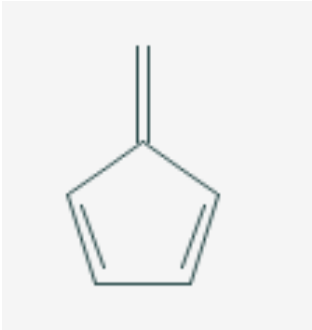
Work plan:

Fulvene calculations:



Task 1

Determine the active space: full valence CAS in the π space

Orbital occupation for scf calculation:

System: Fulvene Point Group: c2v

N. Electrons: 42 Multiplicity: 1

Level: SCF/6-31G

		IRREP							
		a_1	b_1	b_2	a_2				
SCF	DOCC	11	7	2	1				
	OPSH	0	0	0	0				

Task 2:

Perform a closed shell scf calculation (see Appendix for Cartesian geometry); analyze the π orbitals and add the lowest three virtual π orbitals to the active space. What is the resulting CAS orbital scheme?

MCSCF	DOCC	??	??	??	??				
	RAS	0	0	0	0				
	CAS	??	??	??	??				
	AUX	0	0	0	0				

Two states should be calculated: S_0 and S_1. Fill out the table below

States	Multiplicity	N. electrons	Symmetry
1	??	??	?
2	??	??	?
Number of distinct rows (DRTs): ??			

Task 3:

Perform a single point state-averaged SA-CASSCF calculations with two states.

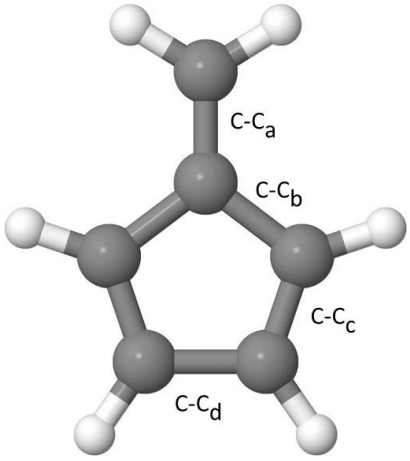
What is the excitation energy, the oscillator strength and the orbital excitation scheme of S_1 in comparison to S_0?

State	ΔE (eV)	Configuration	%	Osc. Str.
		SA2-CASSCF(6,6)		
S_0				-
S_1				

Plot the six π orbitals of the active space.

Task 4

Perform a geometry optimization for the planar S_1 state using the SA2-CASSCF(6,6) method.



	C-C_a	C-C_b	C-C_c	C-C_d
		SA2-CASSCF(6,6)		
S_1				

Task 5

Compute the MXS starting from the planar S_1 fulvene structure using the SA2-CASSCF(6,6) method.

	$C\text{-}C_a$	$C\text{-}C_b$	$C\text{-}C_c$	$C\text{-}C_d$
		SA2-CASSCF(6,6)		
MXS				

Plot or visualize the two vectors of the branching space and characterize the vibrations.

Task 6

Compute the vertical excitation energy at MRCI(CAS6,6) and MRCI(CAS6,6)+Pople correction using the S_0 MRCI geometry

1. Set up the MO occupation table for MRCI

Keep the core orbitals frozen.

MRCI	FC								
	FV								
	DOCC								
	ACT								
	AUX								
	INT								

2. Copy the SA-CASSCF input from Task 3 into a new directory and make only the MRCI input. Do it for S_0 and S_1 separately as they have different symmetries. Use the MRCI S_0 geometry from the Appendix. Extract the vertical excitation energy and compare it with the SA2-CASSCF result.

MRCI/MRCI+P excitation energies using the MRCI S_0 optimized geometry			
State	ΔE (eV)	Configuration	%
S_0			
S_1			

Task 7

Compute the vertical excitation energy at MRCI(CAS6,6) and MRCI(CAS6,6)+Pople correction using the S_1 MRCI geometry

Copy the inputs from Task 6 into separate directories and use the S_1 MRCI optimized geometry (file geom) given in the Appendix. Replace only the old geom file by the new one and do the calculations.

Important: compute all energies relative to the MRCI ground state energy of the S_0 geometry (Task 6).

MRCI/MRCI+P excitation energies using the MRCI S_0 optimized geometry			
State	ΔE (eV)	Configuration	%
S_0			
S_1			

Solutions

Directories on CCR:

	SA2-CASSCF(6,6)/6-31G
S_0 opt	/user/ub2037/fulvene/S0-CAS
S_1 opt	/user/ub2037/fulvene/S1-CAS
MXS	/user/ub2037/fulvene/MXS-CAS/mxs_opt
	MRCI
S_0 opt	/user/ub2037/fulvene/S0-CI
S_1 opt	/user/ub2037/fulvene/S1-CI

Task 2:

CAS orbital scheme

MCSCF	DOCC	11	7	0	0				
	RAS	0	0	0	0				
	CAS	0	0	4	2				
	AUX	0	0	0	0				

States	Multiplicity	N. electrons	Symmetry
1	1	42	A_1
2	1	42	B_1
Number of distinct rows (DRTs): 2			

Task 3:

Vertical excitations at SA2-CASSCF calculation

State	ΔE (eV)	Configuration	%	Osc. Str.
		SA2-CASSCF(6,6) – S_0 optimization		
S_0	0.000	$(1b2)^2(2b2)^2(3b2)^0(4b2)^0$ $(1a2)^2(2a2)^0$	75.7	-
S_1	4.080	$(1b2)^2(2b2)^2(3b2)^1(4b2)^0$ $(1a2)^1(2a2)^0$	72.0	0.0
		$(1b2)^2(2b2)^1(3b2)^2(4b2)^0$ $(1a2)^1(2a2)^0$	14.8	

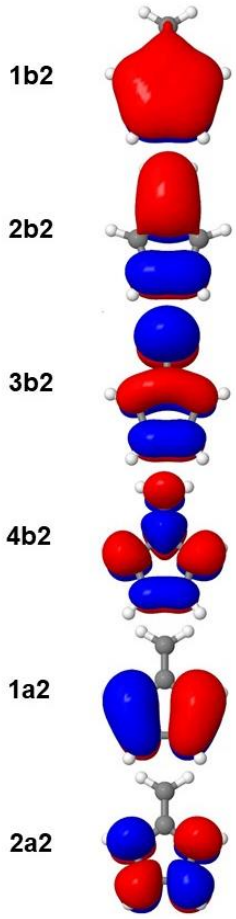


Figure 1: Optimized active orbitals for the S_0 optimized with SA2-CASSCF(6,6)/6-31G.

Task 4

	$C\text{-}C_a$	$C\text{-}C_b$	$C\text{-}C_c$	$C\text{-}C_d$
		SA2-CASSCF(6,6)		
S_0	1.352	1.479	1.360	1.482
S_1	1.497	1.402	1.475	1.363

Task 5

	$C\text{-}C_a$	$C\text{-}C_b$	$C\text{-}C_c$	$C\text{-}C_d$
		SA2-CASSCF(6,6)		
MXS	1.583	1.373	1.538	1.321

Task 6

MRCI Occupation Table

MRCI	FC	4	2	0	0				
	FV	0	0	0	0				
	DOCC	7	5	0	0				
	ACT	0	0	4	2				
	AUX	0	0	0	0				
	INT	7	5	4	2				

MRCI/MRCI+P excitation energies using the MRCI S_0 optimized geometry

State	ΔE (eV)	Configuration	%
S_0	0.000/0.000	$(1b2)^2(2b2)^2(3b2)^0(4b2)^0$ $(1a2)^2(2a2)^0$	69.0
S_1	3.907/3.779	$(1b2)^2(2b2)^2(3b2)^1(4b2)^0$ $(1a2)^1(2a2)^0$	70.1

Task 7

MRCI/MRCI+P excitation energies using the MRCI S_0 optimized geometry

State	ΔE (eV)	Configuration	%
S_0	1.268/1.194	$(1b2)^2(2b2)^2(3b2)^0(4b2)^0$ $(1a2)^2(2a2)^0$	61.8
		$(1b2)^2(2b2)^1(3b2)^1(4b2)^0$ $(1a2)^2(2a2)^0$	10.5
S_1	2.638/2.600	$(1b2)^2(2b2)^2(3b2)^1(4b2)^0$ $(1a2)^1(2a2)^0$	67.3
		$(1b2)^2(2b2)^1(3b2)^2(4b2)^0$ $(1a2)^1(2a2)^0$	10.8

Appendix

Fulvene geom_unique.xyz file containing the symmetry unique atoms using the SA-CASSCF S_0 geometry

7

```
C          0.741279        -0.000000        -2.186935
C          1.177643        -0.000000        -0.898511
C          0.000000         0.000000        -0.004256
C         -0.000000        -0.000000         1.347324
H          1.349366        -0.000000        -3.067414
H          2.192618        -0.000000        -0.559673
H          0.914227         0.000000         1.909820
```

Fulvene geom_unique.xyz file containing the symmetry unique atoms using the MR-CI S_0 geometry

7

```
C          0.746320         0.000000        -2.195217
C          1.187909         0.000000        -0.899709
C          0.000000        -0.000000        -0.001599
C         -0.000000         0.000000         1.356855
H          1.358935         0.000000        -3.087441
H          2.214125         0.000000        -0.555979
H          0.922835        -0.000000         1.928229
```

Fulvene geom file using the MR-CI S_1 geometry

```
C      6.    1.29873323    0.00000000   -4.32672141   12.00000000
C      6.   -1.29873323   -0.00000000   -4.32672141   12.00000000
C      6.    2.14563104    0.00000000   -1.65647062   12.00000000
C      6.   -2.14563104   -0.00000000   -1.65647062   12.00000000
C      6.    0.00000000    0.00000000   -0.06736260   12.00000000
C      6.   -0.00000000   -0.00000000    2.75695396   12.00000000
H      1.    2.53720115    0.00000000   -5.95135381    1.00782504
H      1.   -2.53720115   -0.00000000   -5.95135381    1.00782504
H      1.    4.09852982    0.00000000   -1.04133635    1.00782504
H      1.   -4.09852982   -0.00000000   -1.04133635    1.00782504
H      1.    1.75756975   -0.00000000    3.80378726    1.00782504
H      1.   -1.75756975    0.00000000    3.80378726    1.00782504
```

Directories on CCR:

	SA2-CASSCF(6,6)/6-31G
S_0 opt	/user/ub2037/fulvene/S0-CAS
S_1 opt	/user/ub2037/fulvene/S1-CAS

MXS	/user/ub2037/fulvene/MXS-CAS/mxs_opt
	MRCI
S_0 opt	/user/ub2037/fulvene/S0-CI
S_1 opt	/user/ub2037/fulvene/S1-CI