

A Tale of True & False Positives in Search of Hund's-rule Violating Organic Molecules

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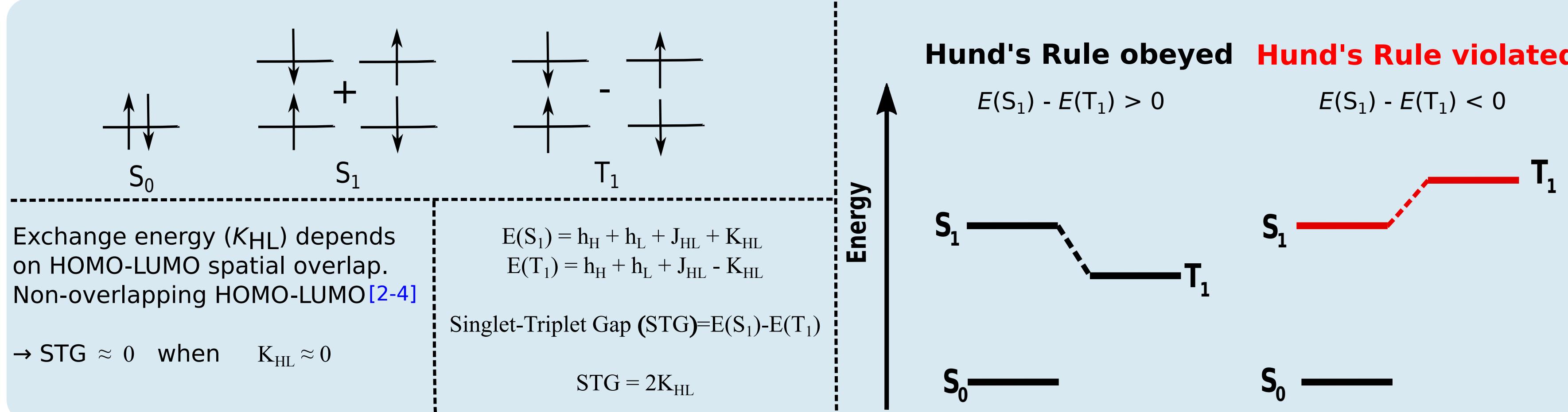
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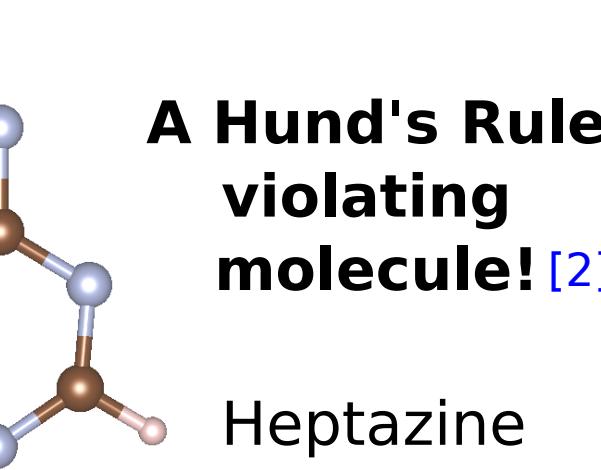
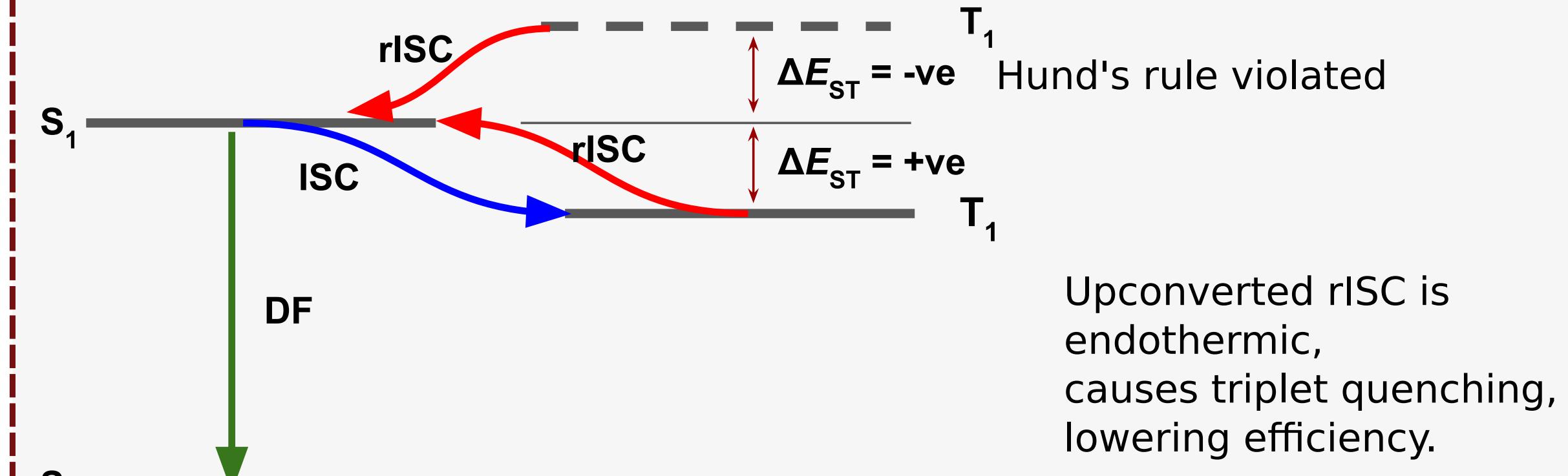
SCIENTIFIC BACKGROUND

Hund's Rule: For a given electronic configuration, the term with maximum multiplicity has the lowest energy. [1]
Energy of a triplet state (spin = 1) < Energy of a singlet state (spin = 0)

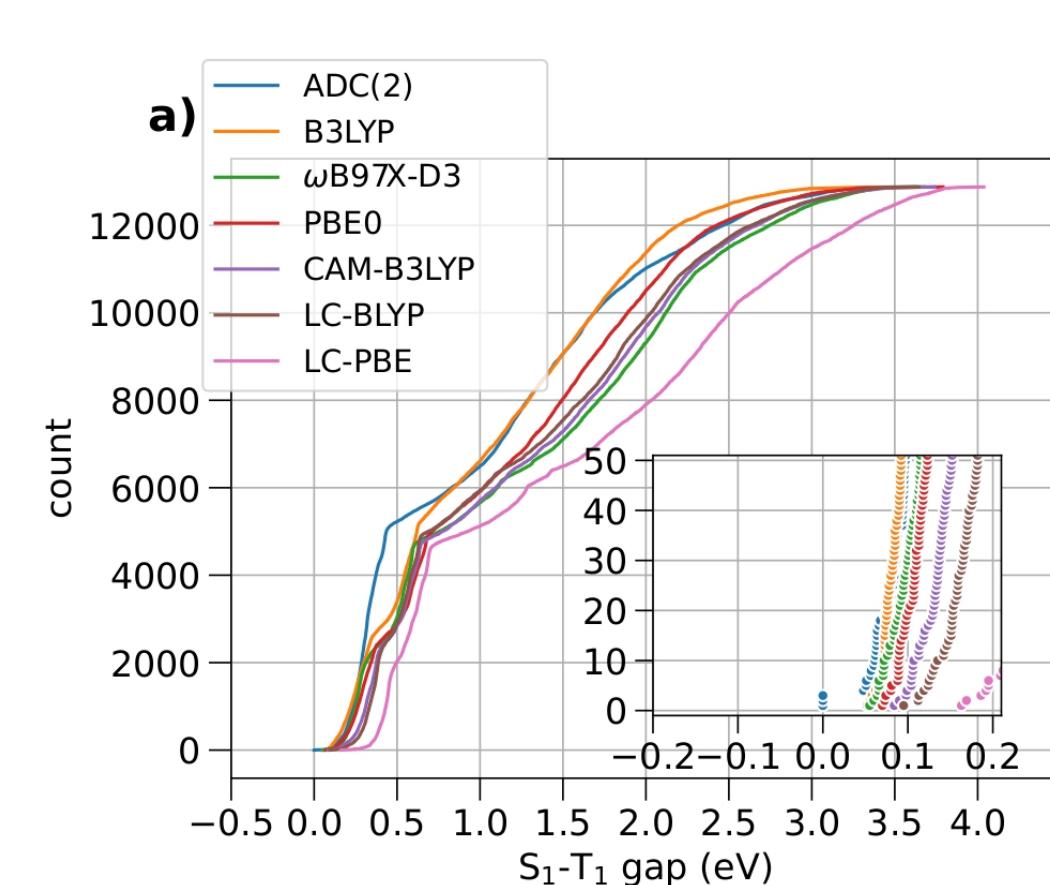


Inverted singlet-triplet (INVEST) emitters have high potential in OLEDs, organic lasers, and photocatalysis. [5,6]

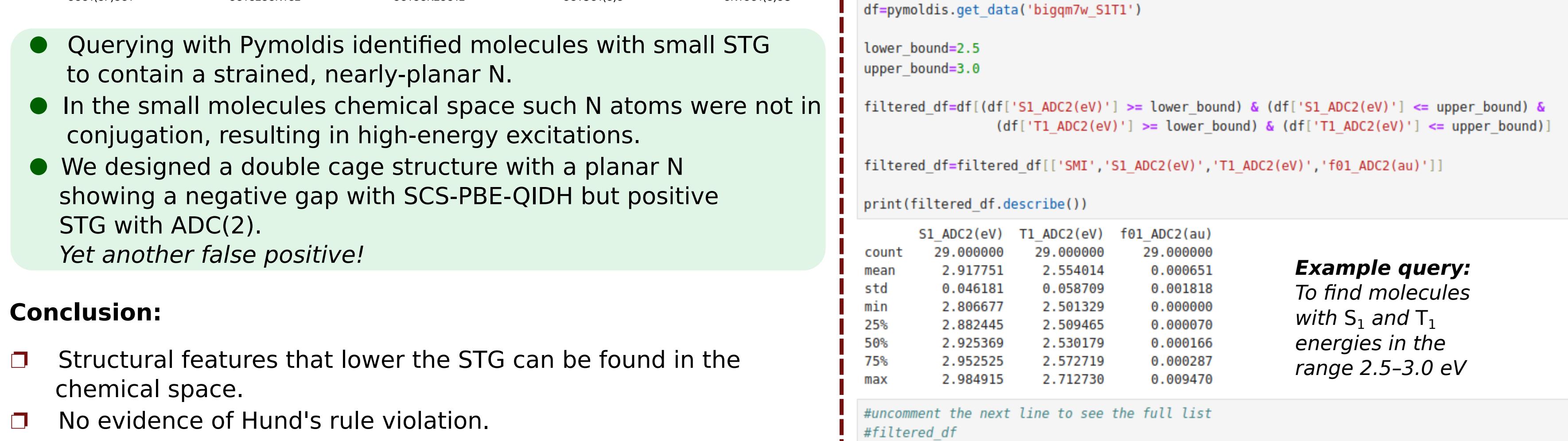
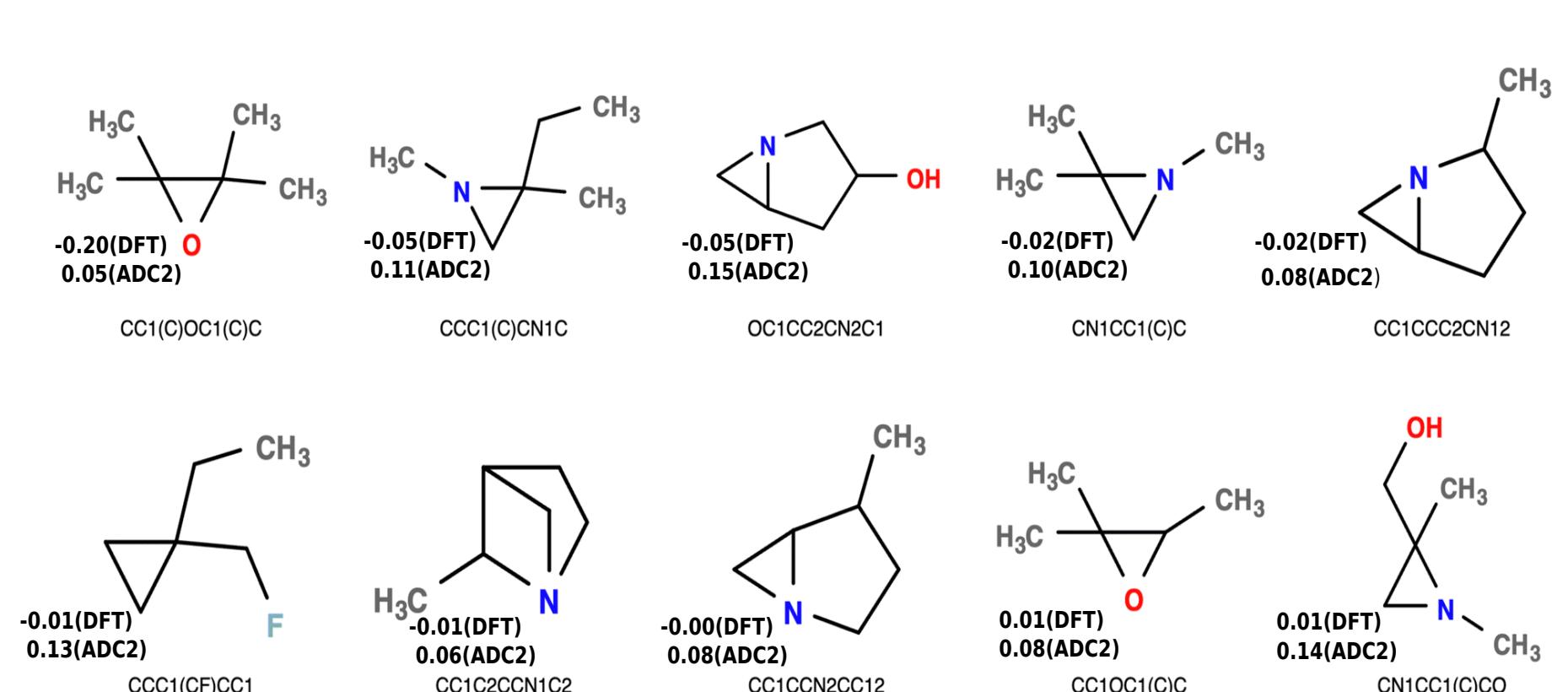
Negative ΔE_{ST} makes rISC exothermic, improving efficiency.



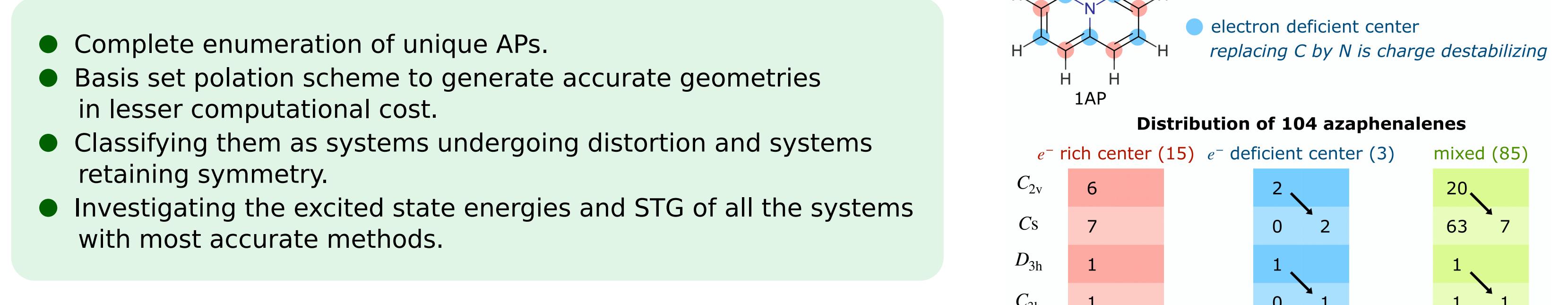
CHEMICAL SPACE ANALYSIS



b) Upon SCS/SOS corrections in DFT, preferentially lower S_1 , hence predict negative STG.



ONGOING WORK



OUTLOOK AND OPEN QUESTIONS

- Hund's rule prevails across thousands of organic molecules with systematically varying structures covering almost all prototypical small organic molecules.
- The chemical space of small molecules lacks features responsible for the negative STG as in molecules such as heptazine showing a downhill rISC mechanism.
- Symmetry lowering in 1AP is confirmed, with the true minimum (C_{3h}) showing a positive STG (~ 0.04 eV), aligning with experiments.
- APs (5AP, 7AP) with N at electron-rich sites retain symmetry and violate Hund's rule, while those with N at electron-deficient sites exhibit stronger symmetry-lowering tendencies, while adhering to Hund's rule.
- Higher-level methods are needed to validate energy differences and ensure accurate modeling.
- How critical are the oscillator strengths of Hund's rule violating molecules for designing efficient emitters?
- What are the quantum chemical reasons for post MP2 treatment of azaphenalenenes?
- What are the insilico design principles for new INVEST molecules?

WORKFLOW

Chemical Space [7,8]

bigQM7w dataset
12,880 small organic molecules

Geometries: ω B97XD/def2-TZVP & ConnGO workflow

Excited state calculations: S_1 and T_1 energies

TDA-TDDFT, def2-TZVP

LC-BLYP B3LYP CAM-B3LYP PBE-QIDH RSX-QIDH
LC-PBE PBE0 ω B97X-D3 SCS-PBE-QIDH SOS-RSX-QIDH
SOS-PBE-QIDH SOS-RSX-QIDH

Data mining
import pymoldis
Query S_1-T_1 gap across chemical space

Hund's rule violation?

Azaphenalenes [9]

Six azaphenalenenes for pseudo-Jahn-Teller analysis

- Z-matrix-based symmetry-constrained geometry optimizations
- CCSD(T)/cc-pVTZ geometry optimizations of high-symmetry structures
- Single-point energy calculations
 - CCSD(T)/cc-pVDZ ground state energy
 - ADC(2)/cc-pVDZ excited state energies (S_1 , T_1 , STG)
- Identify possible low-symmetry minima ($r_1 \neq r_2$, $E^{\text{low-sym}} < E^{\text{high-sym}}$)

Low-symmetry minima

- CCSD(T)/cc-pVTZ, Z-matrix optimizations of low-symmetry structures starting from the structures identified in the Jahn-Teller-Hund's diagnostics analysis.
- S_1 , T_1 , STG calculation with ADC(2)/aug-cc-pVTZ

Software:

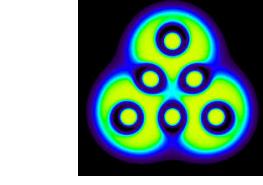
CCSD(T) optimization: Molpro

DFT/TDDFT: Orca, Gaussian



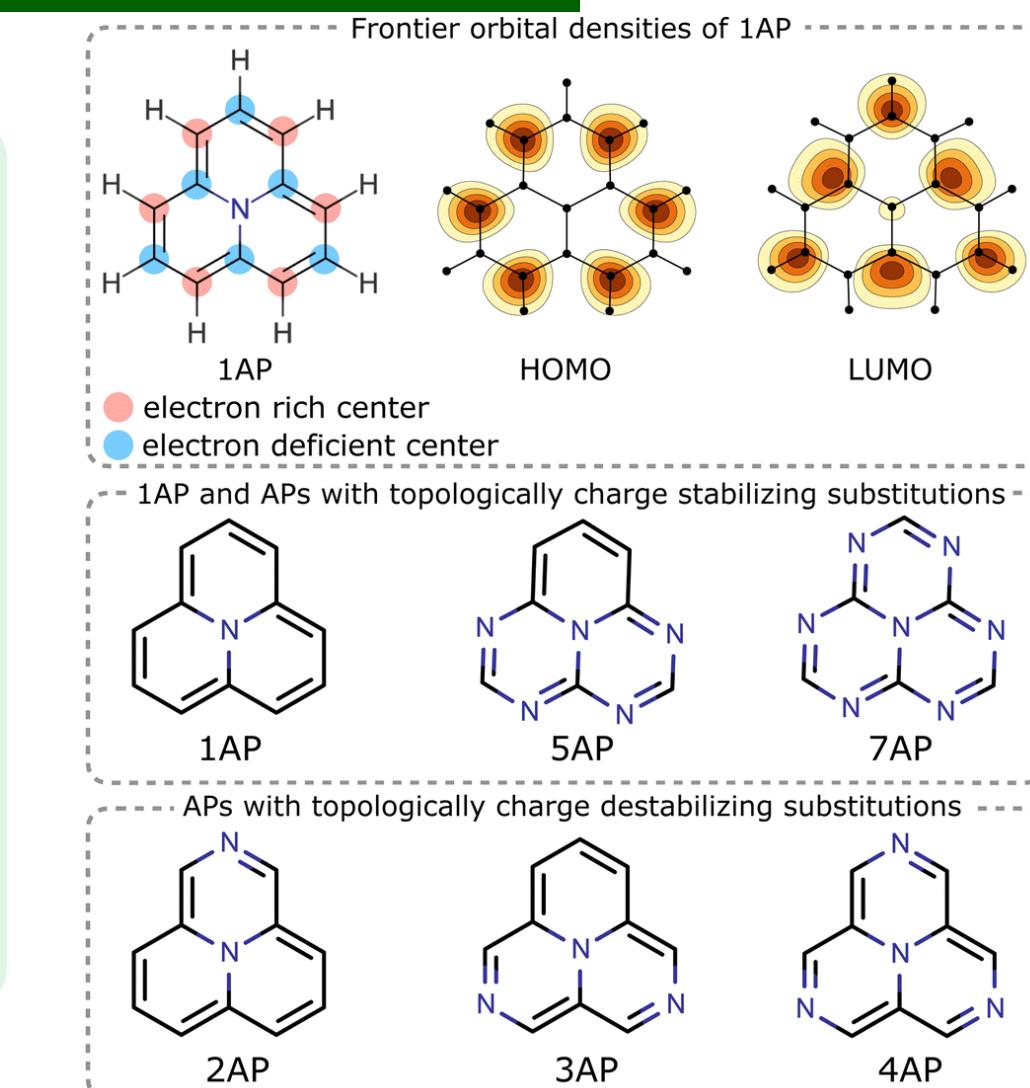
Q-CHEM

Orbital analysis: Multiwfn



CASE STUDY ON AZAPHENALENES [9]

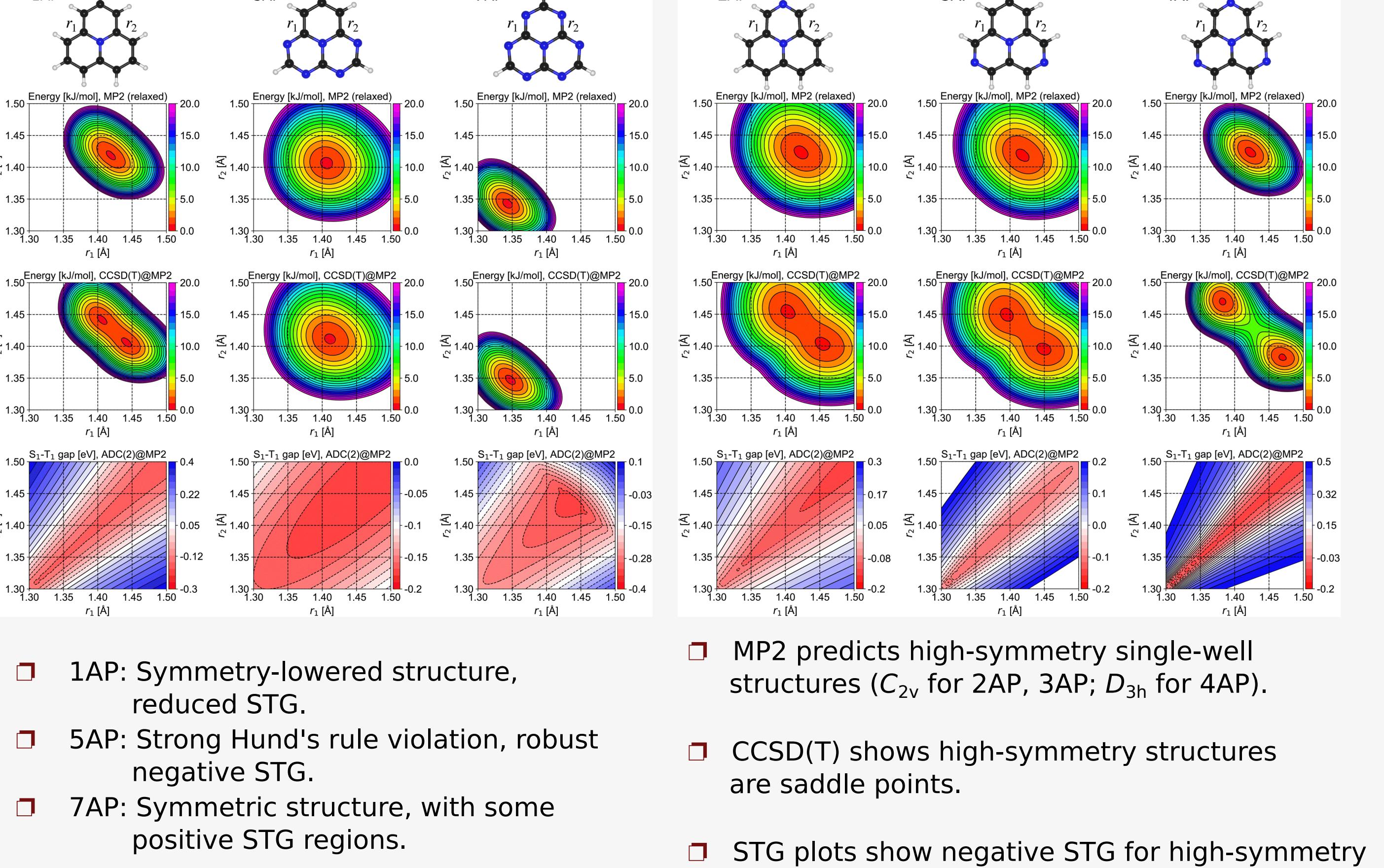
- We focus on 1AP, 5AP, and 7AP, which have already been experimentally studied.
- Additionally we examine 2AP, 3AP, and 4AP, where N is placed at electron-deficient sites of 1AP.
- All six molecules were part of a previous study [10], where TBE predicted negative STG.
- Investigate the potential energy surface at the CCSD(T) level and probe structural distortions and the effect on STG.



Jahn-Teller-Hund diagnostics:

1AP, 5AP, 7AP: Ground state PES (MP2, CCSD(T)) and S_1-T_1 gaps (ADC(2)) shown. Symmetries: C_{3h} for 1AP/7AP, C_s for 5AP; D_{3h} and C_{2v} along $r_1 = r_2$.

2AP, 3AP, 4AP: Symmetries: C_{3h} for 4AP, C_s for 2AP/3AP; D_{3h} and C_{2v} along $r_1 = r_2$.



System	Nature	Energy barrier (kJ/mol)	STG, Our work [9] (eV)	STG, TBE [10] (eV)	STG, Exp (eV)
1AP D_{3h}	TS	0.3	-0.142	-0.131	+0.04 [11]
1AP C_{3h}	Min	-	-0.060	-	-
2AP C_{2v}	TS	2.1	-0.102	-0.071	-
2AP C_s	Min	-	+0.125	-	-
3AP C_{2v}	TS	5.3	-0.079	-0.042	-
3AP C_s	Min	-	+0.274	-	-
4AP D_{3h}	TS	11.1	-0.073	-0.029	-
4AP C_{3h}	Min	-	+0.392	-	-
5AP C_{2v}	Min	-	-0.147	-0.119	-0.047 [4]
7AP D_{3h}	Min	-	-0.253	-0.219	< 0 [2]

- 1AP: STG is nearly zero; 5AP, 7AP: True positives
- 2AP, 3AP, 4AP (studied before, TBE): False positives

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THANK YOU

