

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



- 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: [A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub>] for C<sub>2v</sub>
EE_TRIPLETS = [1,1,1,1] ! for calculating 4 triplet excited states from 4 irreps
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)

CONFICUENCE OF CHEMISTRY ECOM-EE calculation of formaldehyde (CH₂O)

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

1) Excitation energies and orbital description

EOMEE	transitio	on 1/A1						
Total	energy =	-113.79821794	a.u.	Excitation	energy	=	10.4077	eΫ.
R0^2 =	= 0.0012	$R1^2 = 0.9117$	R2^2	= 0.0883 1	Res^2 =	5.	41e-06	

R0^2 = 0.0012 R1^2 = 0.9117 R2^2 = 0.0883 Res^2 = 5.41e-06 Conv-d = yes

Amplitude	Tra	nsit:	ions	between	orbitals				
-0.5796	1	(B2)	A		->	2	(B2)	A	
-0.5796	1	(B2)	в		->	2	(B2)	в	
0.3038	2	(B1)	A		->	3	(B1)	A	
0.3038	2	(B1)	В		->	3	(B1)	в	

Summary of significant orbitals:

Number	Type			Ir	rep	Energy
8	0cc	Alpha		2	(B1)	-0.4369
7	0cc	Alpha		1	(B2)	-0.5329
8	0cc	Beta		2	(B1)	-0.4369
7	0cc	Beta		1	(B2)	-0.5329
11	Vir	Alpha		3	(B1)	0.3336
9	Vir	Alpha		2	(B2)	0.1396
11	Vir	Beta		3	(B1)	0.3336
9	Vir	Beta	1	2	(B2)	0.1396

2) Transition properties

State A: ccsd: 0/A1							
State B: eomee ccsd/rhfref/singlets: 1/A1							
Energy GAP = 0.3825 a.u. = 10.4077 eV							
Transition dipole moment (a.u.):							
A->B: 0.406344 (X 0.000000, Y 0.000000, Z -0.406344)							
B->A: 0.553163 (X 0.000000, Y 0.000000, Z -0.553163)							
Oscillator strength (a.u.): 0.057314							
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: 0.910773; B->A: 0.970106							
gamma^AB * gamma^BA : 0.883547							

EOM-EE state	Energy (eV)	Osc. Strength	EOM-EE state	Energy (eV)	Osc. Strength	
¹ A ₁	10.41	· · 0.06	³ A ₁	6.12	0.0	
¹ A ₂	4.15	0.00	³ A ₂	3.72	0.0	
¹ B ₁	9.71	0.19	³ B ₁	8.68	0.0	
¹ B ₂	9.59	0.003	³ B ₂	8.66	0.0	

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



- 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.

