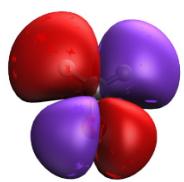
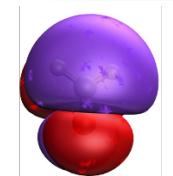
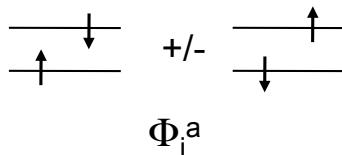
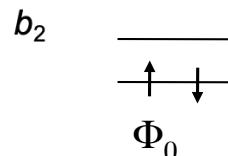


TDDFT calculations of formaldehyde (CH_2O)



TDDFT/CIS ansatz: $\Psi_{\text{ex}} = \sum_{ia} C_i^a \Phi_i^a$



b_1 Reference:
Kohn-Sham or
Hartree-Fock

Excited states

Symmetry of the state: Irrep(Φ_0)xIrrep(i)xIrrep(a)

Multiplicity of the state: $\langle S^2 \rangle$ value

Character of the state: orbitals i,a for the leading amplitude C_i^a

TDDFT method:

Available in RPA and TDA implementations; analytic gradients and frequencies are available.

Strengths: Inexpensive and often accurate.

Weaknesses: Cannot describe doubly-excited states (but SF variant can);

Problems with Rydberg/charge-transfer states (but LRC functionals help).

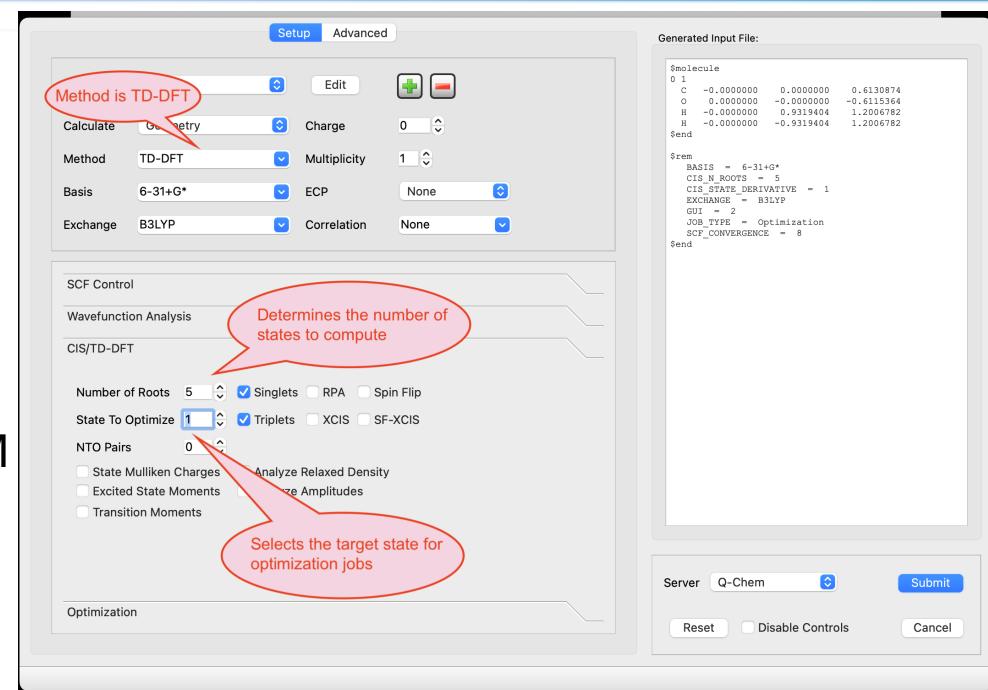
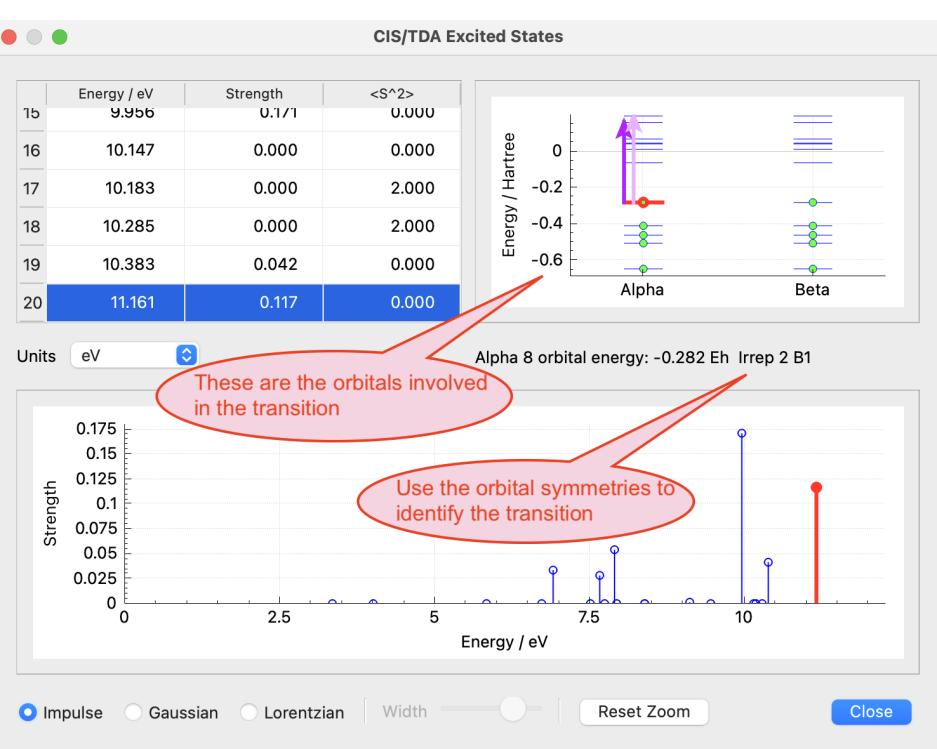
TDDFT calculation of formaldehyde (CH_2O)

Part 1: Excited states of CH_2O

- Import geometry
- Select TD-TDFT
- Specify Functional and basis (wB97-X/6-31+G*)
- Request 4 singlets and 4 triplets
- Analyze excited states and their properties

Part 2: Transient absorption

- Compute 5 lowest triplet states
- Compute absorption spectrum ($\text{T}_0 \rightarrow \text{T}_x$) (STS_MOM = TRUE)
- Compute excited state dipoles (CIS_MOM=TRUE)

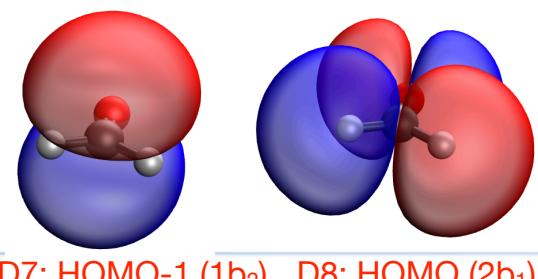


Part 3: Optimize geometry of pi-pi* triplet state

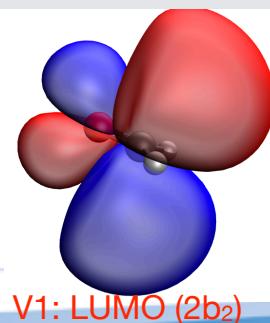
- Compute 5 lowest triplet states
- Use JOBTYPY = OPT to optimize geometry
- CIS_STATE_DERIV=2 to tell which state to optimize)
- Compute adiabatic excitation energy (as difference of S_0 and T_2 total energies at two geometries)
- Compare vertical and adiabatic energies

TD-DFT calculation of formaldehyde: Part I

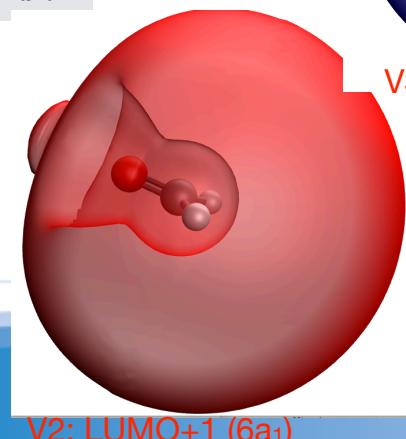
State	E_{ex} (eV)/f _l	Mult	Transition	Character
1	3.46/0.0	triplet	D8->V1	3A_2 ; n-pi*
2	4.07/0.0	singlet	D8->V1	1A_2 ; n-pi*
3	6.03/0.0	triplet	D7->V1	3A_1 ; pi-pi*
4	6.60/0.0	triplet	D8->V2	3B_1 ; n-pi*
5	7.69/0.02	singlet	D8->V2	1B_1 ; n-Ry(s)
6	8.18/0.0	triplet	D8->V3	3B_1 ; n-Ry(p)
7	8.37/0.06	singlet	D8->V3	1B_1 ; n-Ry(p)
8	8.72/0.07	singlet	D8->V4	1A_1 ; n-Ry(p)



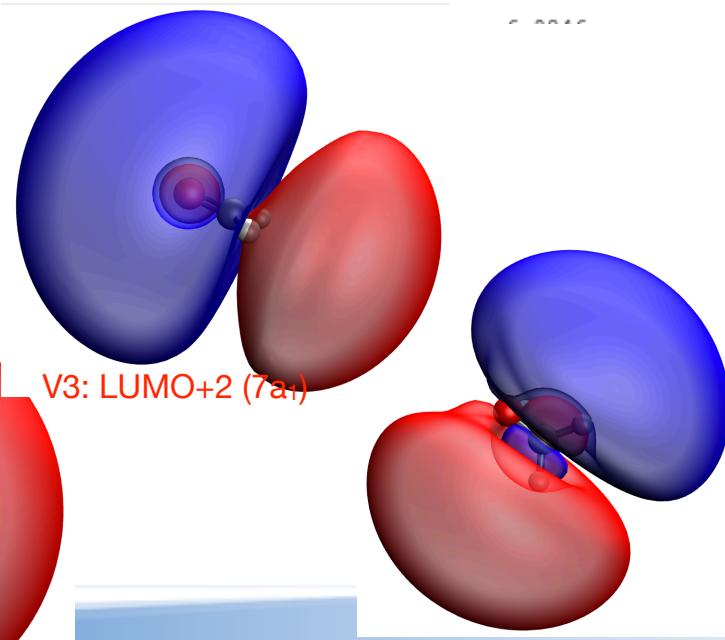
D7: HOMO-1 (1b₂) D8: HOMO (2b₁)



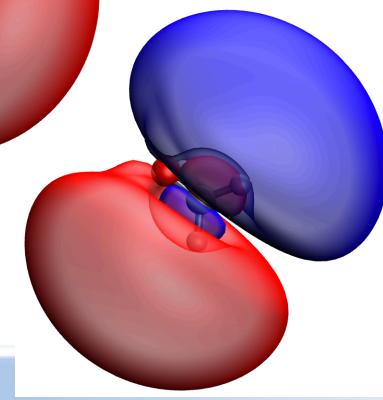
V1: LUMO (2b₂)



V2: LUMO+1 (6a₁)



V3: LUMO+2 (7a₁)



V3: LUMO+2 (3b₁)

To plot orbitals, go to 'Surfaces/Canonical orbitals'

TDDFT/TDA Excitation Energies

Excited state 1: excitation energy (eV) = 3.4593
Total energy for state 1: -114.34467311 au

Multiplicity: Triplet

Trans. Mom.: 0.0000 X 0.0000 Y 0.0000 Z

Strength : 0.0000000000

D(8) --> V(1) amplitude = 0.9647

D(8) --> V(5) amplitude = 0.2427

D: doubly occupied
V: virtual

Excited state 2: excitation energy (eV) = 4.0749
Total energy for state 2: -114.32204800 au

Multiplicity: Singlet

Trans. Mom.: -0.0000 X 0.0000 Y -0.0000 Z

Strength : 0.0000000000

D(8) --> V(1) amplitude = 0.9695

D(8) --> V(5) amplitude = 0.2322

.....

TD-DFT calculation of formaldehyde: Part II

State	E _{ex} , eV	mu, Debye	E(T _x)-E(T ₀), eV	mu _{tr} (T _x -T ₀) , au	fl (T _x -T ₀)
T0	3.46	0.627	0.0		
T1	6.03	0.512	2.57	0.0	0.0
T3	7.60	1.01	4.41	0.534	0.029
T4	8.18	1.32	4.72	0.02	4E-07
T5	8.56	1.31	5.10	0.0	0.0

Ground-state dipole moment: 2.60 Debye

Transition Moments Between Triplet Excited States					
States	X	Y	Z	Strength(a.u.)	
1 2	-0.000000	-0.000000	0.000000	1.593215E-30	
1 3	-0.000000	-0.534483	0.000000	0.02895503	
1 4	-0.000000	-0.001825	0.000000	3.850118E-07	
1 5	0.000000	0.000000	-0.000000	3.233414E-27	
2 3	0.026927	0.000000	-0.000000	2.792231E-05	
2 4	-0.032326	0.000000	0.000000	5.155578E-05	
2 5	0.000000	0.000000	-0.029186	5.293046E-05	
3 4	0.000000	-0.000000	2.237534	0.07146575	
3 5	2.901295	0.000000	0.000000	0.1988884	
4 5	-0.211786	-0.000000	-0.000000	0.0004195352	

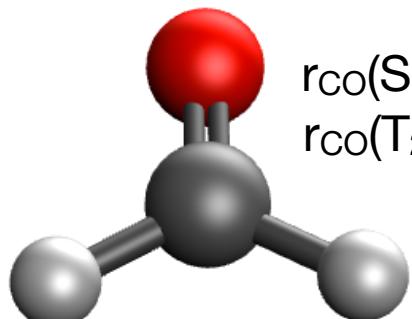
TDA Excited-State Multipoles, State 1					
Charge (ESU x 10^10)					
0.0000					
Dipole Moment (Debye)					
X 0.0000	Y	0.0000	Z	0.6721	
Tot 0.6721					
Quadrupole Moments (Debye-Ang)					
XX -10.1077	XY	-0.0000	YY	-14.2217	
XZ 0.0000	YZ	0.0000	ZZ	-11.8560	
Octopole Moments (Debye-Ang^2)					
XXX 0.0000	XXY	0.0000	YYY	0.0000	
YYY 0.0000	XXZ	0.8971	XYZ	-0.0000	
YYZ -2.4056	XZZ	0.0000	YZZ	0.0000	
ZZZ -1.0310					
Hexadecapole Moments (Debye-Ang^3)					
XXXX -16.1334	XXXY	-0.0000	XXYY	-6.2505	
YYYY -0.0000	YYYY	-18.7325	XXXZ	0.0000	
XXYZ 0.0000	XYYZ	0.0000	YYYZ	0.0000	
XXZZ -8.4097	XYZZ	-0.0000	YYZZ	-12.4081	
XZZZ 0.0000	YZZZ	0.0000	ZZZZ	-46.0558	

TD-DFT calculation of formaldehyde: Part III

E_{gs}	$E(T_2)$ -vert	$E_{ex}(T_2) - \text{vert (eV)}$	$E(T_2)$ -relaxed	$E_{ex}(T_2)$ -ad (eV)
-114.471800	-114.250401	6.02	-114.309328	4.42

-114.471800 -114.250401 6.02 -114.309328 4.42

Total energies are taken from the output at the initial geometry and at the end of optimization (relaxed geometry)



$r_{\text{CO}}(S_0) = 1.203 \text{ \AA}$
 $r_{\text{CO}}(T_2) = 1.444 \text{ \AA}$