EOM-EA and EOM-DEA methods

$$\Psi(N) = R(+1)\Phi_0(N-1)$$

$$\Psi(N) = R(+2)\Phi_0(N-2)$$

- EOM-EA/DEA describe target states by <u>electron-attaching</u> operators
- When using closed-shell reference, target states are naturally spin pure
- EOM-EA is good for certain doublet states (e.g., Na atom in the ground and excited states)
- EOM-DEA can describe diradicals (e.g., methylene) and bond-breaking
- State and transition properties can be computed

EOM-EA: MgOH example

- Alkali-earth atoms like Mg have [core]ns^2 electronic configuration
- They form ionic bonds with halogen-like ligands (e.g. Mg-OH), yielding doublet radicals with an unpaired electron localized on the metal
- EOM-EA can describe its ground and excited states
- Dyson orbitals show where the unpaired electron is

- Import structure to IQmol (mgoh_structure.xyz)
- Use cationic reference ($MgOH^+$, charge=1, multiplicity=1) and EA_STATES
- Compute 3 target states

```
$rem
   method = eom-ccsd
   ea_states = [1, 0, 1, 1]
   basis = 6-31G*
! Dyson orbitals
   cc_do_dyson = true
   print_general_basis = true
$end
```

Note: Largest abelian subgroup is C_{2v}: A_1, A_2, B_1, B_2 irreps
Use MEM_TOTAL=4000

EOM-DEA: Mg-CC-Mg example

- Mg-CC-Mg is a diradical: it has two unpaired electrons
- It is best described by EOM-DEA

- Import structure to IQmol (mgccmg_structure.xyz)
- Use dicationic reference ($MgCCMg^{2+}$, charge=+2, multiplicity=1) and dea_states
- Compute 3 target states in each multiplicity
- Request transition properties between the EOM states

```
$rem
  method = eom-ccsd
  dea_singlets = [1, 0, 0, 0, 0, 0, 1, 1]
  dea_triplets = [0, 0, 0, 0, 0, 1, 1, 1]
  basis = 6-31G*
! transition properties
  cc_trans_prop = 2
$end
```

Note: Largest abelian subgroup is D_{2h}: A_g, B_{1g}, B_{2g}, B_{3g}, A_u, B_{1u}, B_{2u}, B_{3u} irreps
Use MEM_TOTAL=4000

EOM-EA: MgOH example

```
463   EOMEA transition 1/A1
  1   Total energy = -275.26088905 a.u.  Excitation energy = -7.2303 eV.
  2   R1^2 = 0.9901  R2^2 = 0.0099  Res^2 = 1.28e-06
  3   Conv-d = yes
```

Transition	EA, eV	E_{ex} (eV)
$1/A_1$	-7.230	0.000
$1/B_1$	-3.537	3.693
$1/B_2$	-3.537	3.693

IQmol: left panel -> Surfaces

Energy difference relative to reference gives EA=E(EOM) - E(Ref) (electron affinity of $MgOH^+$)

Energy levels in MgOH: difference between the EOM states

EOM-DEA: Mg-CC-Mg example

State	Trans. symm.	E_ex (eV)	Multiplicity	f
0	$1/A_g$	0.000	singlet	--
1	$1/B_{1u}$	0.020	triplet	0.00
2	$1/B_{2u}$	2.873	triplet	0.00
3	$1/B_{3u}$	2.873	triplet	0.00
4	$1/B_{2u}$	2.988	singlet	0.31
5	$1/B_{3u}$	2.988	singlet	0.31

Singlets and triplets are printed separately. Look for a line like:

```
408          Solving for EOMDEA-CCSD Ag transitions to singlet states
```

Transition properties:

```
800   State A: eomdea ccsd/rhfref/singlets: 1/Ag
  1   State B: eomdea ccsd/rhfref/singlets: 1/B2u
  2   Energy GAP = 0.1098 a.u. = 2.9885 eV
  3   Transition dipole moment (a.u.):
  4     A->B: 2.043799 (X 0.000000, Y 2.043799, Z 0.000000)
  5     B->A: 2.071908 (X 0.000000, Y 2.071908, Z 0.000000)
  6   Oscillator strength (a.u.): 0.310042
  7   Transition angular momentum against gauge origin (a.u.):
  8     A->B:  (X 0.000000i, Y 0.000000i, Z 0.000000i)
  9     B->A:  (X 0.000000i, Y 0.000000i, Z 0.000000i)
 10   Norm of one-particle transition density matrix:
 11     A->B: 0.712898;   B->A: 0.709384
 12     ||gamma^AB||*||gamma^BA||: 0.505718
```

The states can be visualized by using natural transition orbitals (NTOs)

A pair of NTOs for the 1/Ag to 1/B2g singlet transition with a SV = 0.33