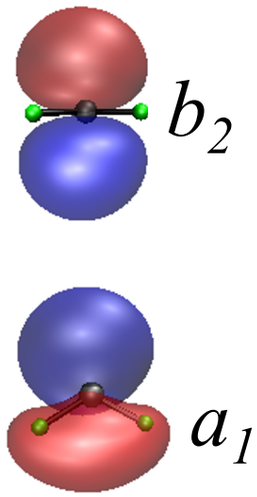
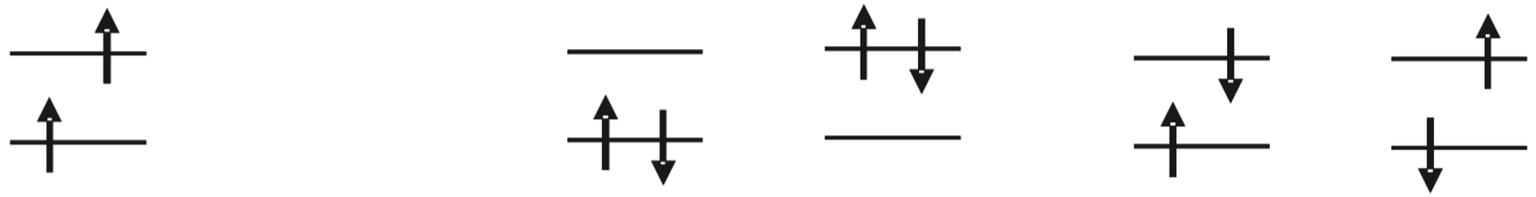
EOM-SF calculation of methylene (CH_2)

EOM-SF: $\Psi(M_s=0)=R(M_s=-1)\Psi_0(M_s=1)$





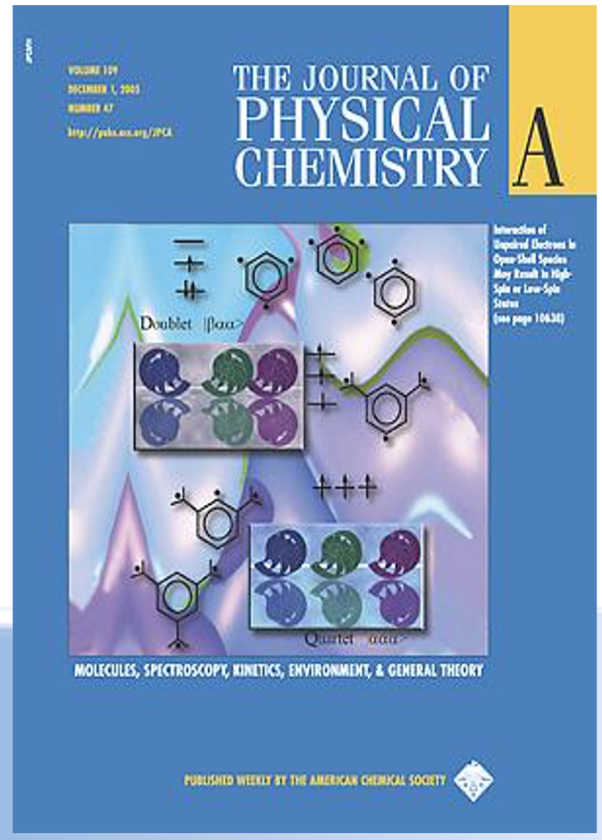
Ψ_0 Reference

Ψ_i^a Target states

EOM-SF method yields:

- accurate singlet-triplet gaps;
- accurate geometries and properties;
- describes closed-shell and open-shell low spin states.

Casanova and Krylov, Spin-flip methods in quantum chemistry, PCCP **22** 4326 (2020)



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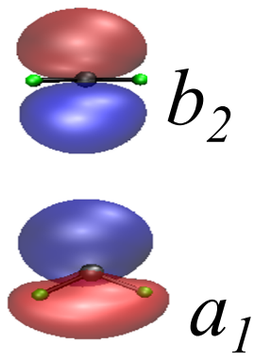
- Import geometry (methylene.xyz) into IQmol
- Use triplet reference (charge=0, multiplicity=3)
- Request ”diradical states” of expected symmetry (see frontier orbitals irreps)
- Request S^2 of CCSD and EOM wavefunctions to check for spin-contamination
- Look at the EOM amplitudes to assign state character.
- Important energy differences: between the EOM states (not reference-EOM).

```
$rem
METHOD              =  EOM-CCSD
SF_STATES           =  [2,0,0,2] ! Request 4 transitions: A1 and B2 irreps
BASIS               =  6-31G
CC_EOM_PROP_TE  =  1        ! Compute S^2 of EOM states
CC_REF_PROP_TE  =  1        ! Compute S^2 of CCSD reference
GUI                 =  2
MEM_TOTAL           =  4000
$end
```



Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Product table for C_{2v} point group

	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

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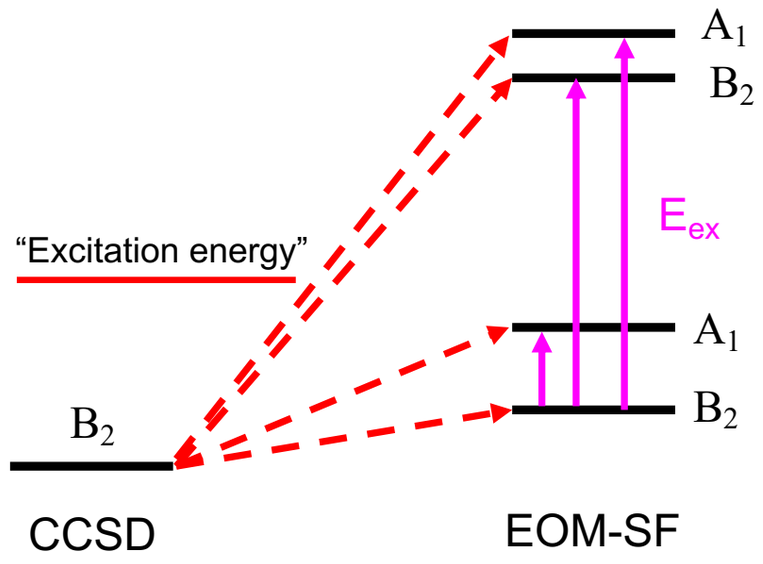
For each EOM-SF state you should get the following sections in the output

1) Excitation energies and orbital description

```
EOMSF transition 1/A1
Total energy = -38.97364719 a.u.  Excitation energy = 0.0086 eV.
R1^2 = 0.9887  R2^2 = 0.0113  Res^2 = 2.06e-06
Conv-d = yes

Amplitude    Transitions between orbitals
-0.6827       1 (B2) A                  ->    1 (B2) B
 0.6698       3 (A1) A                  ->    3 (A1) B
-0.1569       1 (B2) A                  ->    2 (B2) B
-0.1452       2 (A1) A                  ->    3 (A1) B
-0.1126       3 (A1) A                  ->    5 (A1) B

          Summary of significant orbitals:

           Number  Type              Irrep      Energy
           2       Occ   Alpha       2 (A1)     -0.9633
           4       Occ   Alpha       3 (A1)     -0.4731
           5       Occ   Alpha       1 (B2)     -0.4116
           4       Vir   Beta        3 (A1)      0.1363
           9       Vir   Beta        5 (A1)      0.8458
           5       Vir   Beta        1 (B2)      0.1735
           10      Vir   Beta        2 (B2)      0.8981
```

2) State properties and S^2

```
 EOMSF-CCSD transition 1/A1
S^2 calculation will be performed in  double precision
 Excited state properties for  EOMSF-CCSD transition 1/A1
 Dipole moment (a.u.): 0.251378 (X 0.000000, Y 0.000000, Z -0.251378)
 R-squared (a.u.): 23.272158 (XX 10.587846, YY 5.830180, ZZ 6.854132)
 Gauge origin (a.u.): (0.000000, 0.000000, 0.000000)
 Angular momentum (a.u.) against gauge origin:
 (X 0.000000i, Y 0.000000i, Z 0.000000i)
 Traces of the OPDMs: Tr(AA) 4.000000, Tr(BB) 4.000000
 <S^2> = 2.000864
```



Transition irrep.	EOM-SF state	Energy (eV)	S^2	Multiplicity	E_{ex} (eV)
$1/A_1$	$1/B_2$	0.0086	2.00	Triplet	0.0000
$1/B_2$	$1/A_1$	1.1777	0.00	Singlet	1.1691
$2/A_1$	$2/B_2$	2.2171	0.00	Singlet	2.2085
$2/B_2$	$2/A_1$	4.3607	0.00	Singlet	4.3521