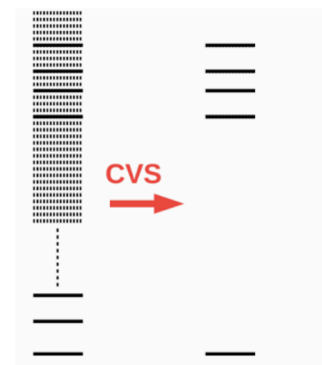


- Core-level states are high in energy
- Core-level states are metastable wrt electron loss
- Core-valence separation (CVS) projects the continuum out and removes low-lying states



- 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)

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

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

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

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

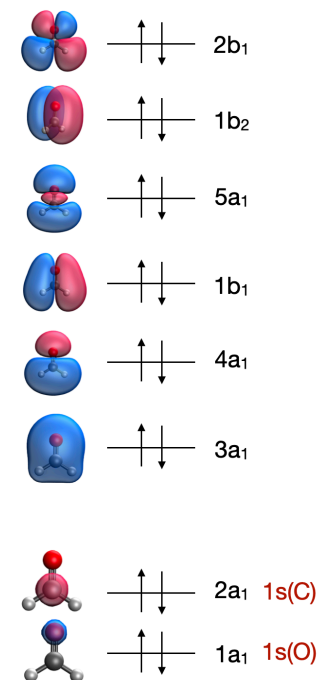
$$\hat{R}_{CVS-EE} = r_0 + \sum_{Ia} r_I^a \hat{a}_a^\dagger \hat{a}_I + \frac{1}{4} \sum_{a,b,I,J} r_{IJ}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_J \hat{a}_I + \frac{1}{4} \sum_{a,b,I,j} r_{IJ}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_I$$

Core-ionized states at carbon edge for CH₂O

- 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.
GUI = 2
$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 in CVS_EE calculation).

CVS-EOM-IP/EE calculation of formaldehyde (CH₂O)

Edge IP, eV

C edge 297.51

Edge Eex, eV f_i

C edge 295.12 0.015

```
EOMIP transition 1/A1
Total energy = -103.10187508 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-06
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 = 6.53e-06
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
```

```
State A: ccscd: 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: 0.045312 (X 0.000000, Y 0.000000, Z -0.045312)
B->A: 0.045092 (X 0.000000, Y 0.000000, Z -0.045092)
Oscillator strength (a.u.): 0.014773
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
```

- 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 CH₂O