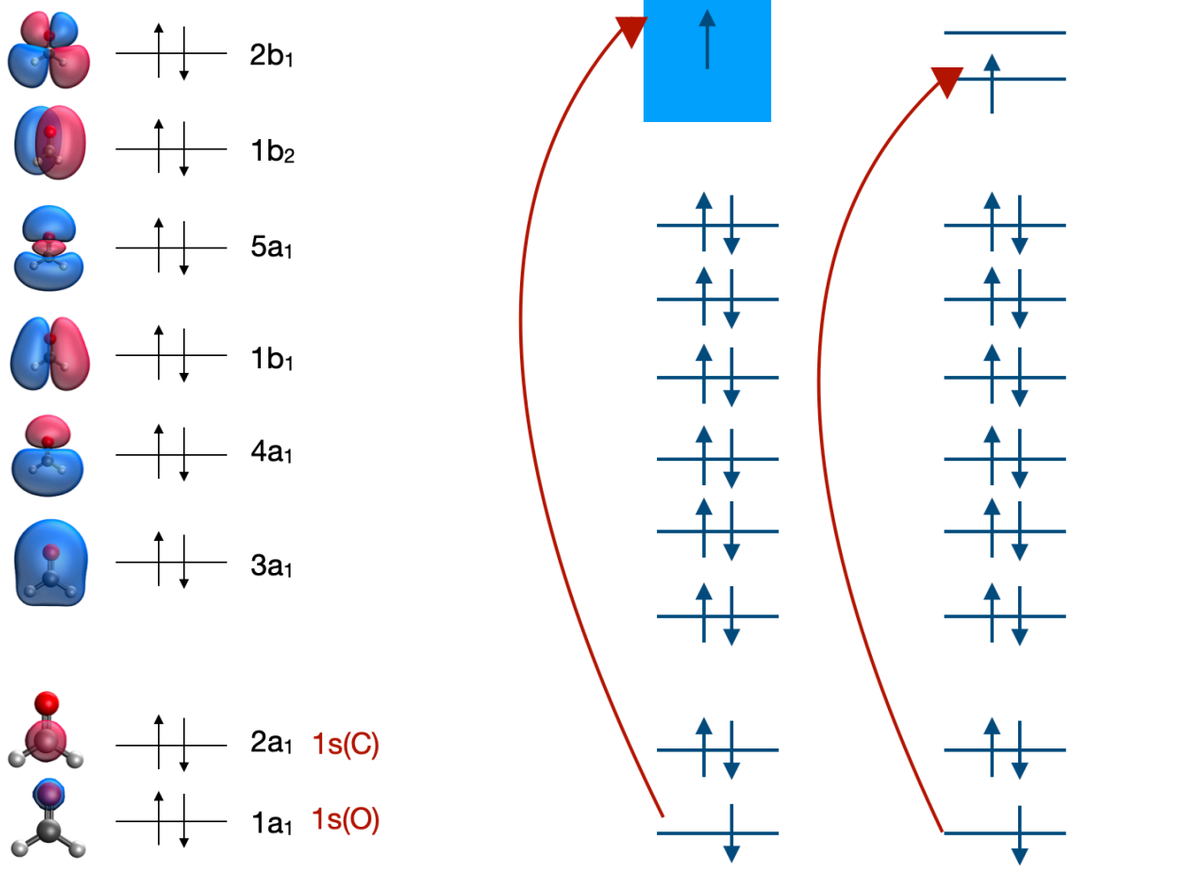
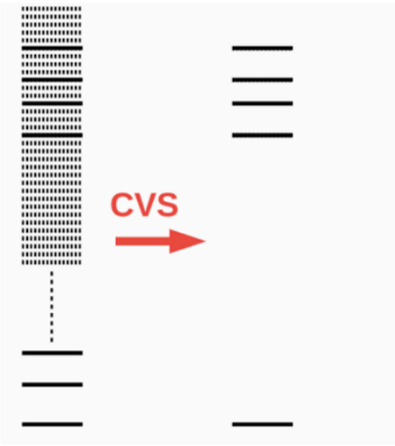
CVS-EOM-IP and CVS-EOM-EE calculations of formaldehyde (CH_2O)



- X-ray spectroscopies are based on transitions involving core electrons
- These states can be computed using CVS-EOM-CC methods (IP and EE)
- Transitions between core-level states and valence states can also be computed (for XES)

- Core-level states are high in energy
- Core-level states are metastable wrt electron loss
- Core-valence separation (CVS) projects the continuum out and removes low-lying states



$$|\Psi_I> = \hat{R}_I e^{\hat{T}} |\Phi_0>$$

$$\bar{H}\hat{R}_I = E_n \hat{R}_I;\ \bar{H} = e^{-\hat{T}} H e^{\hat{T}}$$

$$\hat{R}_{CVS-IP} = \sum_I r_I \hat{a}_I + \frac{1}{2}\sum_{a,I,J} r_{IJ}^a \hat{a}_a^\dagger \hat{a}_J \hat{a}_I + \sum_{a,I,j} r_{Ij}^a \hat{a}_a^\dagger \hat{a}_j \hat{a}_I$$

I, J, K…..- occupied core spin-orbitals
i, j, k…..- occupied valence spin-orbitals
a, b, c…..-virtual spin-orbitals

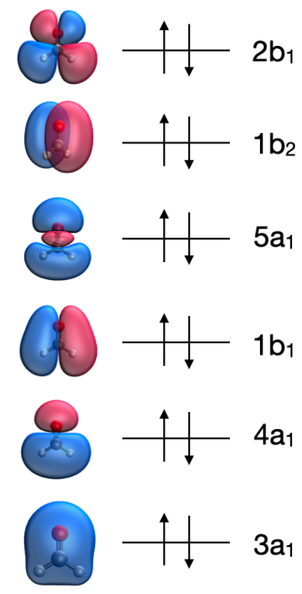
$$\hat{R}_{CVS-EE} = r_0 + \sum_{Ia} r_I^a \hat{a}_a^\dagger \hat{a}_I + \frac{1}{4}\sum_{a,b,I,J} r_{IJ}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_J \hat{a}_I + \frac{1}{4}\sum_{a,b,I,j} r_{Ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_I$$

CVS-EOM-IP/EE calculation of formaldehyde (CH_2O)

Core-ionized states at carbon edge for CH_2O

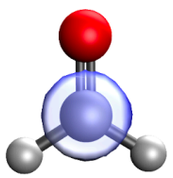
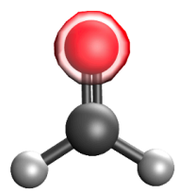
- Import structure (formaldehyde.xyz) to IQmol
- Freeze 2 core orbitals (N_FROZEN_CORE = 2)
- Request one CVS-IP state (of A1 symmetry)

```
$rem
   METHOD  =  EOM-CCSD          !Specify the method
   BASIS  =  6-31g              !Specify the basis for calculation
   CVS_IP_STATES  =  [1,0,0,0]  !Requesting CVS-IP states in A1 symmetry
   N_FROZEN_CORE  =  2          !N_FROZEN_CORE = n will freeze n cores.
   CC_DO_DYSON  =  1            !To obtain Dyson orbitals
   GUI  =  2
   MEM_TOTAL  =  4000
$end
```



- To compute oxygen edge, use N_FROZEN_CORE = 1
- To compute Dyson orbitals, use CC_DO_DYSON = 1
- To compute core-excited states (for XAS) use keywords CVS_EE_STATES = [1,0,0,0]
- Use CC_TRANS_PROP = 1 for transition properties (XAS intensities).

CVS-EOM-IP/EE calculation of formaldehyde (CH_2O)

CVS-EOM-IP state	Energy (eV)	Dyson orbital
1/A_1 C-edge	297.51	
1/A_1 O-edge	544.16	

CVS-EOM-EE state	Energy (eV)	Oscillator strength
1/A_1 C-edge	295.12	0.015
1/A_1 O-edge	543.37	0.005

- The excitation energy in IP and EE calculation gives ionization (XPS) and excitation (XAS) energies, respectively
- The oscillator strength, transition dipole moment are printed out in transition properties section
- Note the huge differences in core-ionization, and excitation energies computed at O-edge and C-edge of CH_2O

```
EOMIP transition 1/A1
Total energy = -103.10187509 a.u.  Excitation energy = 297.5084 eV.
R1^2 = 0.8061  R2_CCVV^2 = 0.0003  R2_COVV^2 = 0.1936  Res^2 = 1.68e-0
Conv-d = yes

Amplitude    Transitions between orbitals
-0.8978       2 (A1) A                  ->    infty

             Summary of significant orbitals:

              Number  Type             Irrep      Energy
              2       Occ  Alpha       2 (A1)    -11.3549
```

```
CVS-EOMEE transition 1/A1
Total energy = -103.18974191 a.u.  Excitation energy = 295.1175 eV.
R0^2 = 0.0000  R1^2 = 0.8313  R2_CCVV^2 = 0.0004  R2_COVV^2 = 0.0842  Res^2 = 6.
Conv-d = yes

Amplitude    Transitions between orbitals
-0.6370       2 (A1) A                  ->    6 (A1) A
-0.6370       2 (A1) B                  ->    6 (A1) B
 0.0868       2 (A1) A                  ->    10 (A1) A
 0.0868       2 (A1) B                  ->    10 (A1) B

             Summary of significant orbitals:

 Number  Type             Irrep      Energy
 2       Occ  Alpha       2 (A1)    -11.3549
 2       Occ  Beta        2 (A1)    -11.3549
 10      Vir  Alpha       6 (A1)      0.2380
 18      Vir  Alpha      10 (A1)      1.1323
 10      Vir  Beta        6 (A1)      0.2380
 18      Vir  Beta       10 (A1)      1.1323
```

```
Start computing the transition properties

-------------------------------------------------------------
State A: ccsd: 0/A1
State B: cvs_eomee_ccsd/rhfref/singlets: 1/A1
Energy GAP = 10.8454 a.u. = 295.1176 eV
Transition dipole moment (a.u.):
  A->B: 0.045179 (X 0.000000, Y 0.000000, Z -0.045179)
  B->A: 0.045092 (X 0.000000, Y 0.000000, Z -0.045092)
Oscillator strength (a.u.): 0.014730
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: 0.904540;   B->A: 0.889668
  ||gamma^AB||*||gamma^BA||: 0.804740
```