ICC Report III

Molecular Orbitals and Charge Decomposition Analysis

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Contents

Expand each MO with N AOs (basis)

$$\phi_i = \sum_k^N C_{ki}\chi_k \tag{1.1}$$

	math variable	subscript	number	number example
MO	ϕ	i	N	420
AO	χ	k	N	420
occupied MO			occ	52
virtual MO			vir	368

N is determined by user, e.g. `def2TZVP`.
$occ = K/2$, where K is the number of electrons (In restricted case).

But How Can I Count ...

Check the `.fchk` file!

```
Title Card Required
SP        RPBE1PBE                              def2TZVP
Number of atoms                            I               29

Full Title                                 C   N=           2
Title Card Required
Route                                      C   N=           8
#p pbe1pbe/def2TZVP geom=allcheck scrf=(smd,solvent=benzene)
nosymm pop=full IOp(3/33=1,3/32=2)
Charge                                     I                0
Multiplicity                               I                1
Number of electrons                        I              104
Number of alpha electrons                  I               52
Number of beta electrons                   I               52
Number of basis functions                  I              420
Number of independent functions            I              420
```

or `.log` file

```
 Standard basis: def2TZVP (5D, 7F)
Ernie: Thresh=  0.10000D-02 Tol=  0.10000D-05 Strict=F.
There are   466 symmetry adapted cartesian basis functions of
     A   symmetry.
There are   420 symmetry adapted basis functions of A
    symmetry.
420 basis functions,   679 primitive gaussians,   466
    cartesian basis functions
52 alpha electrons       52 beta electrons
...
NBasis=   420 RedAO= T EigKep=  6.59D-04  NBF=   420
NBsUse=   420 1.00D-06 EigRej= -1.00D+00 NBFU=   420
```

MO Coefficient and Overlap Matrix

$$K/2 = \sum_{i}^{occ} \langle \phi_i \,|\, \phi_i \rangle = \sum_{i}^{occ} \sum_{k}^{N} \sum_{l}^{N} C_{ki}^{*} C_{li} \langle \chi_k \,|\, \chi_l \rangle \tag{1.2}$$

or

$$K = \sum_{i}^{N} \eta_i \langle \phi_i \,|\, \phi_i \rangle = \sum_{i}^{N} \eta_i \sum_{k}^{N} \sum_{l}^{N} C_{ki}^{*} C_{li} \langle \chi_k \,|\, \chi_l \rangle \tag{1.3}$$

where

$$\eta_i = \begin{cases} 2 & i \in occ \\ 0 & i \in vir \end{cases} \tag{1.4}$$

Moreover, define

$$\text{Density Matrix} \qquad P_{k\ell} = \sum_{i}^{N} \eta_i C_{ki}^{*} C_{\ell i} \tag{1.5}$$

$$\text{Overlap Matrix} \qquad S_{k\ell} = \langle \chi_k \,|\, \chi_\ell \rangle \tag{1.6}$$

thus

$$K = \sum_{k}^{N} \sum_{\ell}^{N} P_{k\ell} S_{k\ell} \tag{1.7}$$

Charge Decomposition Analysis

Charge Decomposition Analysis was proposed by S. Dapprich and G. Frenking, to analyze charge transfer.

Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352–9362

Common approaches for analyzing charge transfer

1. Atomic charges
2. Density difference
3. Charge decomposition analysis

Fragment Orbitals

Recall that

$$\langle \phi_i \,|\, \phi_i \rangle = \sum_k^N \sum_\ell^N C_{ki}^* C_{\ell i} S_{kl} \tag{2.1}$$

where N is the number of AOs, and S is the overlap matrix between AOs. Do SCF calculation for two fragments at same geometry separately, we get two set of MOs of fragments. They are called fragment orbitals, with a total number N.
Expand total MO with FOs instead, we get

$$\eta_i \langle \phi_i \,|\, \phi_i \rangle = \eta_i \sum_m^N \sum_n^N C_{mi}^* C_{ni} S_{mn} \tag{2.2}$$

where

$$S_{mn} = \langle \phi_m \,|\, \phi_n \rangle \tag{2.3}$$

Define

$$d_i = \sum_{m\in A}^{occ}\sum_{n\in B}^{vir} \eta_i C_{mi}^* C_{ni} S_{mn} \tag{2.4}$$

$$b_i = \sum_{m\in A}^{vir}\sum_{n\in B}^{occ} \eta_i C_{mi}^* C_{ni} S_{mn} \tag{2.5}$$

$$r_i = \sum_{m\in A}^{occ}\sum_{n\in B}^{occ} \eta_i C_{mi}^* C_{ni} S_{mn} \tag{2.6}$$

$$d = \sum_i d_i \qquad b = \sum_i b_i \qquad r = \sum_i r_i \tag{2.7}$$

thus
d is the charge transfer from A to B, b is the charge transfer from B to A. $d - b$ is the net charge transfer from A to B.