

Molecular Orbitals and Charge Decomposition Analysis

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Molecular Orbitals

Charge Decomposition Analysis

Expand each MO with N AOs (basis)

$$\phi_i = \sum_k^N C_{ki} \chi_k \quad (1.1)$$

	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

$$K/2 = \sum_i^{occ} \langle \phi_i | \phi_i \rangle = \sum_i^{occ} \sum_k^N \sum_l^N C_{ki}^* C_{li} \langle \chi_k | \chi_l \rangle \quad (1.2)$$

or

$$K = \sum_i^N \eta_i \langle \phi_i | \phi_i \rangle = \sum_i^N \eta_i \sum_k^N \sum_l^N C_{ki}^* C_{li} \langle \chi_k | \chi_l \rangle \quad (1.3)$$

where

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

Moreover, define

$$\text{Density Matrix} \quad P_{kl} = \sum_i^N \eta_i C_{ki}^* C_{li} \quad (1.5)$$

$$\text{Overlap Matrix} \quad S_{kl} = \langle \chi_k | \chi_l \rangle \quad (1.6)$$

thus

$$K = \sum_k^N \sum_\ell^N P_{kl} S_{kl} \quad (1.7)$$

Charge Decomposition Analysis

Fragment Orbitals