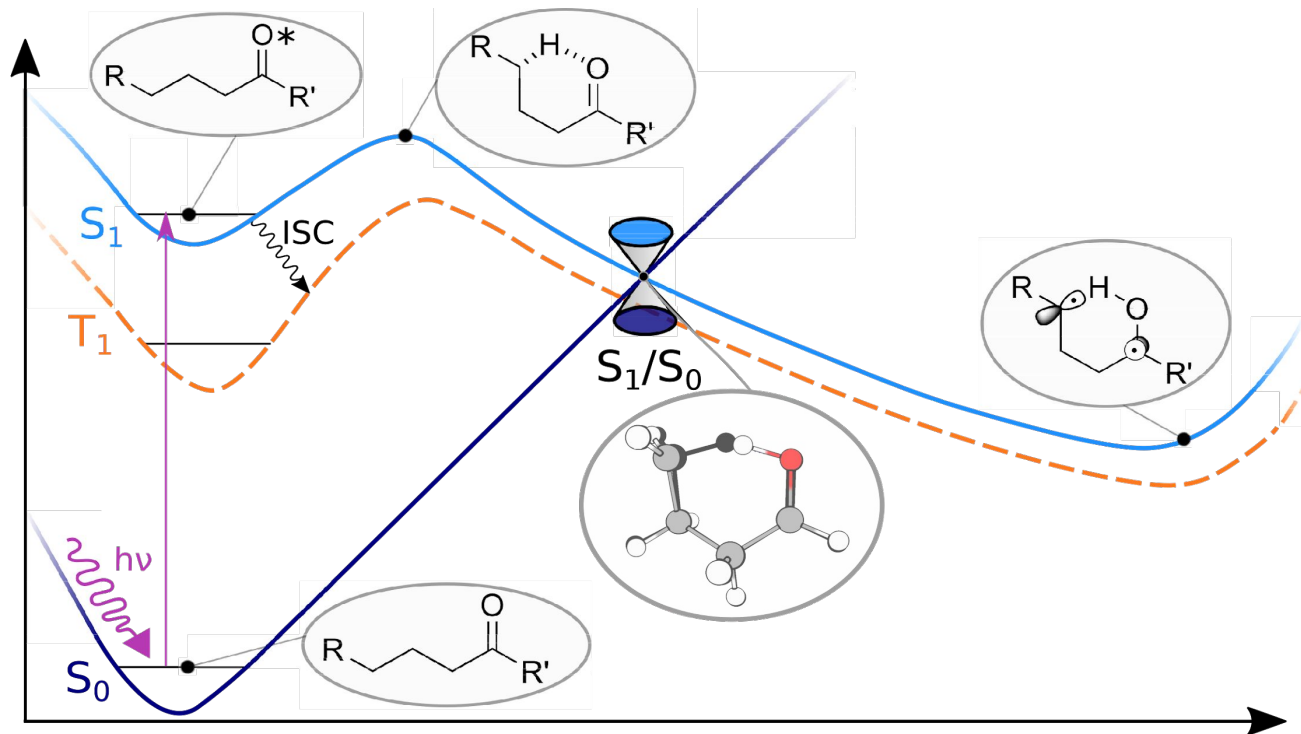# CASPT2 calculations and BAGEL

Keiran Rowell -
Group Meeting Update - 13 Oct 2020

Motivation: Norrish Type II (NTII), dominant in larger carbonyls
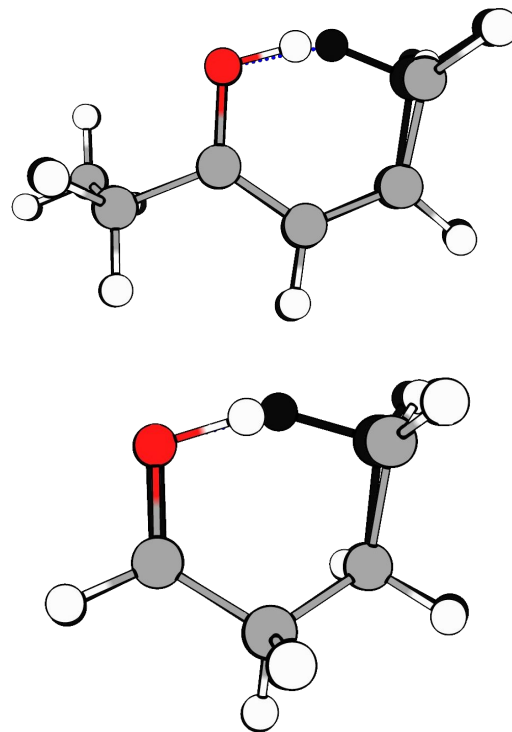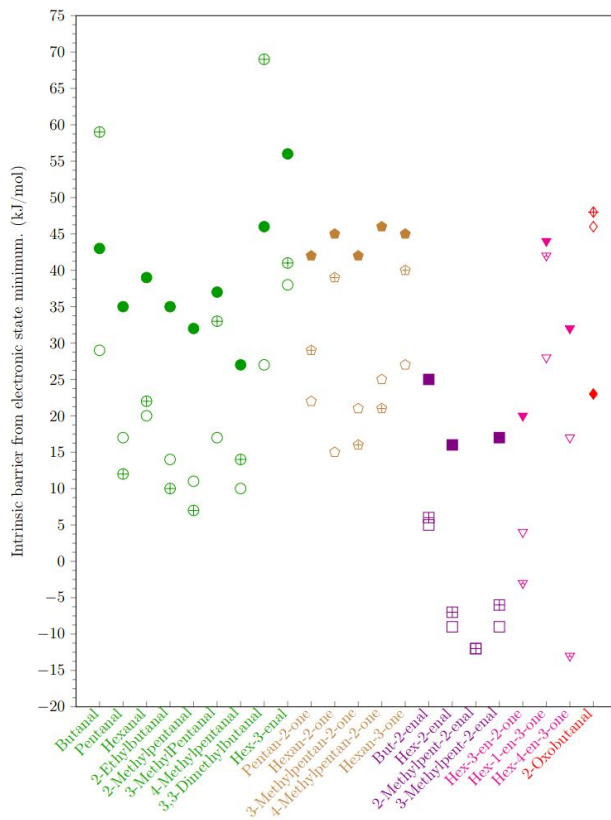
Motivation: CC/DFT excitation energies unsatisfying

Predicting Carbonyl Excitation Energies Efficiently Using EOM-CC Trends

Keiran N. Rowell,[†] Scott H. Kable,[†] and Meredith J. T. Jordan[*,‡]

Motivation: TD-DFT S_1 NTII TSs unreliable

Single point energy:	S_1 NTII intrinsic barrier					ΔE_{ZPVE}
	CAM-B3LYP	M06-2X[a]	B2GP-PLYP	EOM-CCSD	Literature	CAM-B3LYP
Aldehydes:						
Butanal	10	57	29	59	34[b], 13[c], 15[d]	-6
Pentanal	2	62	17	12	16[b], 6[c]	-6
Hexanal	5	17	20	22		-5
2-Ethylbutanal	-2	9	14	10		-7
2-Methylpentanal	-2	7	11	7		-7
3-Methylpentanal	4	16	17	22		-6
4-Methylpentanal	-2	9	10	14		-4
3,3-Dimethylbutanal	12	70	26	69		-7
Hex-3-enal	21	27	38	41		-10
Ketones:						
Pentan-2-one	8	20	28	29	23[b], 14[c]	-9
Hexan-2-one	2	36	15	39	16[b]	-8
3-Methylpentan-2-one	7	17	21	16		-9
4-Methylpentan-2-one	10	11	25	21		-8
Hexan-3-one	11	22	26	40		-9
Enals:						
But-2-enal	-9	4	5	6	-8[c]	-6
Hex-2-enal	-19	-5	-9	-7		-4
2-Methylpent-2-enal	-18	-8	-12	-12		-4
3-Methylpent-2-enal	-16	-2	-9	-6		-4
Enones:						
Hex-3-en-2-one	-6	-3	4	-3		-6
Hex-1-en-3-one	15	14	28	42		-9
Hex-4-en-3-one	2	-13	17	-13		-8
Dicarbonyls:						
2-Oxobutanal	21	30	46	48		-7

[a] GD3 dispersion parameters used since GD3BJ dispersion parameters are not available for M06-2X functional in Gaussian 16.
[b] TD-M06-2X/6-31++G(3df,2p)//TD-M06-2X/6-31++G(d,p) from Shaw.[26]
[c] XMCQDPT2/6-31+G(d)//SA-CASSCF/6-31+G(d) from Kletskii et al.[48]
[d] CIS(D)/cc-pVTZ from Tadić et al.[5]

Motivation: Submerged S_1 NTII barriers in enals?

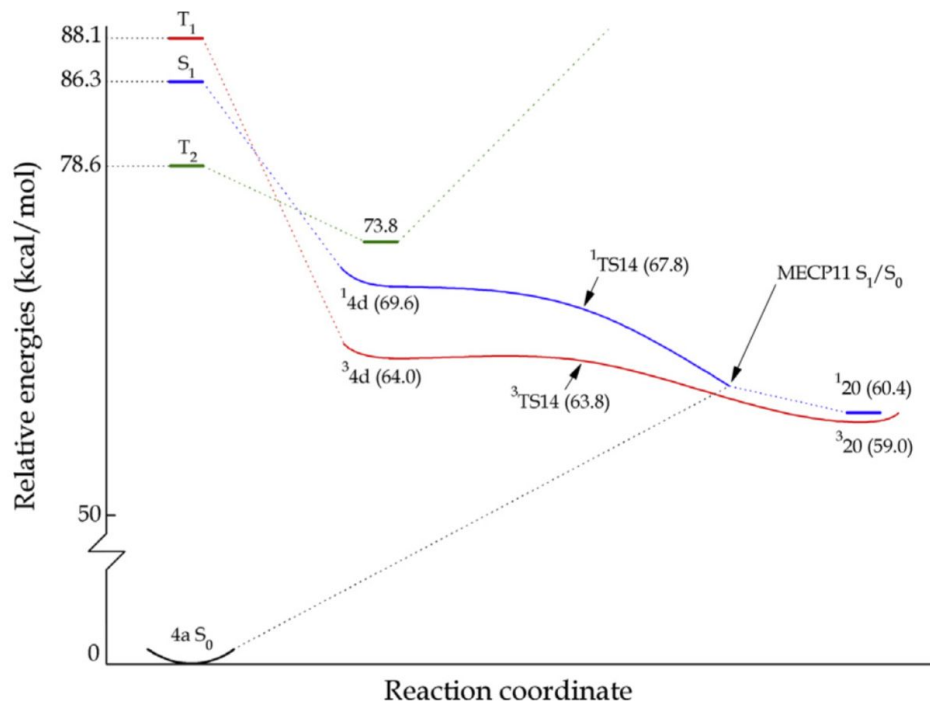| Single point energy:	S_1 NTII intrinsic barrier					ΔE_{ZPVE}
	CAM-B3LYP	M06-2X[a]	B2GP-PLYP	EOM-CCSD	*Literature*	CAM-B3LYP
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Ketones:						
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Hexan-3-one	11	22	26	40		-9
Enals:						
But-2-enal	-9	4	5	6	-8[c]	-6
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2-Methylpent-2-enal	-18	-8	-12	-12		-4
3-Methylpent-2-enal	-16	-2	-9	-6		-4
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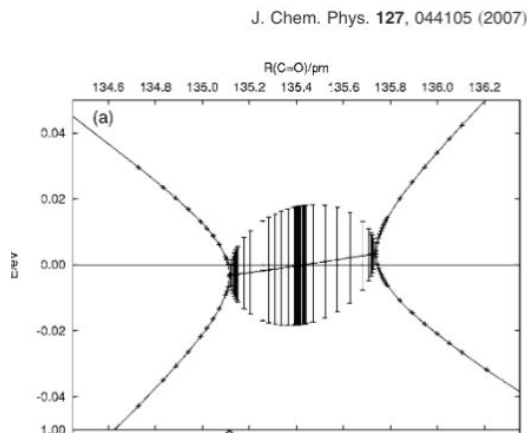[c] XMCQDPT2/6-31+G(d)//SA-CASSCF/6-31+G(d) from Kletskii *et al.*[48]
[d] CIS(D)/cc-pVTZ from Tadić *et al.*[5]

Fig. 15. MEPs of NRII in buten-2-al 4. XMCQDPT2 calculations.

Motivation: **Conical intersections need CAS**

Single-reference methods:
EOM-CC (*left*)
TD-DFT (*right*)

Do not show correct features!

J. Chem. Phys. **127**, 044105 (2007)

Conical intersections and double excitations in time-dependent density functional theory 1049
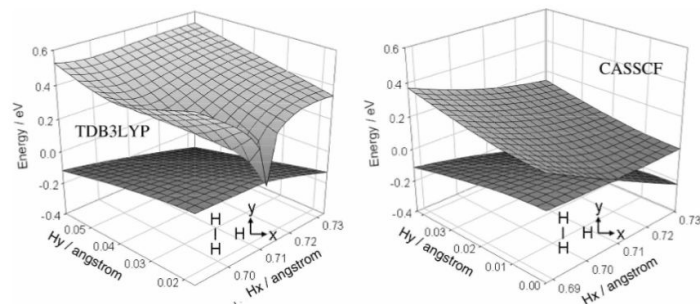
Figure 10. Comparison of PESs of $H_2 + H$ surrounding a conical intersection at CAS(3/3)/6-31G and TD-B3LYP/6-31G levels of theory. The molecule lies in the x–y plane, with the origin at the centre of the H_2 bond (distance fixed to 0.818 Å) and the y axis parallel to the H_2 bond. The position of the third hydrogen atom is varied along the x and y axes. In both cases, two directions split the degeneracy between the surfaces. This is in contrast to the comparison of figures 7–9, and arises because the ground and first excited state in TDDFT can both be represented by the wavefunction ansatz used to generate the density. However, the form of the excited state PES in TDDFT still exhibits unphysical rapid variation near the intersection as seen in figure 9.
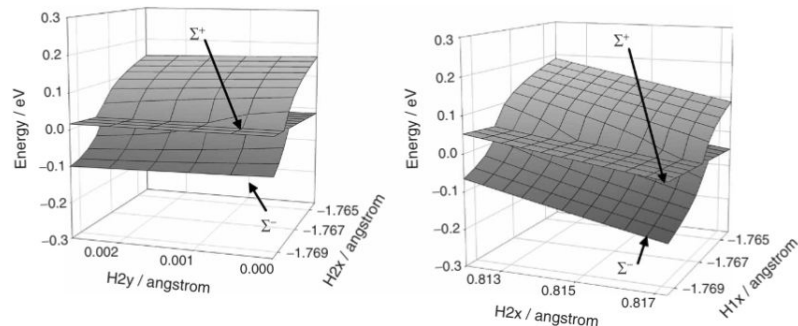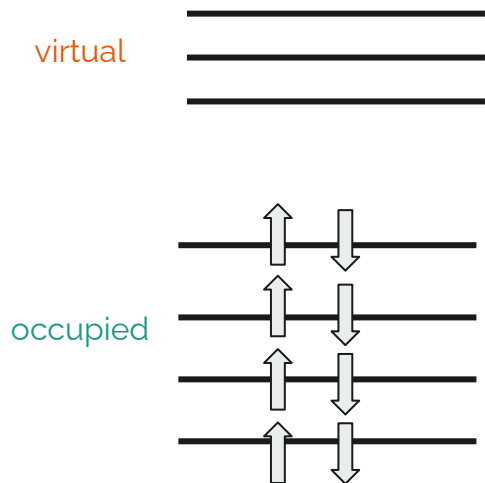
Figure 9. As in figure 7, but using TD-B3LYP/6-31G. As in CIS, only one branching direction is observed instead of the two which should be present. Furthermore, note the change in scale of the energy axis compared to figures 7 and 8.

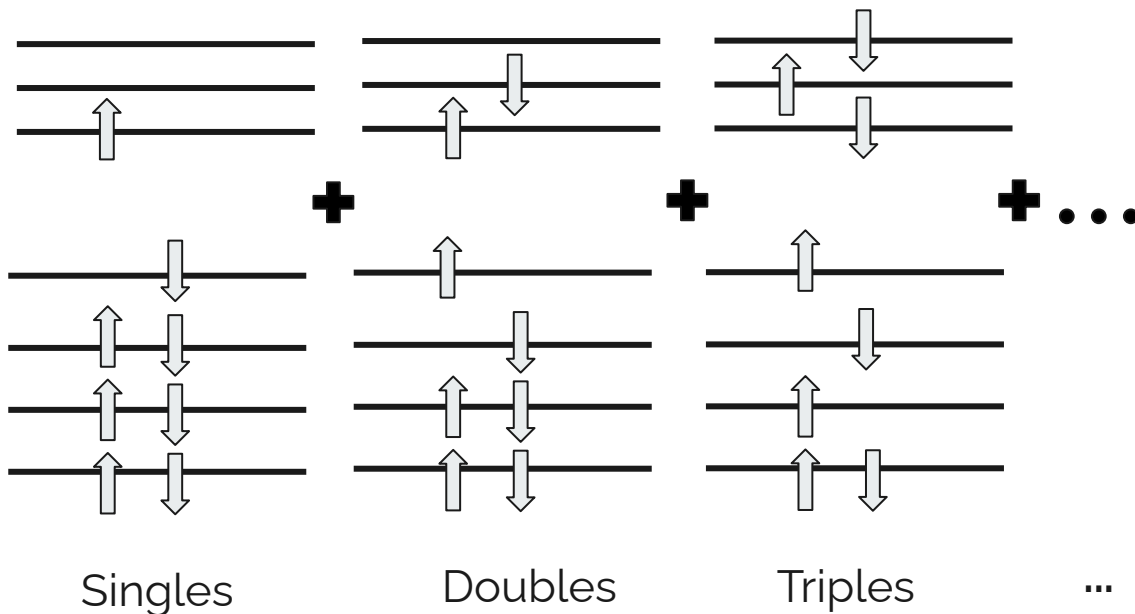# CAS: The complete active space method

Hartree-Fock (**HF**):
Iterative solution of <u>an</u> electronic configuration (Slater determinant)
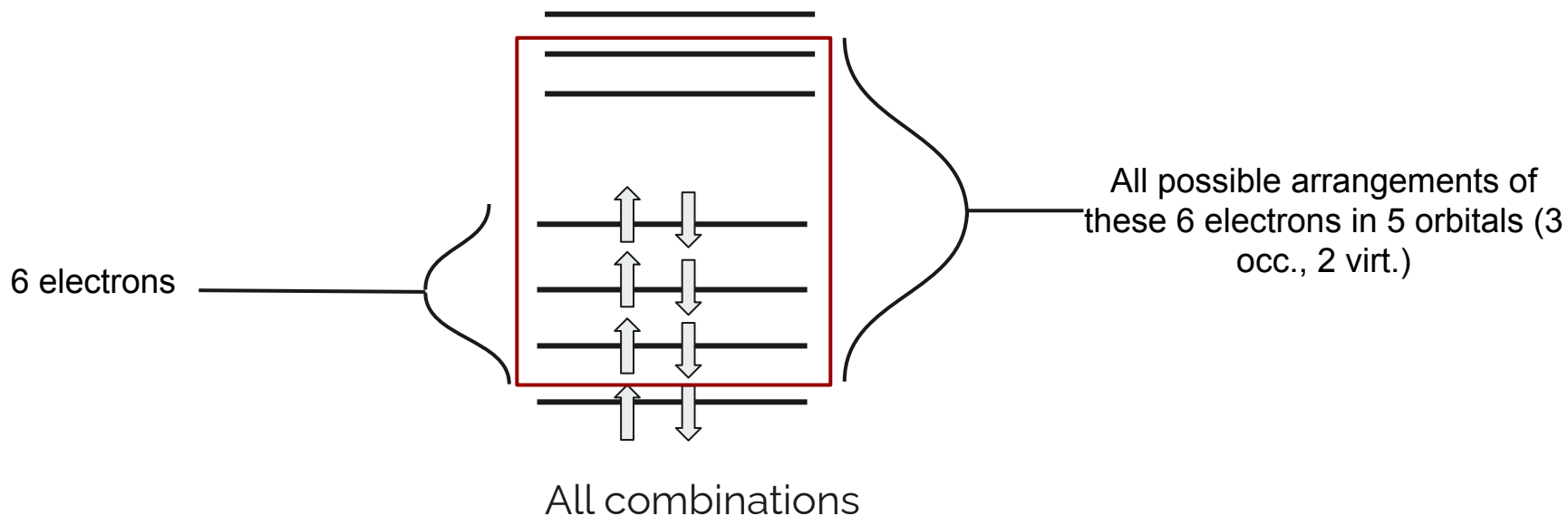
Configuration Interaction (**CI**):
Include other possible Slater determinants.

virtual

occupied

"Zeroth"

Singles   Doubles   Triples   ...

CAS: Full CI in a human-selected active space

Complete Active Space, *n* electrons in *m* orbitals **CAS(*ne,mo*)**:

E.g. CAS(6e,5o)

6 electrons

All combinations

All possible arrangements of these 6 electrons in 5 orbitals (3 occ., 2 virt.)

(MC)SCF: Optimising orbitals (and Slater determinants)

Hartree-Fock (HF):

Slater determinant of one-electron atomic orbitals (χ)

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \chi_3(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \chi_3(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \chi_3(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Optimise molecular orbitals (Φ)

$$\phi_i = \sum_n C_{ni} \chi_n$$

Optimise coeffs of atomic orbital contribution

MCSCF:

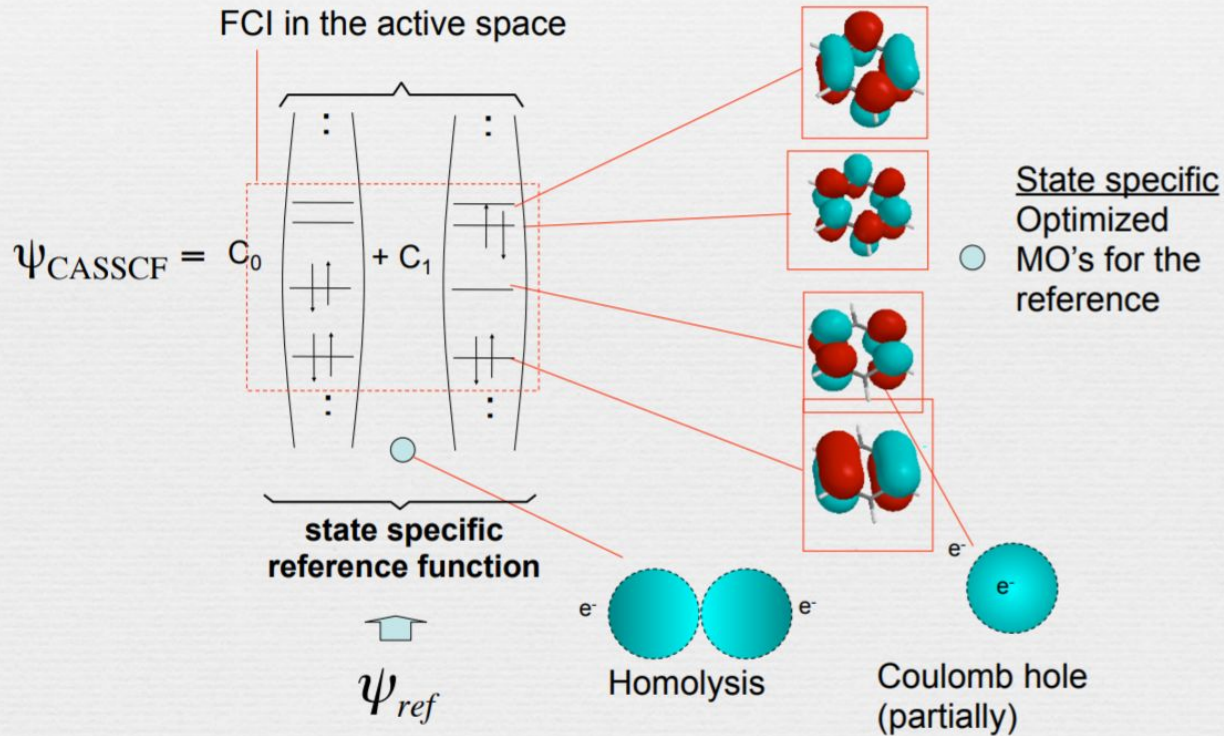Linear combination of multiple Slater determinants

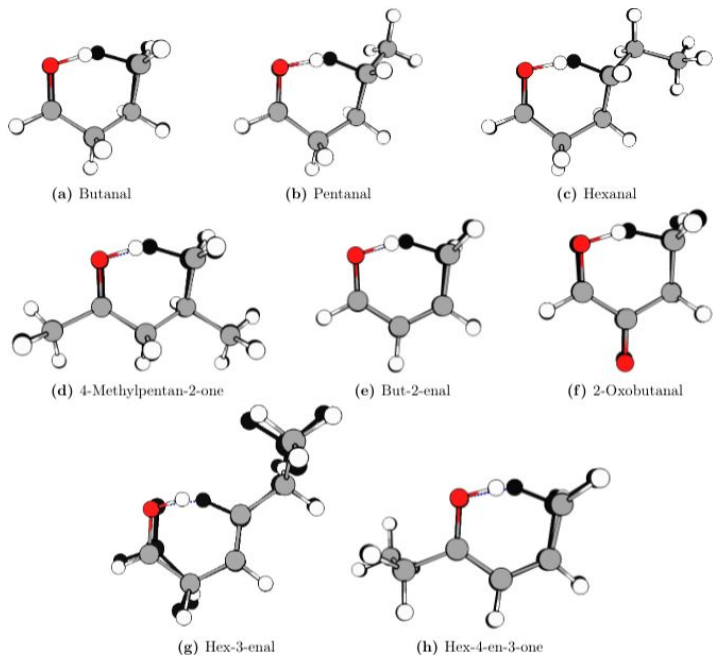$$\psi_{MCSCF} = C_1 \Psi_1 + C_2 \Psi_2 + C_3 \Psi_3 + \ldots$$

CASSCF wavefunctions

$$\psi_{ref} = \psi_{CASSCF} = \sum_i \psi_{ref(i,FCI)}(optMO)$$

FCI in the active space

$$\psi_{CASSCF} = C_0 \begin{vmatrix} \vdots \\ \\ \\ \vdots \end{vmatrix} + C_1 \begin{vmatrix} \vdots \\ \\ \\ \vdots \end{vmatrix}$$

state specific reference function

$$\psi_{ref}$$

State specific
Optimized
MO's for the
reference

Homolysis

Coulomb hole
(partially)

Aims: **Revisit CIs, better NTII energies, branching planes**

S5. S_1/S_0 MECIs overlaid with S_1 NTII transition states

(a) Butanal (b) Pentanal (c) Hexanal

(d) 4-Methylpentan-2-one (e) But-2-enal (f) 2-Oxobutanal

(g) Hex-3-enal (h) Hex-4-en-3-one

Figure S3: Structures of the S_1/S_0 MECIs (*coloured*) overlaid on the NTII S_1 TS structures (*black silhouette*) for several carbonyl species. MECIs are calculated at the CAS(10,8)/6-31G(d) level of theory, while S_1 NTII TS structures are from CAM-B3LYP/def2-TZVP calculations.

My previous work (8 carbonyls):
SA2-CASSCF(10e,8o)/6-31G(d)

Kletskii *et al.* (**2014**) (8 carbonyls):
SA5-XMCQPT2//CASSCF(8e,7o)/6-31G(d)

Marchetti *et al.* (**2018**) (1 carbonyl):
SA7-CASPT2//CASSCF(8e,7o)/6-31G(d)

Small basis sets → poor energies

Aims: triple-zeta basis sets, many stationary points

BAGEL

Brilliantly Advanced General Electronic-structure Library

BAGEL is a parallel electronic-structure program licensed under the GNU General Public License.

The source code can be found at https://github.com/nubakery/bagel. The SMITH3 program that has generated some of the code in BAGEL is hosted at https://github.com/nubakery/smith3.

Pros:
- **Designed for CAS/MRCI**
- **C++/parallel** (some issues)
- **Density fitting**
- **Multistate calculations**
- ***Analytical Nuclear Gradients!***

Cons:
- **In development**
- **Difficult to compile**
- **Little-to-No DFT**

SMITH3: Analytical CASPT2 Nuclear Gradient

Analytical gradients ⟶ Efficient Geom. Opt.

Multireference Electron Correlation Methods: Journeys along Potential Energy Surfaces

Jae Woo Park,* Rachael Al-Saadon, Matthew K. MacLeod, Toru Shiozaki, and Bess Vlaisavljevich*
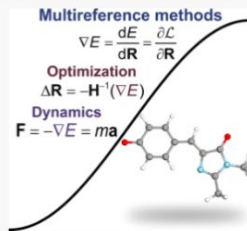
Cite This: *Chem. Rev.* 2020, 120, 5878−5909   Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Multireference electron correlation methods describe static and dynamical electron correlation in a balanced way and, therefore, can yield accurate and predictive results even when single-reference methods or multiconfigurational self-consistent field theory fails. One of their most prominent applications in quantum chemistry is the exploration of potential energy surfaces. This includes the optimization of molecular geometries, such as equilibrium geometries and conical intersections and on-the-fly photodynamics simulations, both of which depend heavily on the ability of the method to properly explore the potential energy surface. Because such applications require nuclear gradients and derivative couplings, the availability of analytical nuclear gradients greatly enhances the scope of quantum chemical methods. This review focuses on the developments and advances made in the past two decades. A detailed account of the analytical nuclear gradient and derivative coupling theories is presented. Emphasis is given to the software infrastructure that allows one to make use of these methods. Notable applications of multireference electron correlation methods to chemistry, including geometry optimizations and on-the-fly dynamics, are summarized at the end followed by a discussion of future prospects.

Multireference methods
$$\nabla E = \frac{dE}{dR} = \frac{\partial \mathcal{L}}{\partial R}$$
Optimization
$$\Delta R = -H^{-1}(\nabla E)$$
Dynamics
$$F = -\nabla E = ma$$

SMITH3:
- Analytical gradients unable to be solved by hand for 20+ years.

- Code avoids direct evaluation of dE/dR. The CI coefficients are geom. dependent. *J. Chem. Phys.*, **2015**, *142*, 051103.

- Used for Extended Multistate (XMS). *J. Chem. Theory Comput.* **2016**, *12*, 3781–3787.

- Recently, XMCQDPT2 like Kletskii *et al.*, agrees with XMS-CASPT2: *J. Chem. Theory Comput.* **2020**, *16*, 5562–557.

Multistate: MS vs XMS-CASPT2 for Conical Intersections

**Multistate (MS):** Diagonalise Hamiltonian w/ state-mixing - energetically close states

Extended (XMS): rotates ref. CAS states, handle degeneracies - conical intersections
J. Chem. Theory Comput. **2016**, *12*, 3781–3787.

Two schemes:

Multistate-Multireference (**MS-MR**): guarantees invariance w/ rotating ref. functions

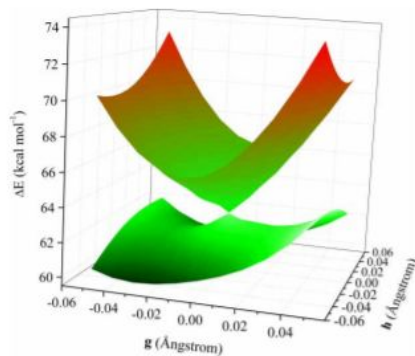Single state-Single reference (**SS-SR**): cost linear w/ number of states
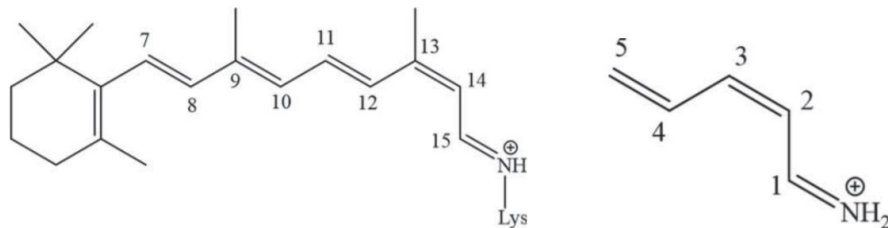
Empirical tests: retinal model, *Mol. Phys.*, **2018**, 116, 19–20, 2571–2582

(X)MS: Branching planes for retinal model
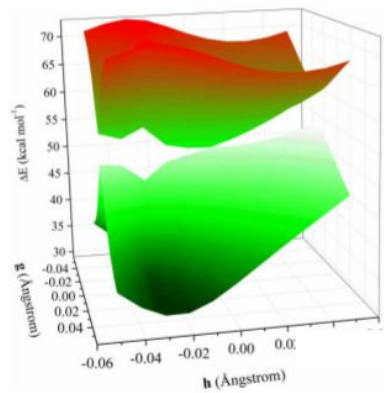
CASSCF

MS

XMS

SS-SR
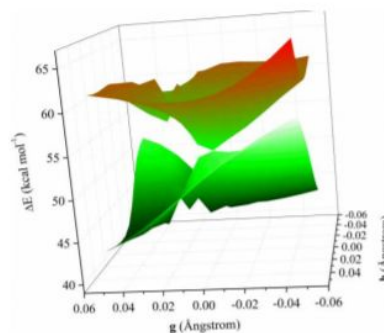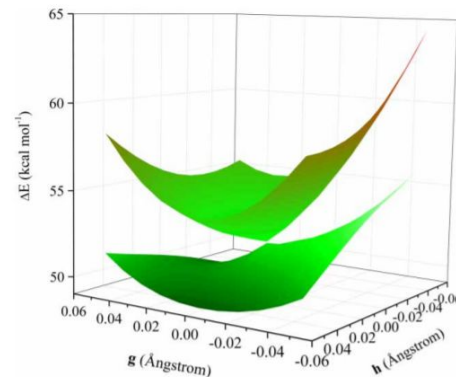
MS-MR
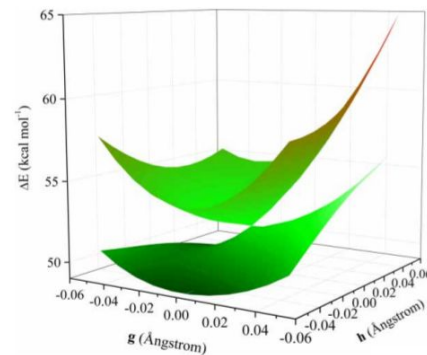
$$\mathbf{g} = \frac{\delta(E_2 - E_1)}{\delta q} \quad \mathbf{h} = \langle \psi_1 | \frac{\delta}{\delta q} | \psi_2 \rangle$$

✔️ Gradient difference (**g**) and non-adiabatic coupling vectors (**h**)
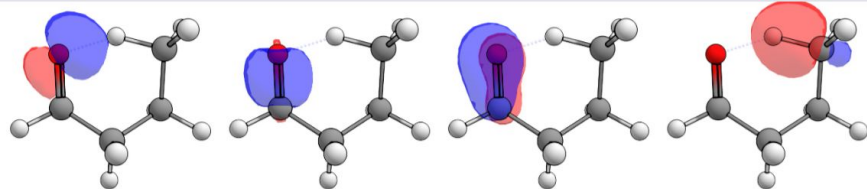
❌ Energy overestimated, topology

Practical: Defining the active space

Guidelines:
- **Guided by chemical problem**
- **Use localised, not canonical, orbitals**
- **Breaking/forming bonds**
- **CAS occupation ≠ 0 or 2**
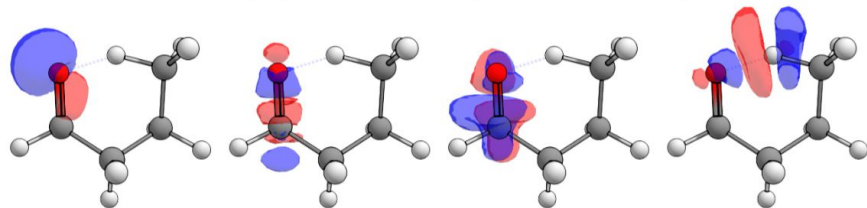- **(Anti)Bonding pairs**
- **State-averaging**

Butanal (10e,8o)

(a) O n **(b)** C—O σ **(c)** C=O π **(d)** γC—H σ

(e) Other O n **(f)** C—O σ^* **(g)** C=O π^* **(h)** γC—H σ^*
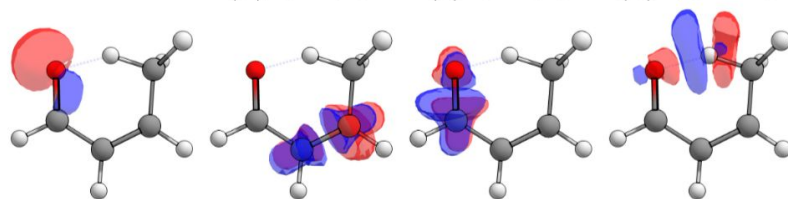
But-2-enal (10e,8o)

(a) O n **(b)** C—C π **(c)** C=O π **(d)** γC—H σ
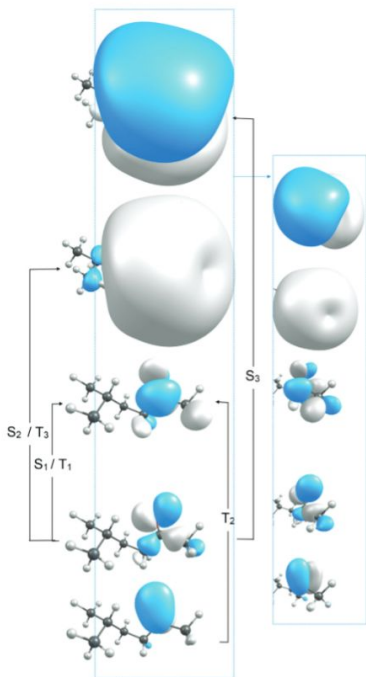
(e) Other O n **(f)** C=C π^* **(g)** C=O π^* **(h)** γC—H σ^*
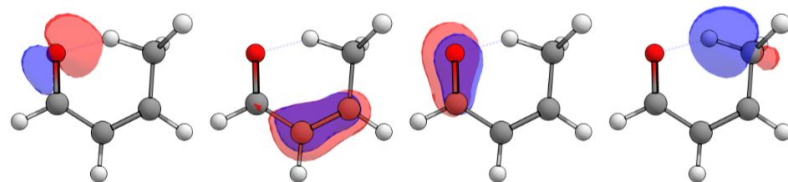
Practical: Which states to include in averaging?

Marchetti includes very high lying states (7 eV)

Kletskii includes states based upon molecule:

S_0, S_1, T_1:

-butanal, pentanal, butanone

S_0, S_1, T_1, T_2:

-but-2-enal, butanimine
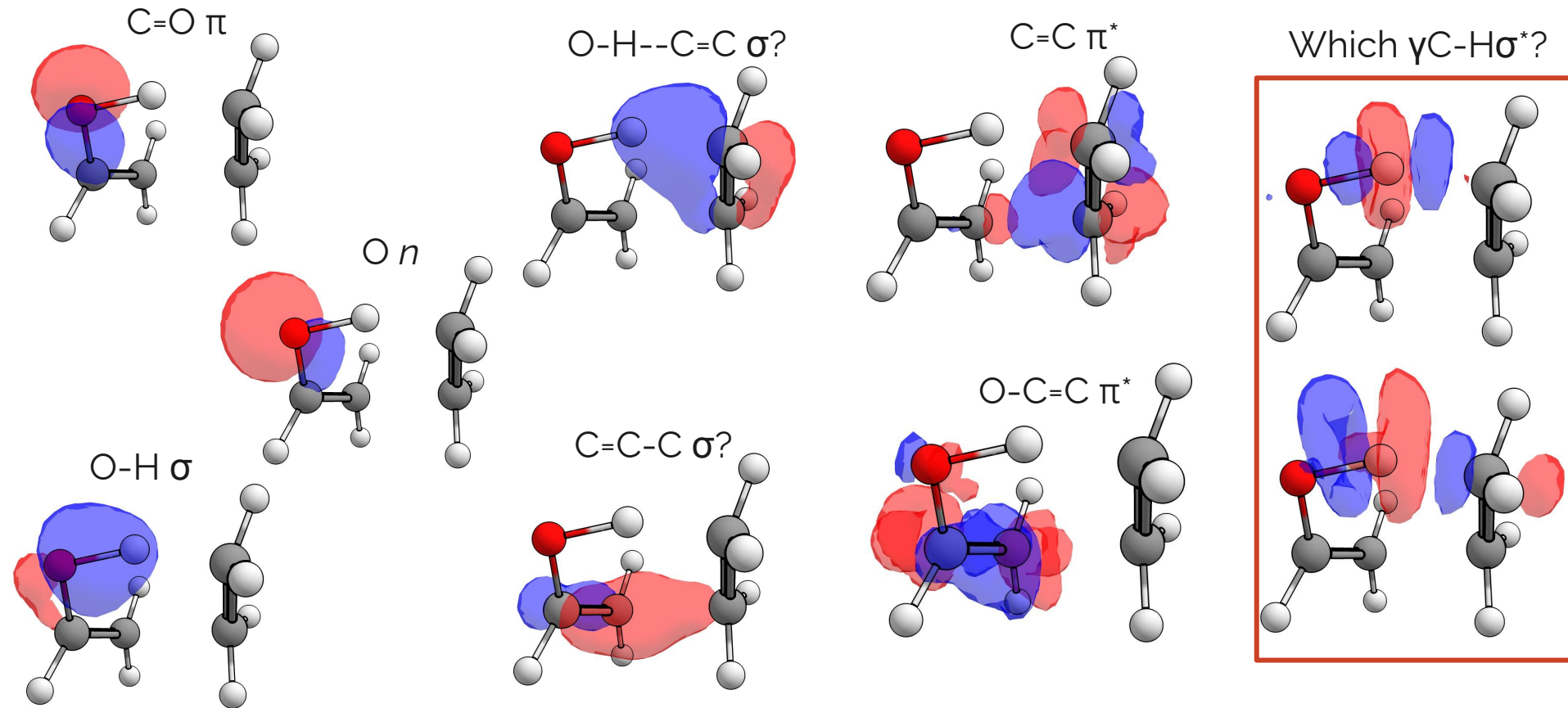
Some considerations with BAGEL

- BAGEL only has state averaging over multiple spins in the relativistic module. Need SOC.

- Carbonyl singlet and triplet structures and orbitals (e.g. S_1 and T_1) are very similar. Is including triplet necessary?

- My calcs so far just include S_0, S_1

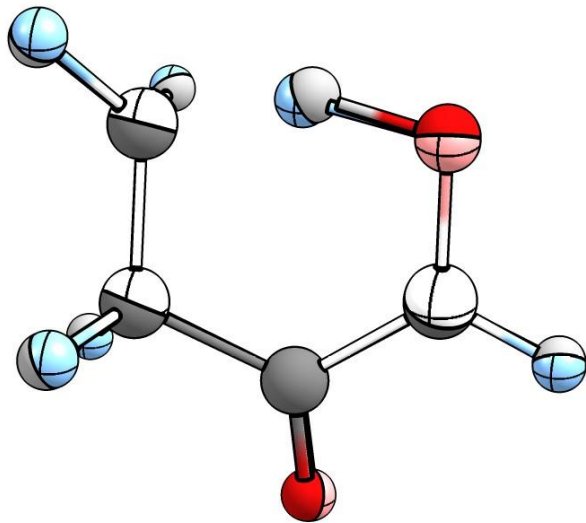# **Difficulties**: Occupied/empty orbitals in minima active space?

Butanal active space at S_1 minimum

O n

C-O σ

C=O π

γC-H σ

Other O n

C-O σ*

C=O π*

γC-H σ*
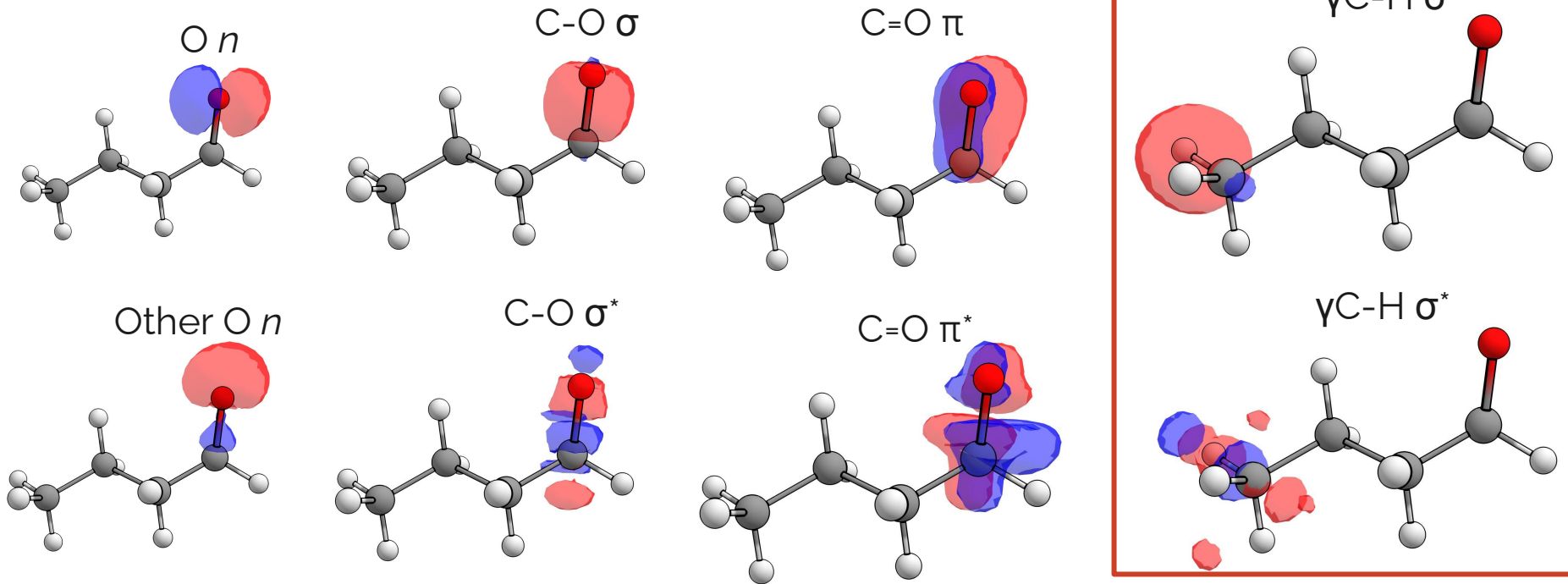
Difficulties: Concerted S_0 NTII reaction - active space

C=O π

O-H--C=C σ?

C=C π*

Which γC-Hσ*?

O n

O-H σ

C=C-C σ?

O-C=C π*

Progress: XMS-CASPT2 S_1/S_0 MECIs

2-oxobutanal CASPT2 vs CASSCF CI

To Do:

- **CASPT2 MECIs** - (8e,6o) done, need (10e,8o)

- **2D branching planes** - working on script

- **Concerted S_0 reaction** - difficulties w/ active space

- **Singlet reaction path** - Some, convergence difficulties. Need to drop γC-H σ(*) from active space?

- **State-averaging** - should I be state-averaging across singlets & triplets?

- **Diradical & dissociation** - singlet CASSCF on UHF orbitals? Localise not implemented for UHF.

Thank you!