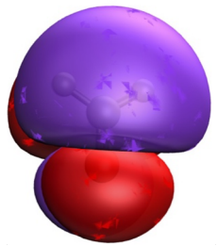
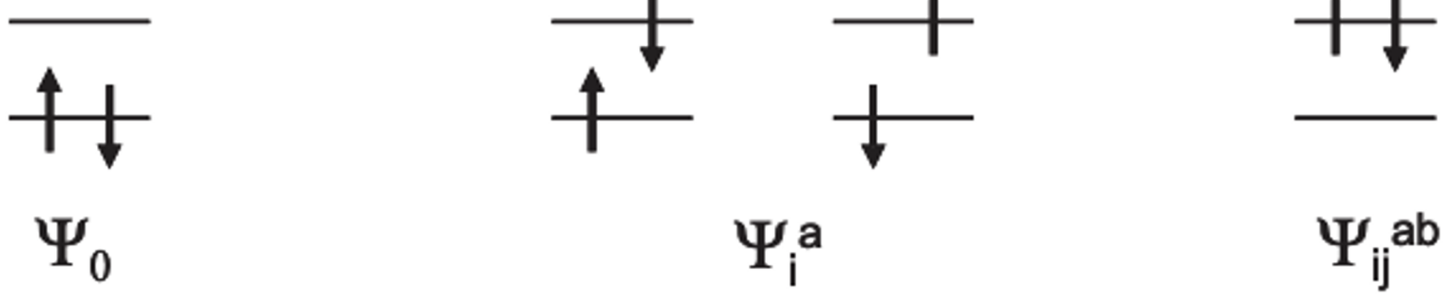
EOM-EE calculation of formaldehyde (CH_2O)



b_2

b_1

EOM-EE: $\Psi(M_s=0) = R(M_s=0)\Psi_0(M_s=0)$



Reference

Target states

EOM-EE method:

- computes excited states (conserving the number of α and β electrons)
- yields accurate excitation energies
- describes multiconfigurational wavefunction with single reference formalism
- can compute excited-state gradients and properties

EOM-EE calculation of Formaldehyde (CH_2O)

- Import geometry (formaldehyde.xyz) into IQmol
- Use singlet reference (charge=0, multiplicity=1)
- Request singlets and triplets using EE_SINGLETS and EE_TRIPLETS
- Request transition properties: CC_TRANS_PROP = true
- Look at the EOM amplitudes and MOs to assign state character

```
$rem
  METHOD  =  EOM-CCSD
   BASIS  =  6-31G**
   EE_SINGLETS  =  [1,1,1,1]   ! for calculating 4 singlet excited states from 4 irreps
   ! the order of irreps are:  [A1, A2, B1, B2] for C2v
   EE_TRIPLETS  =  [1,1,1,1]   ! for calculating 4 triplet excited states from 4 irreps
   MEM_TOTAL  =  4000
   METHOD  =  EOM-CCSD
   CC_TRANS_PROP = true        ! to request transition properties
   !MOLDEN_FORMAT  =  true     ! NTOs are generated in the molden format
   !NTO_PAIRS  =  2            ! 4 NTO pairs per transition
   !STATE_ANALYSIS  =  true
$end
```

For generating NTOs: add STATE_ANALYSIS = true, NTO_PAIRS = 2, and MOLDEN_FORMAT = true

(This is not yet implemented in IQmol, need to visualize separately)

EOM-EE calculation of formaldehyde (CH_2O)

For each EOM-EE state you should get the following sections in the output

1) Excitation energies and orbital description

```
EOMEE transition 1/A1
Total energy = -113.64401221 a.u.  Excitation energy = 10.6423 eV.
R0^2 = 0.0006  R1^2 = 0.9034  R2^2 = 0.0966  Res^2 = 8.21e-06
Conv-d = yes

Amplitude    Transitions between orbitals
-0.5231       1 (B2) A                  ->    2 (B2) A
-0.5231       1 (B2) B                  ->    2 (B2) B
 0.3878       2 (B1) A                  ->    3 (B1) A
 0.3878       2 (B1) B                  ->    3 (B1) B
-0.1152       1 (B1) A                  ->    3 (B1) A
-0.1152       1 (B1) B                  ->    3 (B1) B

Summary of significant orbitals:

 Number  Type          Irrep      Energy
 5       Occ  Alpha    1 (B1)     -0.7024
 8       Occ  Alpha    2 (B1)     -0.4394
 7       Occ  Alpha    1 (B2)     -0.5360
 5       Occ  Beta     1 (B1)     -0.7024
 8       Occ  Beta     2 (B1)     -0.4394
 7       Occ  Beta     1 (B2)     -0.5360
 11      Vir  Alpha    3 (B1)      0.3229
 9       Vir  Alpha    2 (B2)      0.1271
 11      Vir  Beta     3 (B1)      0.3229
 9       Vir  Beta     2 (B2)      0.1271
```

2) Transition properties

```
State A: ccsd: 0/A1
State B: eomee_ccsd/rhfref/singlets: 1/A1
Energy GAP = 0.391097 a.u. = 10.642306 eV
Transition dipole moment (a.u.):
  A->B: 0.183608 (X 0.000000, Y 0.000000, Z 0.183608)
  B->A: 0.381190 (X 0.000000, Y 0.000000, Z 0.381190)
Oscillator strength (a.u.): 0.018249
Transition angular momentum against gauge origin (a.u.):
  A->B:  (X 0.000000i, Y 0.000000i, Z 0.000000i)
  B->A:  (X 0.000000i, Y 0.000000i, Z 0.000000i)
Norm of one-particle transition density matrix:
  A->B: 0.909370;   B->A: 0.968533
  ||gamma^AB||*||gamma^BA||: 0.880755
```

EOM-EE state	Energy (eV)	Osc. Strength	EOM-EE state	Energy (eV)	Osc. Strength
$^1A_1$	10.64	0.02	$^3A_1$	6.08	0.0
$^1A_2$	3.98	0.00	$^3A_2$	3.58	0.0
$^1B_1$	9.56	0.19	$^3B_1$	8.56	0.0
$^1B_2$	9.42	0.01	$^3B_2$	8.46	0.0

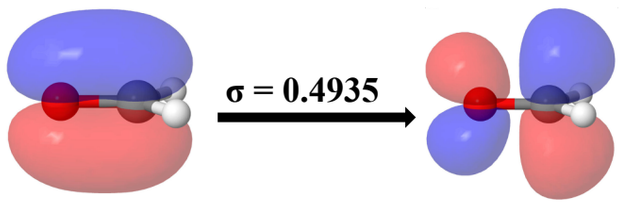
- The oscillator strength for the triplet states is zero as they are spin-forbidden
- Transition between the excited states can also be computed

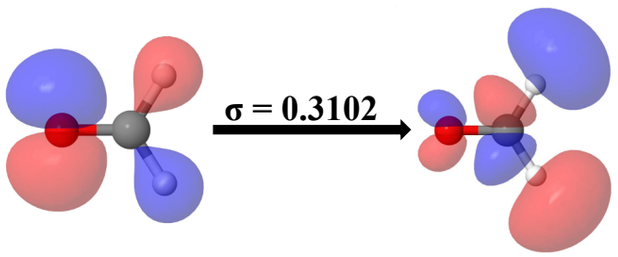
EOM-EE calculation of formaldehyde (CH_2O)

1. NTOs are in the *filename*.out.plots folder. The NTOs are named as ccsd_eomee_ccsd_rhfref_singlets_i_j_nto.mo (for jth state in the ith irrep). We plotted the NTOs with the jmol plotting software.
2. Each NTO pair is associated with a singular value (σ). It is negative for holes and positive for particles. σ = 0.49738 means 49% of the wavefunction is accounted for by this NTO pair.
3. The number of NTO pairs we need to consider depends on the participation ratio (PR_NTO). If PR_NTO is close to 1, we take 1 NTO pair.
4. NTOs for some electronic excitations in formaldehyde are shown below.

$^1A_1$ transition

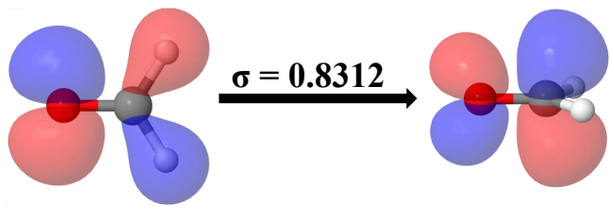
PR_NTO = 2.012





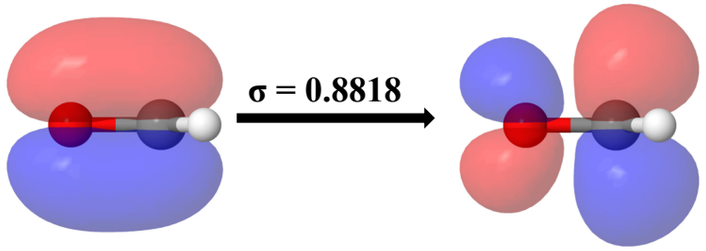
$^1A_2$ transition

PR_NTO = 1.003



$^3A_1$ transition

PR_NTO = 1.072



$^3A_2$ transition

PR_NTO = 1.004