fragment B), **the OFOs of fragment B with the UFOs of fragment A** (charge donation from fragment B to fragment A).

In addition to the LONG FORM, you can use the SHORT FORM section of *AOMix-CDA* output files to see the MO compositions in terms of fragment molecular orbitals. The SHORT FORM includes information about all occupied MOs and up to 50 lowest unoccupied MOs. The short form lists up to eight FOs with largest LCFO-MO coefficients (and each contribution is greater than 1%). For a given MO, FO components are printed in the order of decreasing importance:

```
LUMO+0[#9, -0.117 eV]= 79.1%L+1(2) 16.5%L+0(2)  2.7%H-0(1)
HOMO-0[#8,-11.072 eV]= 95.1%H-0(1)  3.2%L+1(2)  1.3%H-2(2)
HOMO-1[#7,-11.072 eV]= 95.1%H-1(1)  3.2%L+0(2)  1.3%H-1(2)
HOMO-2[#6,-14.111 eV]= 56.5%H-0(2) 26.4%H-2(1) 16.0%L+0(1)
                        1.0%L+1(1)
```

To save space, the notation in the SHORT FORM section of *AOMix-CDA* outputs is:
`H-3(1)`=HOFO-3 of Fragment 1, `L+0(1)`=LUFO of Fragment 1, `H-0(2)`=HOFO of Fragment 2, `L+1(2)`=LUFO+1 of Fragment 2, etc.

Open-shell calculations

If you study orbital interactions between open-shell fragments, you may have a situation when, using the default *AOMix-CDA.exe* settings, you will not be able to complete calculations because of non-conservation of the number of α- and β-spin electrons:

$$n_\alpha^{molecule} \neq \sum_i^{NF} n_\alpha^{fragment.i}\ ,\quad n_\beta^{molecule} \neq \sum_i^{NF} n_\beta^{fragment.i}\ .$$

For instance, if you want to study orbital interactions between two CH radicals forming the C_2H_2 molecule, you have the following situation: the C_2H_2 molecule (closed-shell) has 7 α-spin and 7 β-spin electrons, however each CH radical (in the quartet spin state) has 5 α-spin and 2 β-spin electrons adding to a total of 10 α-spin and 4 β-spin electrons in the default spin coupling scheme (ferromagnetic):

[CDA example 2]

-------- the input file for the whole molecule --------

```
#P B3LYP/TZVP SCF=Tight Pop=Full IOp(3/33=1)

The HC-CH molecule

0 1
H                   0.000000    0.000000    1.661837
C                   0.000000    0.000000    0.599005
C                   0.000000    0.000000   -0.599005
H                   0.000000    0.000000   -1.661837
```

----- the input file for Fragment 1 --------

```
#P UB3LYP/TZVP SCF=Tight Pop=Full IOp(3/33=1) NoSymm

Fragment 1, HC

0 4
H                     0.000000    0.000000    1.661837
C                     0.000000    0.000000    0.599005
```

----- the input file for Fragment 2 --------

```
#P UB3LYP/TZVP SCF=Tight Pop=Full IOp(3/33=1) NoSymm

Fragment 2, CH

0 4
C                     0.000000    0.000000   -0.599005
H                     0.000000    0.000000   -1.661837
```

(the above example shows *Gaussian 03* input files for the *AOMix-CDA* calculation)

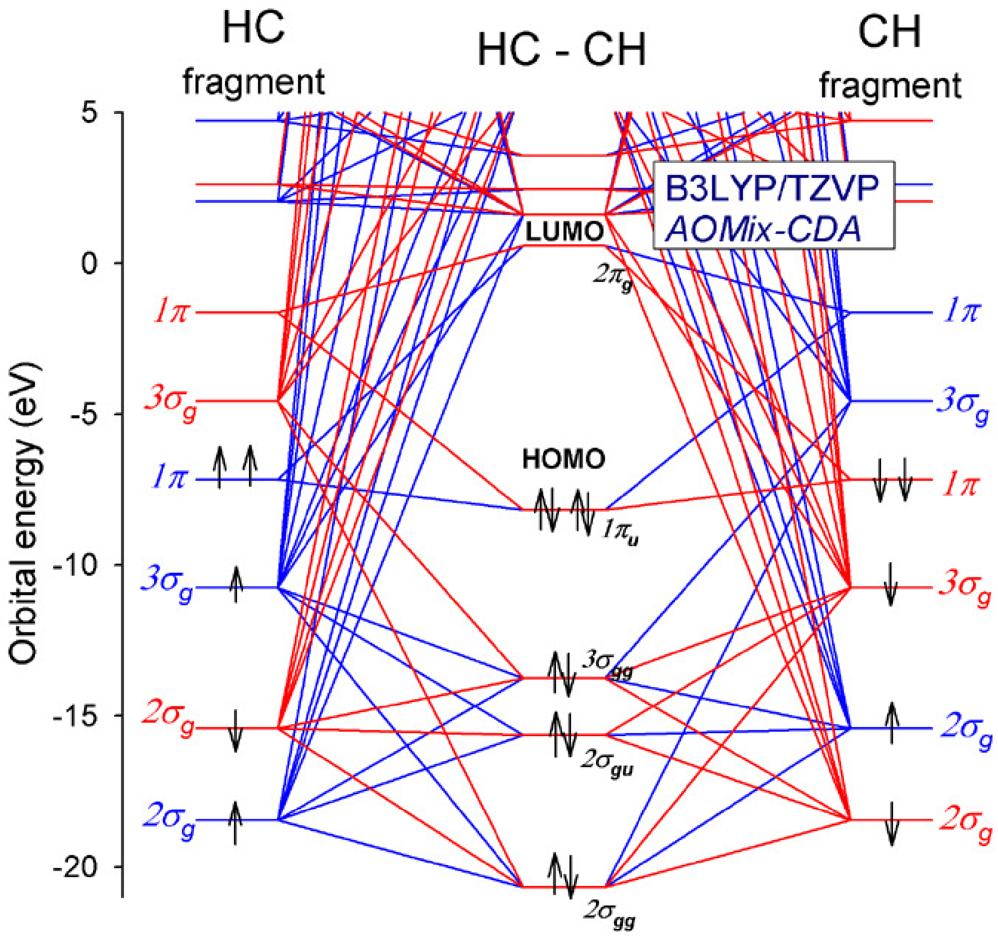
In this situation, you want to *couple* the α-spin FOs of the 1st fragment with the β-spin FOs of the 2nd fragment (anti-ferromagnetic spin coupling).

The anti-ferromagnetic spin-coupling scheme is added in *AOMix-CDA* by the use of the **FLIP *i*x** keyword in the *aomixpar.txt* file. This keyword instructs *AOMix-CDA* to exchange (swap) *α*-spin and *β*-spin orbitals for fragment *i*.

Going back to the C_2H_2 example. After application of the **FLIP 2x** keyword, the second CH fragment has **2 α-spin and 5 β-spin electrons**. Thus,

$$n_\alpha^{molecule} = \sum_i^{NF} n_\alpha^{fragment.i}\ ,\ n_\beta^{molecule} = \sum_i^{NF} n_\beta^{fragment.i}\ ,$$

and the number of α- and β-spin electrons in the whole molecule is correct.



Orbital interaction diagram for the HC-CH molecule which is formed by two CH radicals (B3LYP/TZVP calculation, α-spin orbitals are shown in blue, β-spin orbitals are shown in red).

***AOMix-CDA* calculations with mixed basis sets**

AOMix-CDA can process calculations with **mixed basis sets** but one has to ensure that **the number of *d* orbitals in each shell (five vs. six) remains the same in the whole molecule and fragment calculations**. In *Gaussian 98/03*, this can be done by using the **5D** keyword for calculations with five *d* functions (pure *d* functions) and the the **6D** keyword for calculations with six *d* functions (Cartesian *d* functions) per shell.

[CDA example 3]

The following example shows how to setup *Gaussian 03* calculations for the *AOMix-CDA* analysis of the [Fe(CO)$_4$(C$_2$H$_4$)] complex (with Fe(CO)$_4$ and C$_2$H$_4$ as fragments) when using a mixed all-electron basis set (TZVP for Fe and 6-31G(d) for the other atoms) with pure d functions (5D):

-------- the input file for the Fe(CO)$_4$(C$_2$H$_4$)

```
#P B3LYP/GEN 5D SCF=Tight Pop=Full IOp(3/33=1)

The Fe(CO)4(C2H4) complex, the molecule is in standard orientation (NOSYMM is not
necessary)

0 1
Fe    0.000000            0.000000     0.018179
C     1.821462            0.000000     0.090291
C    -1.821462            0.000000     0.090291
C     0.000000            1.503897    -0.976361
C     0.000000           -1.503897    -0.976361
O     0.000000            2.460510    -1.620978
O     0.000000           -2.460510    -1.620978
O    -2.968878            0.000000     0.160975
O     2.968878            0.000000     0.160975
C     0.000000           -0.704147     2.039071
C     0.000000            0.704147     2.039071
H     0.910796           -1.252234     2.262845
H     0.910796            1.252234     2.262845
H    -0.910796            1.252234     2.262845
H    -0.910796           -1.252234     2.262845

Fe 0
TZVP
****
O C H 0
6-31G*
****
```

----- the input file for Fragment 1 --------

```
#P B3LYP/GEN 5D SCF=Tight Pop=Full IOp(3/33=1) NOSYMM

Fragment 1, Fe(CO)4

0 1
Fe    0.000000            0.000000     0.018179
C     1.821462            0.000000     0.090291
C    -1.821462            0.000000     0.090291
C     0.000000            1.503897    -0.976361
C     0.000000           -1.503897    -0.976361
O     0.000000            2.460510    -1.620978
O     0.000000           -2.460510    -1.620978
O    -2.968878            0.000000     0.160975
O     2.968878            0.000000     0.160975

Fe 0
TZVP
****
O C 0
6-31G*
****
```

----- the input file for Fragment 2 --------

```
#P B3LYP/6-31G(d) 5D SCF=Tight Pop=Full IOp(3/33=1) NOSYMM

Fragment 2, C2H4

0 1
C     0.000000           -0.704147     2.039071
C     0.000000            0.704147     2.039071
H     0.910796           -1.252234     2.262845
H     0.910796            1.252234     2.262845
H    -0.910796            1.252234     2.262845
H    -0.910796           -1.252234     2.262845
```

[CDA example 4]

The following example shows how to setup *Gaussian 03* calculations for the *AOMix-CDA* analysis of the [Fe(CO)$_4$(C$_2$H$_4$)] complex (with Fe(CO)$_4$ and C$_2$H$_4$ as fragments) when using a mixed basis set with ECP (LanL2DZ for Fe and 6-31G(d) for the other atoms):

-------- the input file for the Fe(CO)$_4$(C$_2$H$_4$)

```
#P B3LYP/GEN SCF=Tight Pop=Full IOp(3/33=1) Pseudo=Read

The Fe(CO)4(C2H4) complex, the molecule is in standard orientation (NOSYMM is not
necessary)

0 1
Fe    0.000000              0.000000      0.018179
C     1.821462              0.000000      0.090291
C    -1.821462              0.000000      0.090291
C     0.000000              1.503897     -0.976361
C     0.000000             -1.503897     -0.976361
O     0.000000              2.460510     -1.620978
O     0.000000             -2.460510     -1.620978
O    -2.968878              0.000000      0.160975
O     2.968878              0.000000      0.160975
C     0.000000             -0.704147      2.039071
C     0.000000              0.704147      2.039071
H     0.910796             -1.252234      2.262845
H     0.910796              1.252234      2.262845
H    -0.910796              1.252234      2.262845
H    -0.910796             -1.252234      2.262845

Fe 0
LANL2DZ
****
O C H 0
6-31G*
****

Fe 0
LANL2DZ
```

----- the input file for Fragment 1 --------

```
#P B3LYP/GEN SCF=Tight Pop=Full IOp(3/33=1) Pseudo=Read NOSYMM

Fragment 1, Fe(CO)4

0 1
Fe    0.000000              0.000000      0.018179
C     1.821462              0.000000      0.090291
C    -1.821462              0.000000      0.090291
C     0.000000              1.503897     -0.976361
C     0.000000             -1.503897     -0.976361
O     0.000000              2.460510     -1.620978
O     0.000000             -2.460510     -1.620978
O    -2.968878              0.000000      0.160975
O     2.968878              0.000000      0.160975

Fe 0
LANL2DZ
****
O C 0
6-31G*
****

Fe 0
```

```
LANL2DZ
```

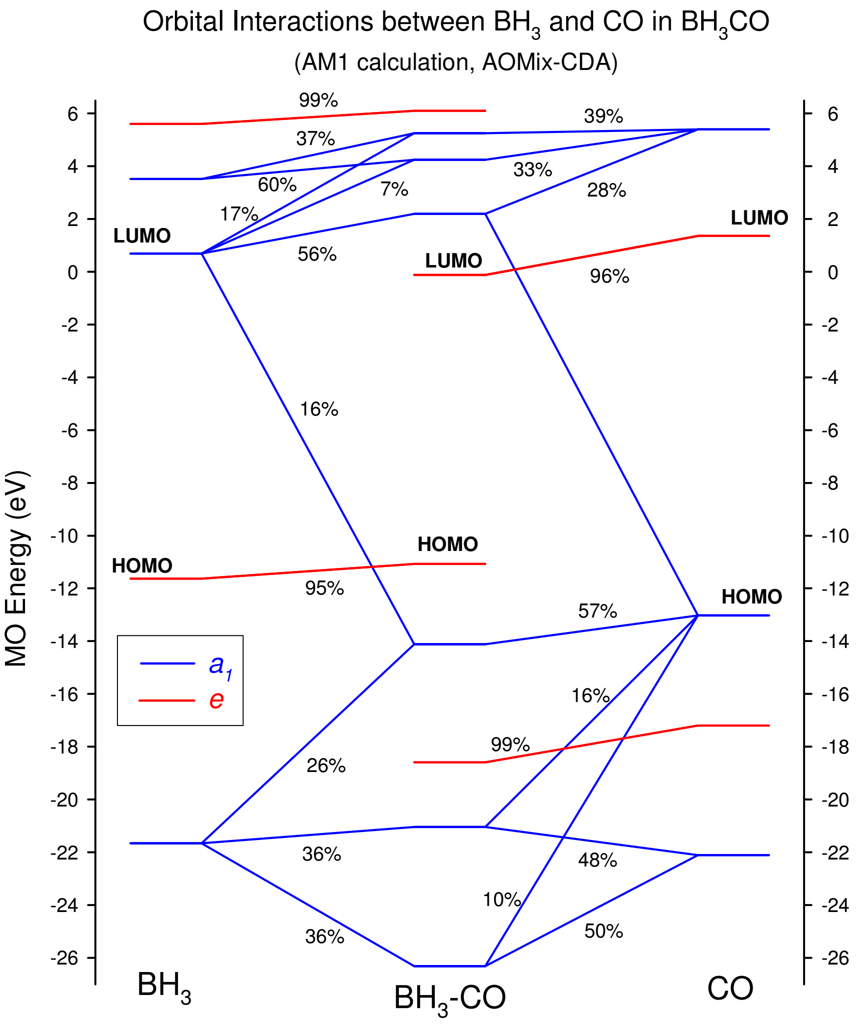
----- the input file for Fragment 2 --------

```
#P B3LYP/6-31G(d) SCF=Tight Pop=Full IOp(3/33=1) NOSYMM

Fragment 2, C2H4

0 1
C     0.000000              -0.704147      2.039071
C     0.000000               0.704147      2.039071
H     0.910796              -1.252234      2.262845
H     0.910796               1.252234      2.262845
H    -0.910796               1.252234      2.262845
H    -0.910796              -1.252234      2.262845
```

Construction of Orbital Interaction Diagrams (NF = 2)

Orbital interaction diagrams are constructed easily from *AOMix-CDA* output files.

For molecular systems with no symmetry, *AOMix-CDA.exe* will create files *AOMix-MO-FO-alpha.dat* and *AOMix-MO-FO-beta.dat* which contain orbital interaction plot data for α- and β-spin orbitals respectively. For molecular systems with symmetry, *AOMix-CDA.exe* will create files *AOMix-MO-FO-alpha-Γ.dat* and *AOMix-MO-FO-beta-Γ.dat* for orbitals of each irreducible representation Γ. For example, for H_3B-CO complex which has C_{3v} symmetry, *AOMix-CDA.exe* will create files *AOMix-MO-FO-alpha-a1.dat* and *AOMix-MO-FO-alpha-e.dat* which will contain interaction diagrams for orbitals with a_1 and e symmetry respectively (see Figure below).



Orbital interaction diagram for the H_3B-CO molecule which is formed by BH_3 and CO (the AM1 calculation, orbitals with ***a*₁** symmetry are shown in blue, orbitals with ***e*** symmetry are shown in red).

In the current version, *AOMix-CDA.exe* reads symmetry information from the *aomix.g* file. This information can read by *AOMix.exe* from electronic structure output files (*Gaussian/Jaguar/HyperChem*, etc).

Some irreducible representations, such as ***a"*** and ***e_1"***, include the *"* symbol which cannot be included in file names. *AOMix-CDA.exe* will replace the *"* symbol with the ***X*** symbol in the *AOMix-MO-FO-*.dat* file names.

By default, *AOMix-CDA.exe* connects MO-FO pairs for which corresponding contributions are greater than 4%. It is possible to change the value of this parameter. You can use any graph software of your choice (*SigmaPlot 2000, Excel*, etc.) to create orbital interaction diagrams from *AOMix-CDA* output files. To create the orbital interaction plot:

1. Import each of the *AOMix-MO-FO-alpha-Γ.dat* files (for α-spin orbitals) or each of the *AOMix-MO-FO-beta-Γ.dat* files (for β-spin orbitals) as plain text files in your favorite graph software.
2. Create a *line plot* (or a *line plot* with multiple ***XY*** pairs in case of a symmetrical molecule) and, for each imported *AOMix-MO-FO-*.dat* file, define the 1st Column from each *AOMix-MO-FO-*.dat* file as ***X*** and the 2nd Column as ***Y***. If a molecule has symmetry and you can import and plot data for each irreducible representation by selecting appropriate *AOMix-MO-FO-*.dat* files and using different color to highlight different orbital symmetries. Most likely, you may want to re-scale the ***Y*** axis to focus your plot on the MO energy region near the HOMO-LUMO gap. The orbital interaction plot is ready.

The *aomixpar.txt* file can be used to define the non-default parameters for creating orbital interaction diagrams. To enter new parameters, edit the line after the **CDA** keyword:

```
4.0  0.0  0.0
```

If the above line is modified to be:

```
3.0  1.55 -1.41
```

AOMix-CDA.exe will connect all MO-FO pairs for which the FO contributions are greater than 3.0% and it will shift the FO energies of Fragment 1 and Fragment 2 by 1.55 eV and -1.41 eV, respectively.

The option of adjusting the MO energies of fragments is useful for constructing orbital interaction diagrams for complexes containing ions. The SHORT FORM of an *AOMix-CDA* output will print the recommended MO energy shifts for each fragment. They appear in the format like this:

```
HOMO-7[#4,-44.373 eV]= 99.6%H-4(2) VShift= -1.41 eV
HOMO-8[#3,-205.70 eV]=100.0%H-3(1) VShift=  1.55 eV
```

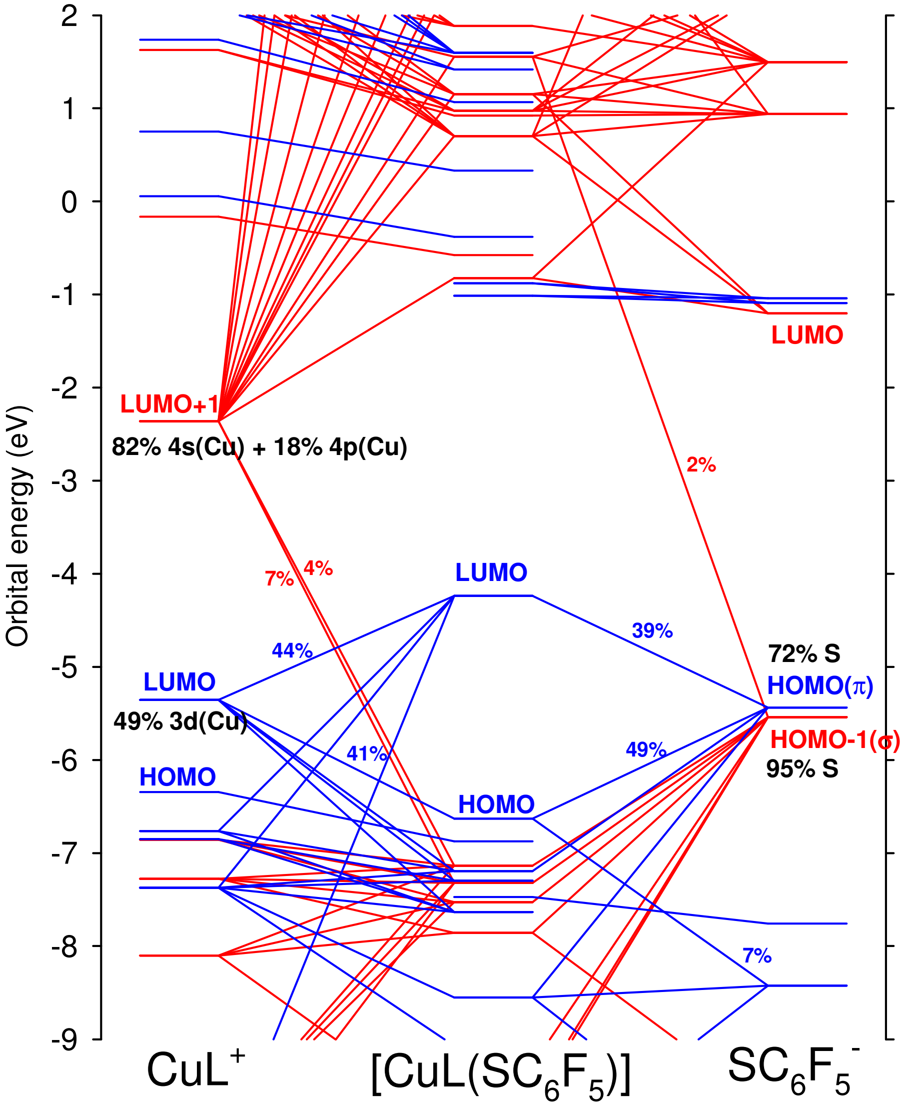
Here, the recommended shift values are 1.55 eV for Fragment 1 and -1.41 eV for Fragment 2.

If the **FO OVERLAP** keyword is included in the *aomixpar.txt* file, the SHOFT FORM of the *AOMix-CDA* output will include the overlap integrals $\mathbf{S}_{ab}^{FO} = \left\langle \psi_a^{FO} \middle| \psi_b^{FO} \right\rangle$ and overlap populations ($2\mathbf{c}_{ai}\mathbf{c}_{ai}\mathbf{S}_{ab}^{FO}$ where the are the LCFO-MO coefficients $\mathbf{c}_{ai}$ from the $\psi_i^{MO} = \sum_k^{NF} \sum_a \mathbf{c}_{ai}\psi_{a,k}^{FO}$ expansions):

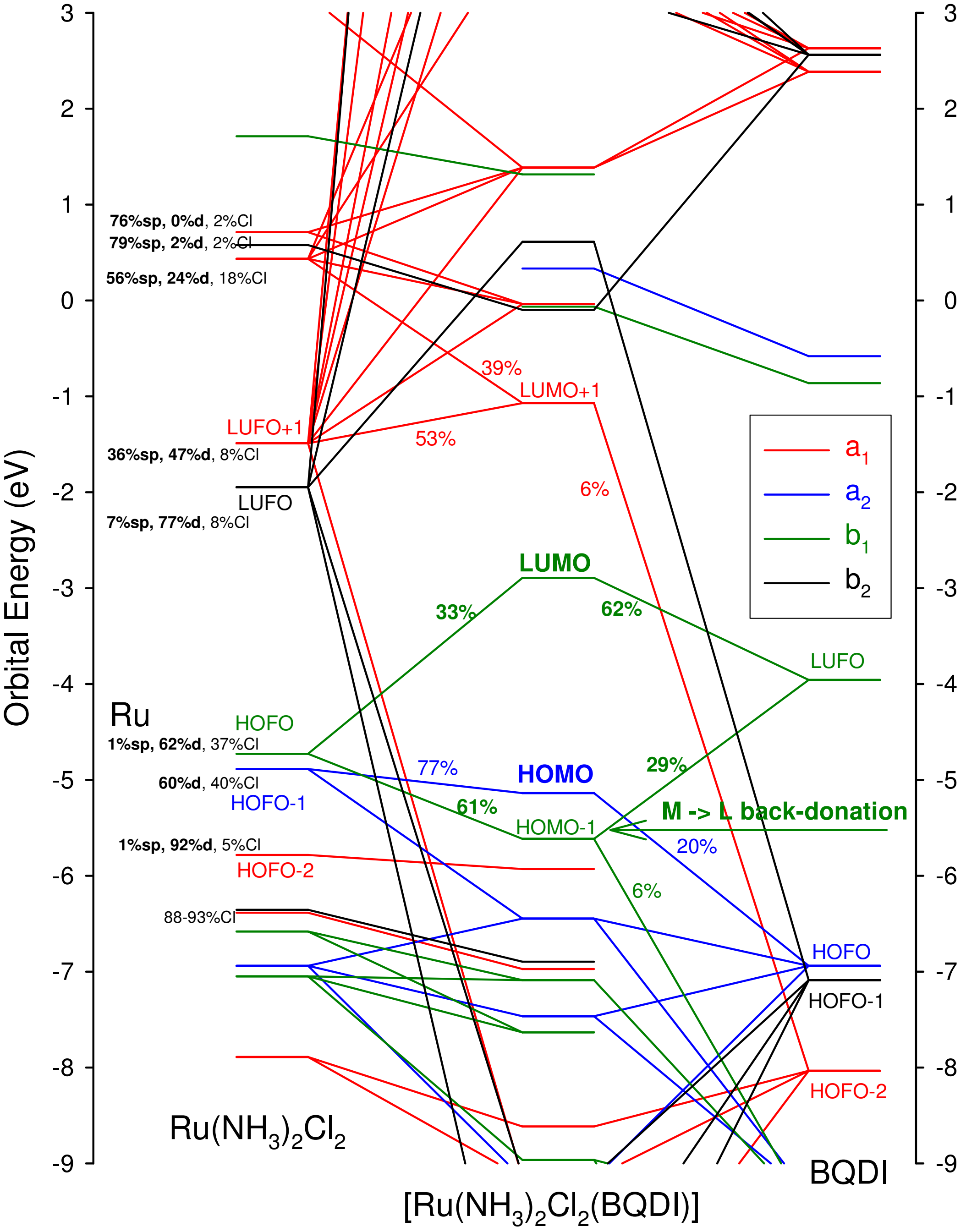
```
--- ALPHA-SPIN ORBITALS ---
  Mol. Orbital         Compositions in terms of dominant FO contributions
                       FO Overlap integrals S(ab) and
                       overlap populations, OP=2*c(ai)*c(bi)*S(ab)

==========================================================================
...

 LUMO+0[#12, 3.161   eV]=  Fr 1: 7.1%L+1 3.0%H-0 1.9%L+2
 Fr 2: 46.7%L+1 S(0.32 0.24 0.09 ) OP(0.07 -0.10 -0.01 )
       40.0%L+0 S(0.09 0.06 -0.32 ) OP(0.02 -0.02 0.04 )

 HOMO-0[#11, -12.718 eV]=  Fr 1: 94.9%H-0
 Fr 2: 3.6%L+1 S(0.24 ) OP(0.05 )
       1.4%H-1 S(0.06 ) OP(-0.02 )

 HOMO-1[#10, -12.718 eV]=  Fr 1: 94.9%H-1
 Fr 2: 3.6%L+0 S(0.24 ) OP(0.05 )
       1.4%H-2 S(0.06 ) OP(-0.02 )

 HOMO-2[#9, -15.102 eV]=  Fr 1: 57.3%H-2 14.5%L+0
 Fr 2: 25.9%H-0 S(0.35 -0.62 ) OP(-0.36 0.18 )
       1.1%L+5 S(0.43 -0.24 ) OP(0.02 0.00 )
```

In the above example, the HOMO of the complex (orbital #11 with the eigenvalue of -12.718 eV) is a mixture of 94.9% HOMO of Fragment 1 and 3.6% LUMO+1 and 1.4% HOMO-1 of Fragment 2. The overlap integral between the HOMO of Fragment 1 and LUMO+1 of Fragment 2 is 0.24 while the overlap population for this FO pair in the HOMO is 0.05 (indicating bonding interaction between HOFO(1) and LUFO+1(2)). The overlap integral between the HOMO of Fragment 1 and HOMO-2 of Fragment 2 is 0.06 while the overlap population for this FO pair is -0.02.

Examples of orbital interaction diagrams from *AOMix-CDA* are presented in this manual, on the www.sg-chem.net website, and in References[39,65] If time will permit, the author will add additional educational examples for the analysis of chemical bonding in different systems in the near future.



β-Spin orbital interaction diagram illustrating the coupling of the metal and thiolate fragments in the [CuL(SC$_6$F$_5$)] complex (the *AOMix-CDA* calculation, based on B3LYP/TZVP results; MOs with ***a'*** and ***a"*** symmetries are shown in red and blue respectively; molecular orbitals of the ML$^+$ and SC$_6$F$_5^-$ fragments are shifted by 4.0 eV and -4.5 eV respectively).[39]



The orbital interaction diagram illustrating the coupling of the Ru(NH$_3$)$_2$Cl$_2$ and BQDI fragments in the [Ru(NH$_3$)$_2$Cl$_2$(BQDI)] complex with *C*$_{2V}$ symmetry (the *AOMix-CDA* calculation, based on B3LYP/LanL2DZ results; molecular orbitals of the Ru(NH$_3$)$_2$Cl$_2$ and BQDI fragments are shifted by 0.7 eV and -0.7 eV, respectively).[65]

In the above figure, **donation** from the BQDI ligand to the $Ru(NH_3)_2Cl_2$ fragment can be clearly seen (LUFO and LUFO+1 of $Ru(NH_3)_2Cl_2$ interact with HOFO-1 and HOFO-2 of the BQDI ligand, respectively; black and red lines corresponding to orbitals of b_2 and a_1 symmetry) and strong **back-donation** from the $Ru(NH_3)_2Cl_2$ fragment to the BQDI ligand is present too (the HOFO of $Ru(NH_3)_2Cl_2$ is mixing with the LUFO of the BQDI ligand, green lines). As a result, the *AOMix-CDA* results for this complex are:

```
Electron donation between fragments
======================================

                  Ru->BQDI    BQDI->Ru
--------------------------------------
 b2     orbitals:  0.000       0.140
 a1     orbitals:  0.025       0.156
 b1     orbitals:  0.100       0.001
 a2     orbitals:  0.000       0.000
--------------------------------------
 Total  over OMOs  0.110       0.289
======================================
 Total ALPHA+BETA  0.220       0.579
```

Since, no charge donation occurs via the MOs with a_2 symmetry, these orbitals play no role in covalent bonding between the metal fragment and the BQDI ligand.[65]

Practical Recommendations

Electron population analysis and the related concepts (bond orders, valence indices, etc.) are extremely useful for the wave function analysis. However, one has to remember that

1. Resulting quantities are not quantum mechanical observables;
2. Results are dependent on the quality of the basis set. What makes this dependence problematic is that the improvement in basis set (resulting in lowing of the total electronic energy) can make results of the population analysis (MPA in particular) worse or even completely unrealistic.

My experience with different basis sets shows that basis sets, such as 6-31G*, 6-311G*, TZV, and TZVP, do not usually cause failures in calculations of MPA-derived MO compositions, CDA, and bond orders. However, basis sets with very diffuse functions (such as 6-311+G*) may cause unrealistic results.

The indicators of this problem are:

1. **negative** MO contributions from fragments (in the MO composition analysis using MPA or MMPA);
2. MO contributions from fragments that are **greater than 100%** (in the MO composition analysis using MPA or MMPA);
3. **negative** partial DOS values;
4. **large negative** charge donation and back-donation values between fragments (using CDA); and
5. **large negative** 2-center bond order indices.

If you encounter any of the above and your basis set contains diffuse functions, you will need to check your population results with a well behaving basis set. The **TZVP** basis set[66] **is recommended** for population analysis calculations. It is a high-quality basis set with enough flexibility to produce accurate results for structures, thermochemistry, and electronic structure analysis. As a more economic alternative, the **DZVP** basis set[67] can be used.

When you run *AOMix-CDA* calculations, it is important to remember about the basis set superposition error (BSSE) effects.[68]

Usually, the BSSE is discussed for calculations of energies of formations, but it is also relevant for construction of MO-FO interaction diagrams. It is clear that the BSSE is expected to be particularly significant when small, inadequate basis sets are used. These do not provide an accurate description and lack the necessary flexibility. Thus, I recommend the use of basis sets such as TZVP to run *AOMix-CDA* calculations and to build MO interaction diagrams. The large, flexible triple-zeta basis sets minimize the BSSE to a small, negligible value.

In future releases, *AOMix-CDA.exe* will include the capability to deal with the BSSE explicitly.

Limitations:

Program	**Max. number of fragments**	**Max. number of orbitals / basis functions**
AOMix	**7**[a]	**2000**[a,b]
AOMix with the **LARGE** keyword	**4000**	**4000**
AOMix-prep	# of basis functions	No program limit[c]
AOMix with the **CDA** keyword	**99**[d]	**4000**
AOMix-S	# of basis functions	No program limit[c]
AOMix-L	# of basis functions	No program limit[c]
AOMix-CDA	**99**[d]	No program limit[c]

a) If there is a need to obtain information for a larger number of fragments or orbitals, execute the *AOMix.exe* program with the **LARGE** keyword and, then, run the *AOMix-S.exe* program (see the instructions related to the *AOMix-S.exe* program in this manual).

b) The 2000 orbital limit does not apply if you prepare *AOMix-x* input files using the **CDA** and **LARGE** keywords.

c) The programs use dynamic memory allocation techniques for storage and transformation of integrals and matrices. The only real limitation is the amount of virtual memory (RAM) in your computer. Typically, a PC with 512 MB RAM can handle *AOMix* calculations with up to 2500 basis functions. If you plan to run larger calculations, you may need a computer with 1-2 GB RAM.

d) This number will be expanded to **9999** in the future release.

Keywords in the *AOMix* parameter file (*aomixpar.txt*)

All lines with a hash symbol # in this file are treated as comments and will be ignored by the program.

Keyword (and its possible and default values)	**Program affected by keyword**	**Keyword description**
SCPA	*AOMix* *AOMix-S*	Specifies SCPA as a method for population analysis (**instead of** MPA) for ab initio/DFT calculations
MMPA	*AOMix-S*	Specifies MMPA as **an additional** method (to MPA) for population analysis for ab initio/DFT calculations.
SPDF=ALL, **OFF**, **NOSINGLE**, or a list of fragments (up to 20 integer numbers in a list)	*AOMix-S*	**SPDF=ALL** instructs *AOMix-S* to print S,P,D,F, etc. orbital contributions for all atoms (or fragments) **SPDF=NOSINGLE** instructs *AOMix-S* to print S,P,D,F, etc. orbital contributions for all atoms (or fragments) except those with one type of orbitals (typically these are hydrogen atoms) **SPDF= 1 15 31 45** instructs *AOMix-S* to print S,P,D,F orbital contributions for atoms/fragments 1, 15, 31, and 45
NETPOP=ON, **OFF**	*AOMix-S*	The keyword controls printing of net orbital populations.
OP=ON, **OFF**	*AOMix-S*	The keyword controls printing of overlap populations.
OP-CONTRIBUTIONS= ON, **OFF**	*AOMix-S*	The keyword instructs *AOMix-S* to print contributions to overlap populations. Currently, it only works if NF=2
CUBE=OFF, **5**, **10**, **20**, **ALL**, **ESP**	*AOMix-S*	The keyword instructs the program to create a script for the *Gaussian cubegen* utility; *X* is a number of frontier occupied and unoccupied orbitals to be included in the script; the **ESP** sub-keyword indicates that the script will include the command to generate the CUBE file for the electrostatic potential.
ENERGYRANGE *E1 E2*	*AOMix-S*	The keyword instructs the program to use user-defined energy range (from *E1* to *E2* eV) for DOS calculations.
FORMAT.P=0, **1**, **2**	*AOMix* *AOMix-CDA*	Specifies the number of digits after the decimal point in MO compositions (%) of *AOMix* output files. It also defines the cutoff limit for the LONG FORM of *AOMix-CDA* output files.
POP=FULL or **positive integer number**	*AOMix*	**POP=FULL** instructs the program to include all MOs in output. If **POP=20**, printing will be limited to 20 HOMOs and 20 LUMOs only; if **POP=50**, printing will be limited to 50 HOMOs and 50 LUMOs; etc.

FILEFORMAT= CHECK, NOCHECK	*AOMix*	**FILEFORMAT=CHECK** instructs the program to verify the MS-DOS ASCII format of user's output files. **FILEFORMAT=NOCHECK** disables this feature.
LARGE[a]	*AOMix*	Turns on the input preparation for *AOMix-L,P,S*
CDA[b]	*AOMix*	Turns on the input preparation for *AOMix-CDA.exe*
NOSYMM	*AOMix-CDA* *AOMix-L*	If the keyword is included in *aomixpar.txt*, the use of symmetry is turned off.
FLIP *i***x** *i* = **1**, ..., **NF**	*AOMix-CDA*	Exchanges (swaps) α- and β-spin molecular orbitals for a selected molecular fragment: **FLIP 1x** applies the orbital swap to Fragment 1, **FLIP 2x** applies the orbital swap to Fragment 2, etc. A user can apply this keyword to as many fragments as necessary. For example, **FLIP 2x 4x** applies the orbital swap to Fragments 2 and 4.
FO OVERLAP=ON, OFF	*AOMix-CDA*	The keyword controls printing of the FO overlap matrix.
LCFO=ON, OFF	*AOMix-CDA*	The keyword controls printing of the LCFO-MO matrix.
CORE *X* *X must be a real number (50.0, 100.0, 200.0, etc.)*	*AOMix-CDA*	Include MOs within the ±*X* eV range in the MO interaction plot.
CLEANUP	*AOMix-CDA*	If the keyword is included in *aomixpar.txt*, at the end of the AOMix-CDA.exe run, all *AOMix* temporary files will be deleted.
3-CENTER=ON, OFF	*AOMix-L*	**3-CENTER=ON** turns on printing of the 3-center bond order indices
4-CENTER=ON, OFF	*AOMix-L*	**4-CENTER=ON** turns on printing of the 4-center bond order indices. Note that, if **3-CENTER=OFF** is selected, then **4-CENTER=OFF** is set.
S-EIGV=ON, OFF	*AOMix-L*	the **S-EIGV=ON** and **LOWDIN=ON** keywords turn on printing of all eigenvalues and eigenvectors of the overlap matrix and the $\mathbf{S}^{1/2}$ and $\mathbf{S}^{-1/2}$ matrices*;* if the keyword is absent or commented, the program will print six lowest eigenvalues.
LOWDIN=OFF, ON, ALWAYS	*AOMix-L*	**LOWDIN=ON** Instructs the program to perform LDA if the number of orbitals is 500 or less; **LOWDIN=ALWAYS** Instructs the program to perform LPA for all calculations.
PROJECTION=FULL, OCCUPIED, S, OFF	*AOMix-L*	The keyword controls printing of the overlap matrix between α- and β-spin MOs.
GUESS=CARDS	*AOMix-L*	If the keyword is included in *aomixpar.txt*, *AOMix-L.exe* will generate the Gaussian input file

		that contains the converged wave function as an initial guess (see Appendix I for details).
PSEUDOBONDS= *i X color*	*AOMix-L*	Assigns the print format, threshold value and color to bond orders in *UCSF Chimera* PseudoBond attribute files. Default is **PSEUDOBONDS= 3 0.1 blue**
AOMIX-S TO-FOLLOW	*AOMix-L*	If the keyword is included in *aomixpar.txt*, *AOMix-S* calculations will start automatically after *AOMix-L* execution. At the end of the run, all temporary files will be deleted.

Several new program keywords have not been documented yet. Watch for the updates of this manual. a,b) In order to use these keywords, a user must have an appropriate license.

AOMix Error Codes:

AOMix.exe and other programs in the *AOMix* package perform multiple checks during calculations and may stop when they detect an error or give you a warning massage. The list error codes is shown in the table below:

Error code	**Error description**
100	One or more of the *AOMix* executable files (*aomix-p#.exe*) are missing. Make sure that you have downloaded the complete *AOMix* package with all executable (.exe) files.
111	The software license number is incorrect or the program could not read it.
113	The program could not find registered MAC address or license file.
114	*aomixpar.txt* is missing from the *AOMix* directory. Execute *AOMix.exe*
200	The correct ASCII format of the output file is not detected. Convert your input files to the MS-DOS ASCII format (using the *U2WIN* program or any other available method).
201	The output file does not match the format of the quantum-chemical package.
202	*AOMix.exe* could not determine the quantum-chemical package.
203	*AOMix.exe* could not find the TITLE line in your output file.
220	*AOMix.exe* could not find the number of electrons in the output file.
239	*AOMix.exe* cannot process *ADF* calculations with core basis functions. Please use the all-electron basis sets without core functions.
240	*AOMix.exe* could not find the number of orbitals in the output file.
242	Number of orbitals exceeds the program limit. To proceed: 1. Run *AOMix.exe* with the **LARGE** keyword to generate *AOMix-x* input files and 2. Run *AOMix-S.exe* to finish the calculation.
243	Number of canonical orbitals is not valid.
250	*AOMix.exe* could not find the LCAO-MO expansion in the output file you selected. Make sure that it is in your output file.
251	There was a problem while reading the LCAO-MO data. Inspect your output file.
255	*AOMix.exe* could not find the LCAO-MO expansion for beta-spin orbitals in the output file you selected.
260	*AOMix.exe* could not find the overlap matrix. Make sure that it is in your output file.
261	There was a problem when reading the overlap matrix. Inspect your output file.
287	Output files for less than 2 fragments were found. CDA calculations require at least 2 fragments (with the output file names *fragm1.log* and *fragm2.log*). Make sure that the output files for fragments are present in the *AOMix* directory.
288	There is only one fragment in the fragment list and this fragment represents the entire molecule. This is not allowed. Make sure that there will be at least 2 fragments in your calculation.
289	Number of fragments is incorrect. Make corrections to your fragment list file.
290	Number of fragments exceeds the *AOMix.exe* limit. Use *AOMix-S.exe* for this calculation.
291,292	The wrong fragment list specification. Fix your fragment list file.
293	You cannot use a list of atoms to process this output file. Specify molecular fragments as a list of atomic orbitals.
295	There is a duplication in the fragments. Fix your fragment list file.
296	The wrong fragment list specification. Fix your fragment list file.

If you run *AOMix* and experience a problem, please check sample input and output files **http://www.sg-chem.net/download** to make sure that you run your calculations correctly and also read the FAQ page (**http://www.sg-chem.net/NP/faq.php**).

When new versions of the quantum-chemical software packages (Gaussian, Jaguar, Q-Chem, etc.) are released, there can be changes in output file formatting and/or modifications in keyword functionalities. These changes can affect *AOMix* execution. In this situation, please inspect your output files from the new version of the software and, if possible, compare them with output files from the old version of the software.

If, after reading the *AOMix* manual and the FAQ webpage, you cannot resolve your problem, contact the *AOMix* developer with the detailed description of your problem.

Abbreviations

AO	Atomic orbital
BSSE	Basis set superposition error
CDA	Charge decomposition analysis
CMO	Canonical molecular orbital
COOP	Crystal orbital overlap population, identical to OPDOS
CT	Charge transfer
DFT	Density functional theory
DOS	Density-of-states
ECP	Effective core potential
EDA	Energy decomposition analysis
ESP	Electrostatic potential
FMO	Frontier molecular orbital
FO	Fragment molecular orbital
GP	Gross population
HF	Hartree-Fock
HOFO	Highest occupied fragment molecular orbital
HOMO	Highest occupied molecular orbital
LCAO	Linear combination of atomic orbitals
LCFO	Linear combination of fragment orbitals
LPA	Löwdin population analysis
LUFO	Lowest unoccupied fragment molecular orbital
LUMO	Lowest unoccupied molecular orbital
MO	Molecular orbital
MPA	Mulliken population analysis
MMPA	Modified Mulliken population analysis
NBF	Number of basis functions
NF	Number of fragments
NP	Net population
NPA	Natural population analysis
OFO	Occupied fragment molecular orbital
OP	Overlap population
OPDOS	Overlap-population density-of-states
PB	Pseudobond
PDOS	Partial density-of-states
PUHF	Projected unrestricted Hartree-Fock method
RHF	(Spin)-restricted Hartree-Fock method
QC	Quantum chemistry
SCPA	c^2 population analysis
TDOS	Total density-of-states
TOP	Total overlap population
UFO	Unoccupied (vacant) fragment molecular orbital
UHF	(Spin)-unrestricted Hartree-Fock method
ZDO	Zero differential overlap

APPENDIX I

Anyone who has been running large-size QM calculations knows how important it is to be able to restart your calculations from the converged wave functions. Usually, this is achieved by using checkpoint files. If you lose these files or you have switched from one operating system to other and forgot to keep formatted checkpoint files, you have to re-run your calculations from scratch to obtain converged wave functions. For small molecule calculations, it is not a big problem: new single-point calculations will take seconds or minutes on a modern workstation. For large molecule calculations with more than 1000 orbitals, you may lose hours or days of CPU time to recover your converged wave functions. Keeping the checkpoint files is not necessary anymore! *AOMix-L.exe* can recover the converged wave function from an output. To activate this option, include the **GUESS=CARDS** keyword in the *aomixpar.txt* file. Then, run *AOMix-L.exe* as you would run it for regular *AOMix-L* calculations.

For *Gaussian* calculations, *AOMix-L.exe* will generate the *AOMix-guess-cards.gjf* file that contains the atomic coordinates of the whole molecule and the complete initial guess (data after the (5E16.5) Fortran format line) that represents the converged wave function. For example:

```
%chk=BH3CO

#P HF/6-31G(d) SCF=Tight GUESS=CARDS

BH3-CO

0 1
B        0.90571        0.71072        1.31687
H        0.83756        1.90583        1.19882
H        2.00975        0.24811        1.19883
H        0.25148        0.24811        2.21397
C        0.13818        0.16800       -0.01251
O       -0.38420       -0.20138       -0.91730

(5E16.5)
   -1
     1.00000E-05    -2.00000E-04    -1.50000E-04     0.00000E+00     0.00000E+00
    -4.10000E-04     6.00000E-05     0.00000E+00     0.00000E+00     3.80000E-04
     4.00000E-05     4.00000E-05     0.00000E+00     0.00000E+00     0.00000E+00
     1.00000E-05     7.00000E-05     1.00000E-05     7.00000E-05     1.00000E-05
     7.00000E-05    -4.00000E-05     0.00000E+00     6.30000E-04     0.00000E+00
     0.00000E+00    -9.80000E-04     8.40000E-04     0.00000E+00     0.00000E+00
    -1.31000E-03     6.00000E-05     6.00000E-05     0.00000E+00     0.00000E+00
     0.00000E+00     9.94670E-01     2.11400E-02     2.03000E-03     0.00000E+00
     0.00000E+00     5.61000E-03     5.90000E-04     0.00000E+00     0.00000E+00
    -3.10000E-03    -4.26000E-03    -4.26000E-03     0.00000E+00     0.00000E+00
     0.00000E+00
    -7.00000E-05    -3.00000E-05    -2.00000E-04     0.00000E+00     0.00000E+00
     8.11000E-03    -2.90000E-03     0.00000E+00     0.00000E+00    -7.80000E-04
…
```

APPENDIX II

AOMix-CDA.exe provides a method to use the converged wave functions of fragments to generate a guess wave function for a whole molecular system. This option can be very helpful to 1) generate a high-quality initial guess for multi-fragment molecular systems and 2) to setup open-shell calculations of low-spin, anti-ferromagnetically coupled systems[63,69-71] such as, for example, a pentalene-bridged V^{II}-V^{II} complex[63] where the two ions are separated by 2.54Å[72] and anti-ferromagnetically coupled to yield a ground state wave function with $S_{total}=0$.

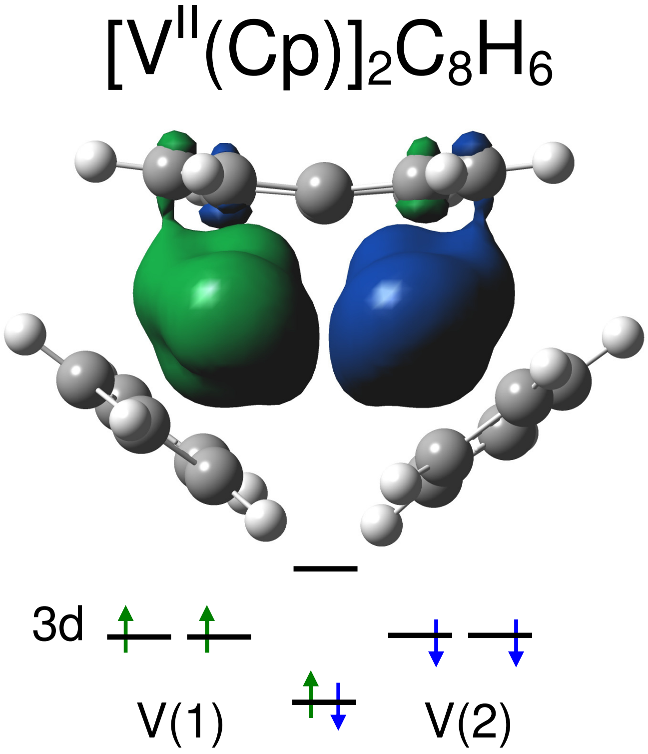


Figure A-II. Spin density of the broken-symmetry state for $[V(Cp)]_2(C_8H_6)$ (open-shell singlet) from the PBE/TZVP calculation.[63] The initial guess wave function was generated from the fragment wave functions by *AOMix-CDA*. For this complex, the closed-shell singlet description with a triple vanadium-vanadium bond (proposed in Ref.[72]) is incorrect (see the gray line for the S=0 CS state in Figure A-III) and there is only a weak single V-V bond in the true ground state.[63]

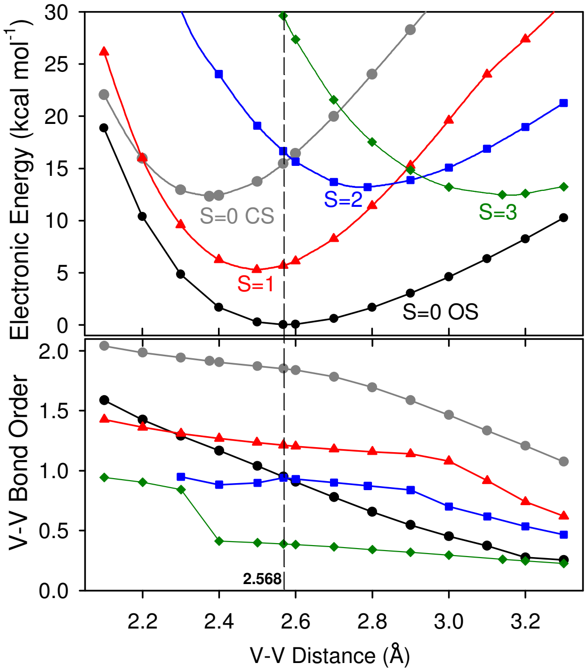


Figure A-III. (Upper) Potential energy surfaces and (lower) Mayer V-V bond orders for electronic states of different spin multiplicity of $[V(Cp)]_2(C_8H_6)$ as a function of the V-V internuclear distance (the PBE/TZVP calculations).[63]

The way to employ *AOMix-CDA* for initial guess wave function calculations is almost identical to regular *AOMix-CDA* calculations:

1. Build your molecular system as in the following order:

```
(fragment 1)      atom1 x1  y1  z1
                  atom2 x2  y2  z2
                  atom3 x3  y3  z3
(fragment 2)      atom4 x4  y4  z4
                  atom5 x5  y5  z5
(fragment 3)      atom6 x6  y6  z6
                  atom7 x7  y7  z7
                  …
Etc.
```

2. Calculate the MOs of molecular fragments using atomic coordinates in Step 1.

Output files for molecular fragments are outputs of single-point calculations. They must contain the LCAO-MO and overlap matrices.

IMPORTANT! The atom order* and xyz atomic coordinates in fragments must match those in an entire molecule! If a default setting in your QC package is to rearrange atoms* or/and reorient a molecule when it starts a calculation, you should disable such software features using appropriate keywords (such as **NoSymm** in *Gaussian 98/03*)**.**

Fragment file names are pre-defined as described below. For correct *AOMix* and *AOMix-CDA* execution, output files from your electronic structure package (*ADF, Gaussian, GAMESS,* etc.) must be named as follows:

Output for	Output File Name
Fragment #1	*fragm1.log*
Fragment #2 (if present)	*fragm2.log*
Fragment #3 (if present)	*fragm3.log*
…	…
Fragment #99 (if present)	*fragm99.log*
…	…

Let's take the BH_3CO complex as an example and define BH_3 and CO as two fragments. Then, the input structures for the single-point calculations must be given as shown below:

[EXAMPLE 1] Building the wave function of the BH_3CO molecule from the wave functions of BH_3 and CO.

1st fragment, BH_3; the *Gaussian 03* input file:

```
#P HF/6-31G(d) NoSymm Pop=Full IOp(3/33=1) SCF=Tight

Fragment 1, BH3

0 1
B        0.90571        0.71072        1.31687
H        0.83756        1.90583        1.19882
H        2.00975        0.24811        1.19883
H        0.25148        0.24811        2.21397
```

2nd fragment, CO; the *Gaussian 03* input file:

```
#P HF/6-31G(d) NoSymm Pop=Full IOp(3/33=1) SCF=Tight

Fragment 2, CO

0 1
C        0.13818        0.16800       -0.01251
O       -0.38420       -0.20138       -0.91730
```

3. Uncomment (remove #) the **CDA** keyword in the *AOMix* parameter file (*aomixpar.txt*). If you are using "**non-Latin**" MS Windows version, execute the **US** command in the Windows command prompt.
4. Start the *AOMix.exe* program and run it with single-point output files you prepared in Step 2. First, you should see the message:

```
Preparing the AOMix-CDA input files -  ON
```

Then, *AOMix.exe* will create several files:

aomix.c1, aomix.e1, (*aomix.o1* if it's a non-ZDO calculation)*,*

aomix.c2, *aomix.e2*, (*aomix.o2* if it's a non-ZDO calculation), etc.

which will be used in the next step.

5. Run the *AOMix-CDA.exe* program in the same directory where the *AOMix* files from Step 4 are located. *AOMix-CDA.exe* will generate the *AOMix-fragment-wave.gjf* file that contains the wave function (the AO coefficients after the (5E16.8) Fortran format line) that is constructed from the converged wave functions of the fragments.

As in regular *AOMix-CDA* calculations, the anti-ferromagnetic spin-coupling scheme can be added (if necessary) by the use of the **FLIP *i*x** keyword in the *aomixpar.txt* file. This keyword instructs *AOMix-CDA* to exchange (swap) α-spin and β-spin orbitals for fragment *i*.

After *AOMix-CDA* execution, modify the keywords of the *AOMix-fragment-wave.gjf* file to suit your needs. The following example shows the input file for the BH_3CO molecule:

```
#P HF/6-31G(d) SCF=Tight Guess=Cards

The spin-restricted wave function from the molecular fragments.
Frag.  1: AE=   4, BE=   4, BH3
Frag.  2: AE=   7, BE=   7, CO

0 1
B        0.90571        0.71072        1.31687
H        0.83756        1.90583        1.19882
H        2.00975        0.24811        1.19883
H        0.25148        0.24811        2.21397
C        0.13818        0.16800       -0.01251
O       -0.38420       -0.20138       -0.91730

(5E16.8)
   -1
 9.96240000E-01  2.36300000E-02  0.00000000E+00 -2.00000000E-05 -1.02000000E-03
-1.15100000E-02  0.00000000E+00  0.00000000E+00 -1.80000000E-04  5.00000000E-05
 5.00000000E-05 -9.60000000E-04  0.00000000E+00  0.00000000E+00 -3.00000000E-05
-1.20000000E-04  2.29000000E-03 -1.20000000E-04  2.29000000E-03 -1.20000000E-04
 2.29000000E-03  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
 0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
 0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
 0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00  0.00000000E+00
...
```

Currently, this *AOMix-CDA* functionality to build wave functions of multi-fragment molecular systems from fragment wave functions can be used for *Gaussian* calculations only. In future releases, similar functionality can be added for use with other quantum-mechanical packages if they allow the same functionality as *Gaussian*'s **Guess=Cards** keyword.

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> **Percentage compositions of molecular orbitals, the overlap populations and bond orders between molecular fragments, and density-of-states spectra were calculated using the *AOMix* program [1, 2].**

Or

> **Molecular orbitals were analyzed using the *AOMix* program [1,2].**

1. **S. I. Gorelsky, *AOMix: Program for Molecular Orbital Analysis*; University of Ottawa, 2008, http://www.sg-chem.net/**
2. **S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* 2001, *635*, 187-196.**

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