L10

Computational chemistry: Critical appraisal

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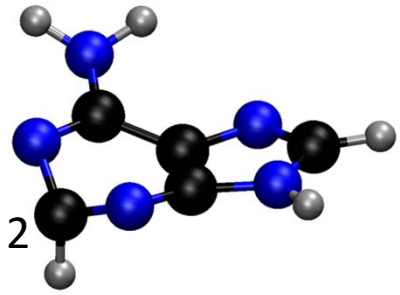
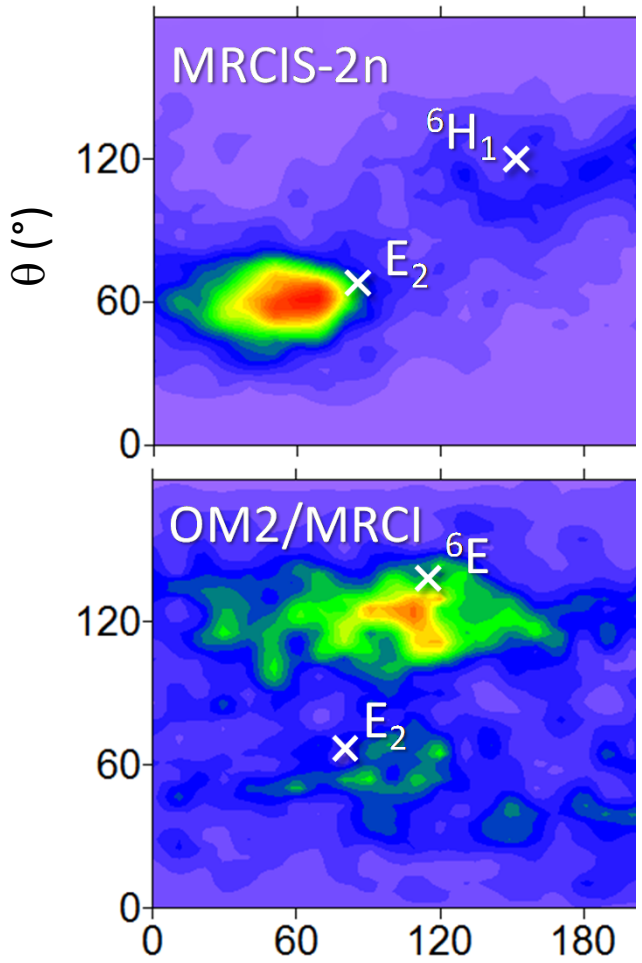
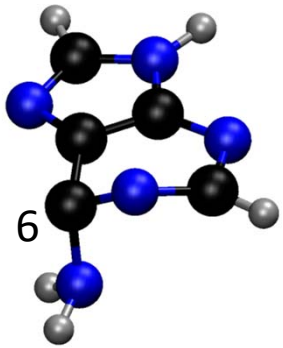
Results depend on the method

Adenine: Ab Initio x Empirical

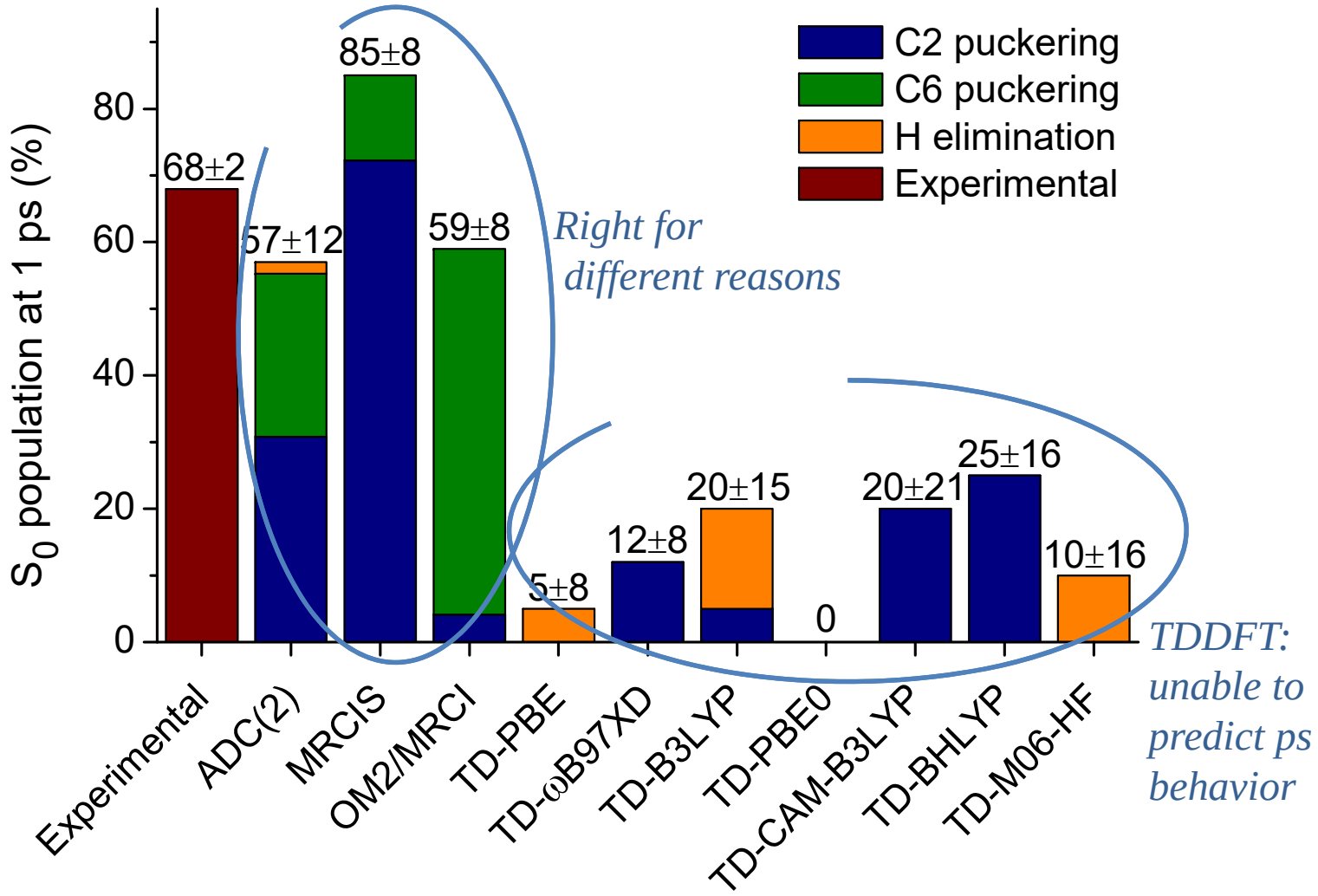






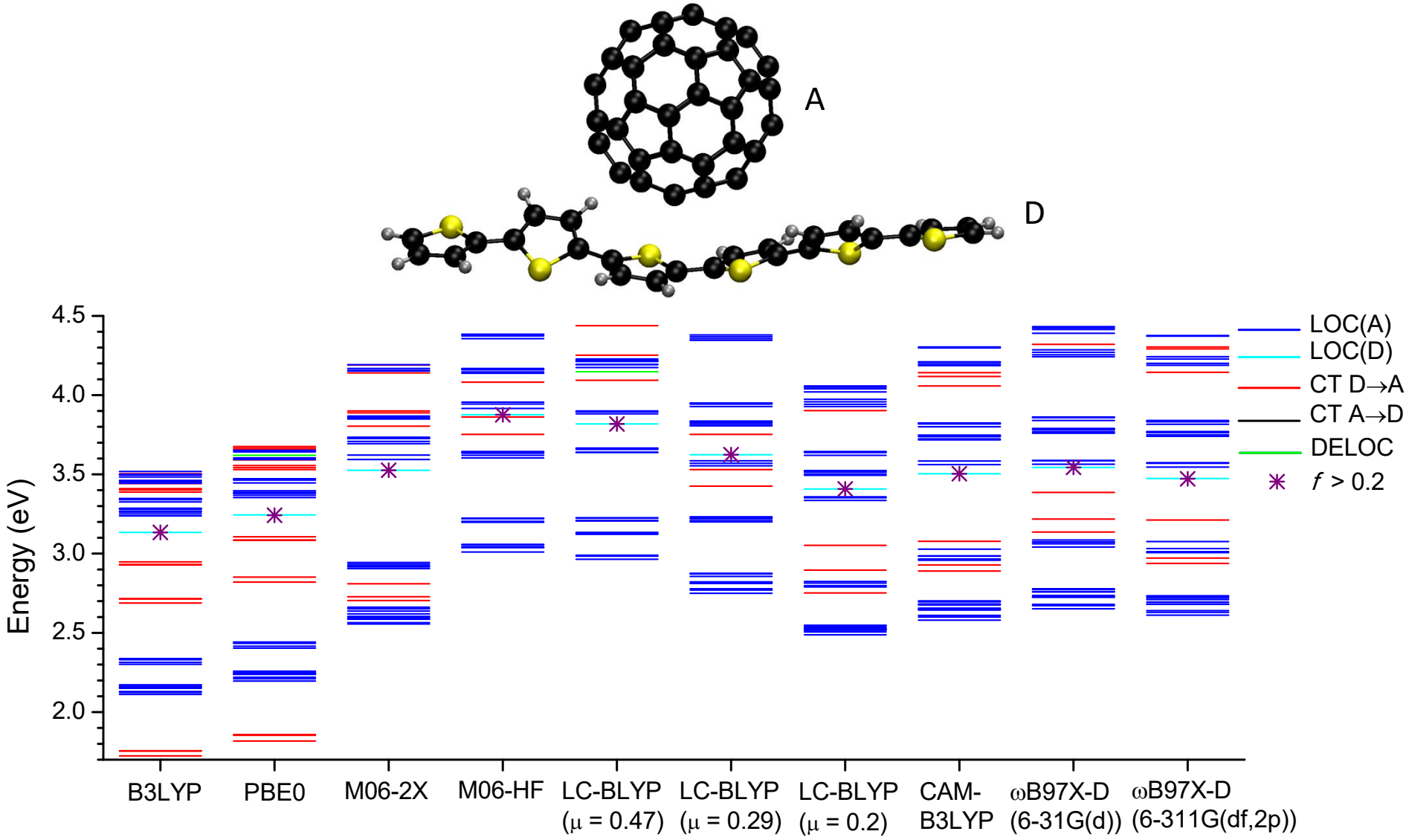
Ab initio and semiempirical MRCI produce **divergent results**

Ground-State Population at 1 ps (Ade)



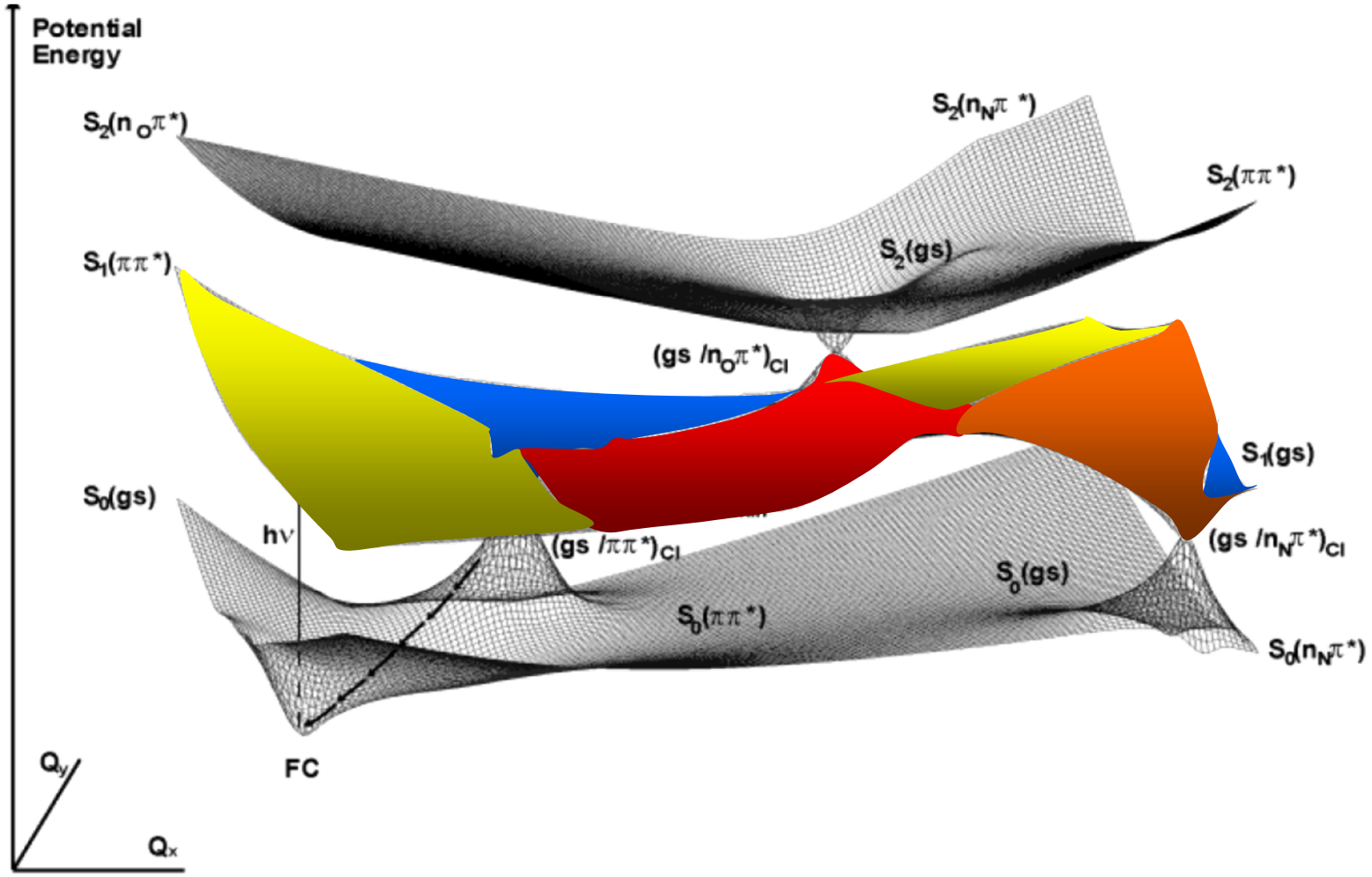
- Plasser, Crespo-Otero, Pederzoli, Pittner, Lischka, Barbatti, JCTC **10**, 1395 (2014)

Problem isn't only Adenine



- Sen, Crespo-Otero, Weingart, Thiel, Barbatti, JCTC **9**, 533 (2013)

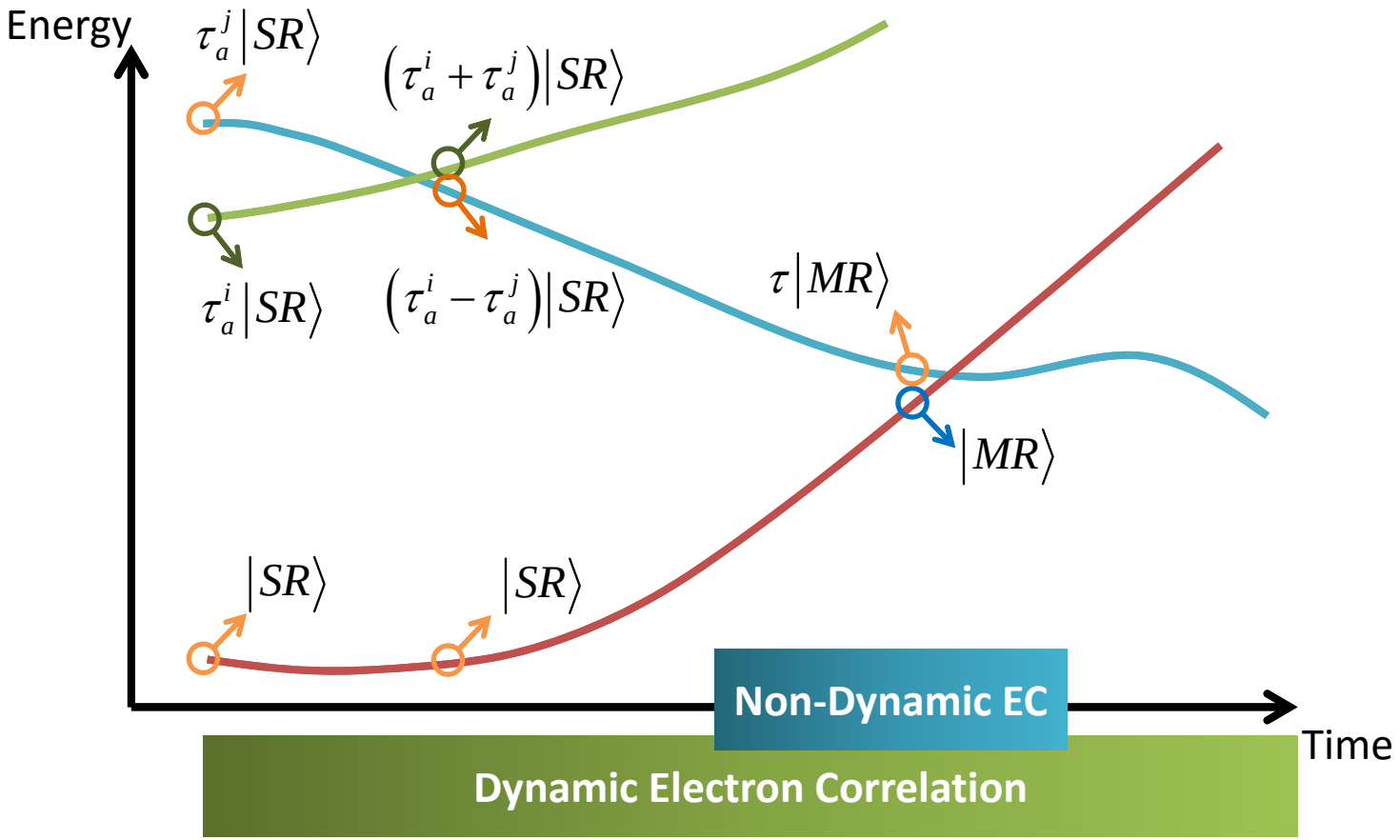
The Root of All Evil



- Excited-state spectral region has high density of states
- Small variation in geometry leads to a change of electronic character
- No affordable method can describe all characters at the same level

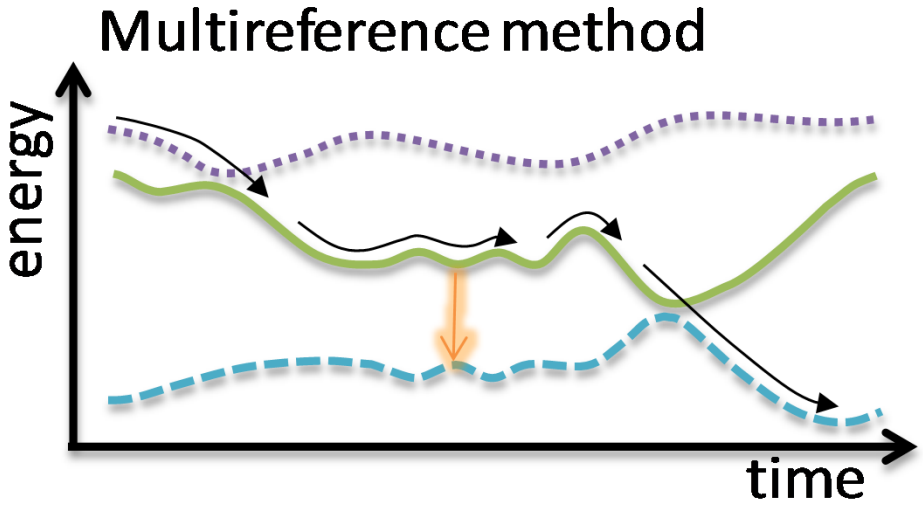

Till where Can We Go
with Single-Reference Methods?

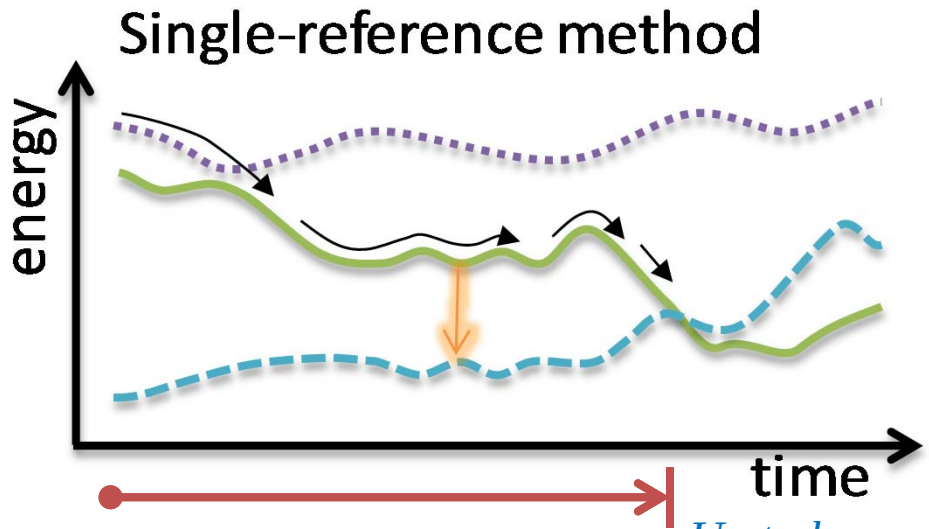
Electron Correlation: Dyn x Non-Dyn



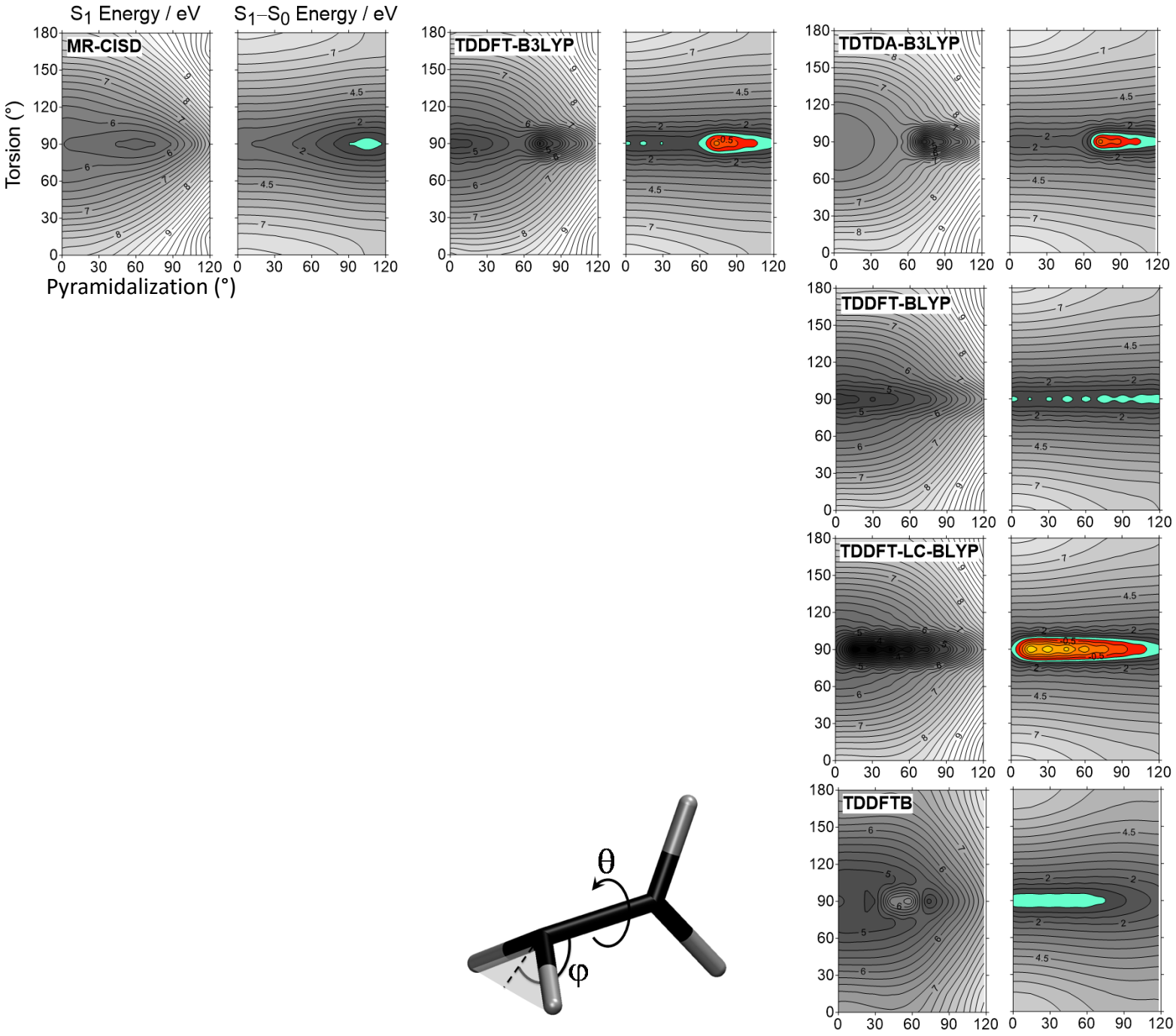
If DEC is needed everywhere and NDEC only at the intersection, why choosing CASSCF (only DEC) for dynamics?

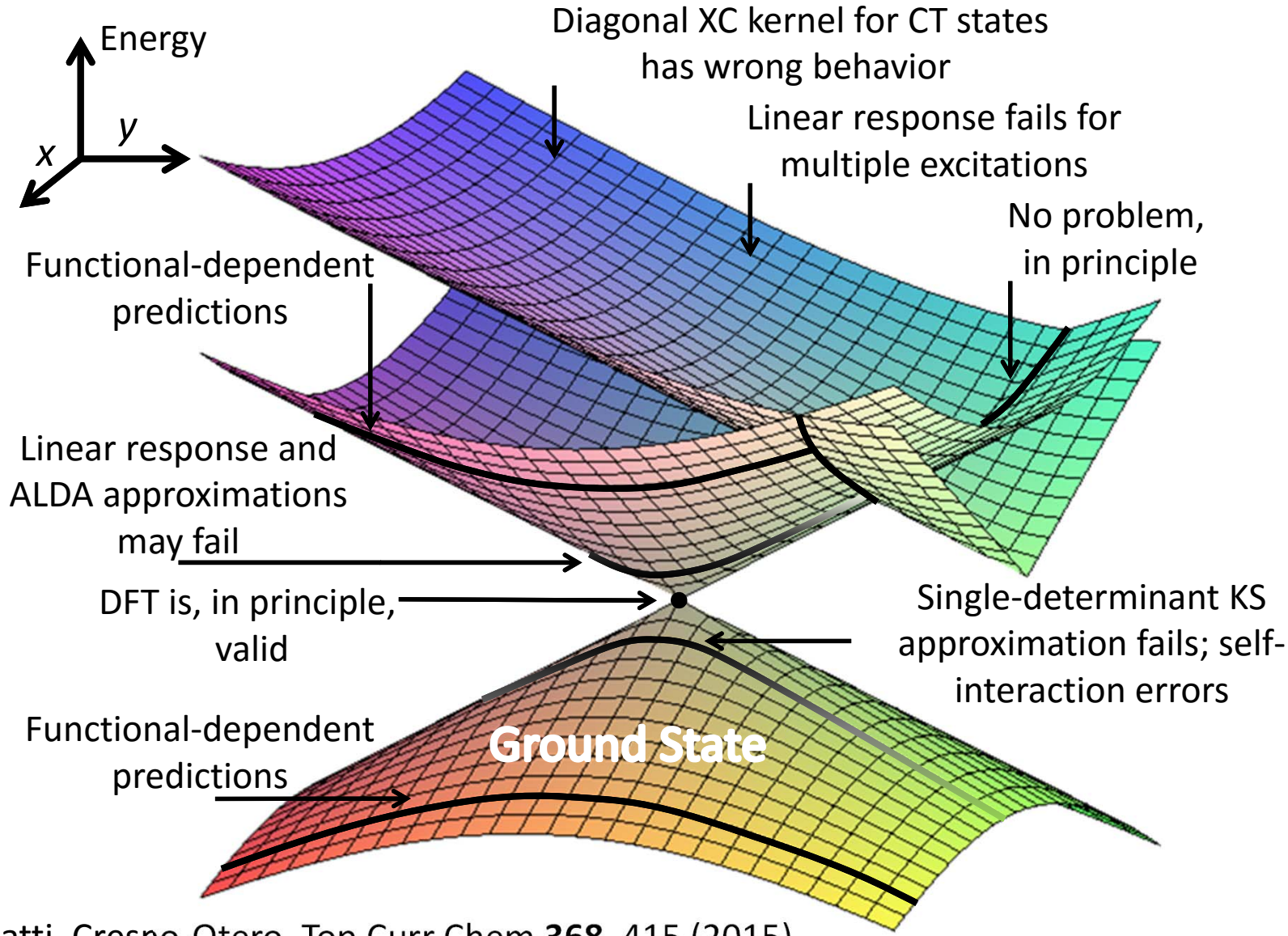
Dynamics with Single Reference





Up to here, dynamics may be OK.
But we ***need better research protocols*** *to guarantee quality*


S1 Energy / eV
S1–S0 Energy / eV
MR-CISD
TDDFT-B3LYP
TDTDA-B3LYP
TDDFT-BLYP
TDDFT-LC-BLYP
TDDFTB
Torsion (°)
Pyramidalization (°)
θ
φ



- Barbatti, Crespo-Otero, Top Curr Chem **368**, 415 (2015)

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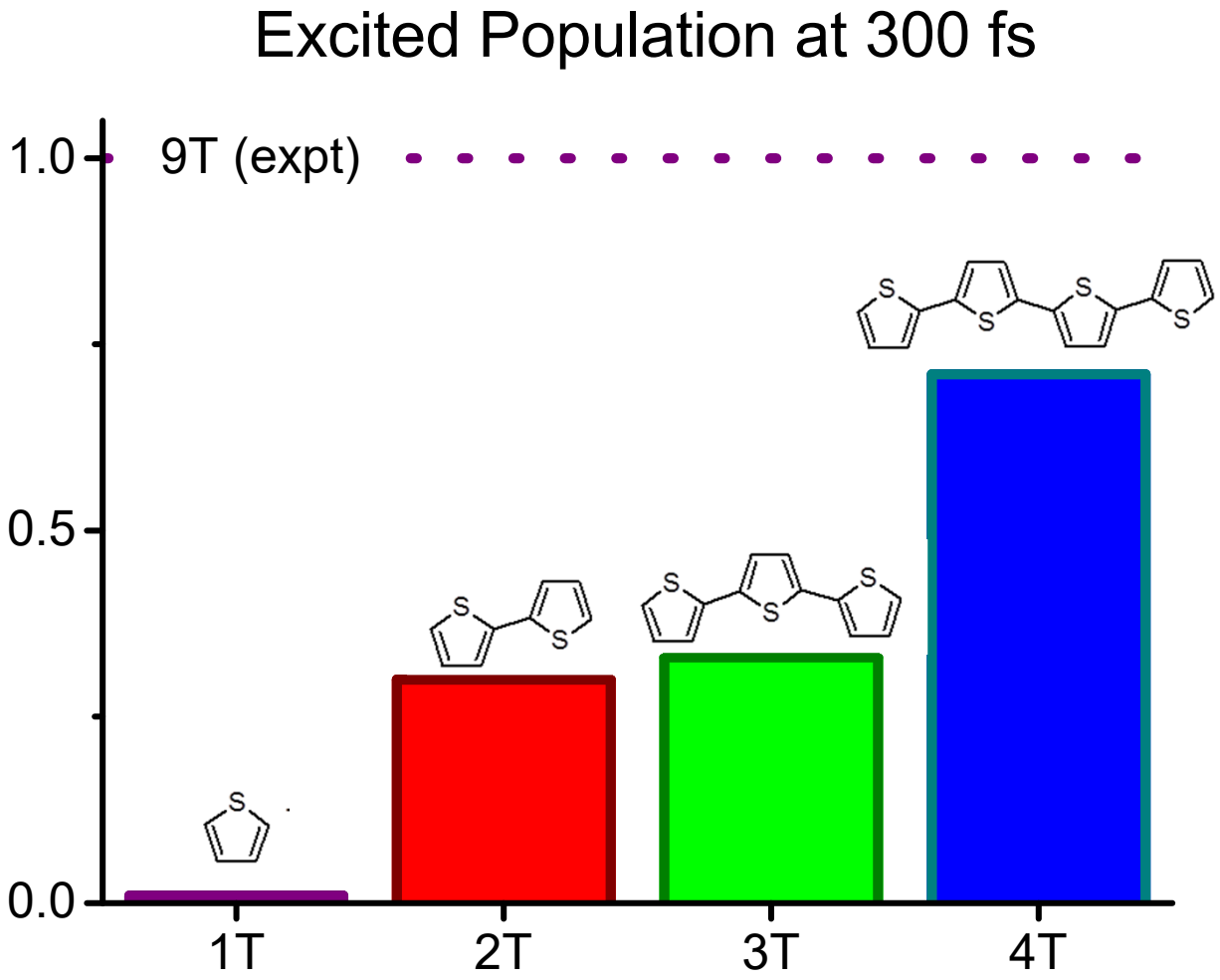


- Fazzi, Barbatti, Thiel, PCCP, accepted (2015)

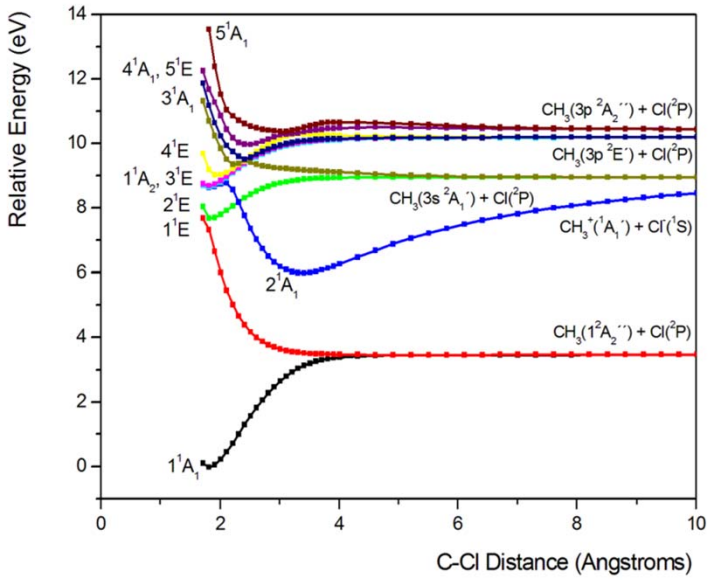

The best strategy

Computational chemistry of excited states:

- Powerful tool to understand mechanisms and interpret experiments
- Due to very complex electronic densities, they demand high expertise
- Used like black-box they may lead to qualitatively wrong results

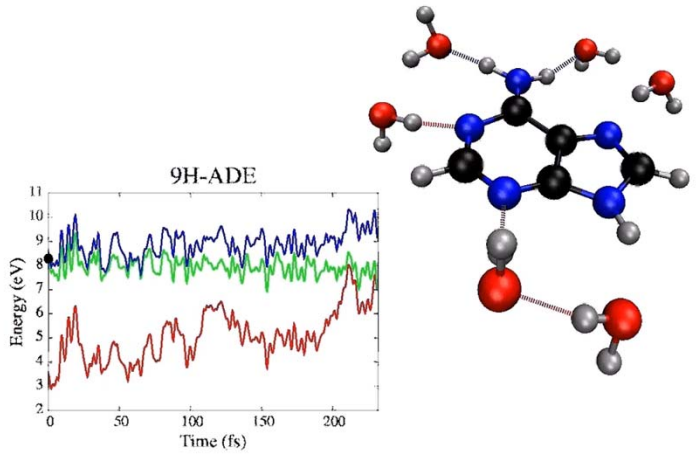
Reaction pathways:

- They can be computed with very high computational levels
- However, they are limited to few *biased* coordinates based on “educated guess”



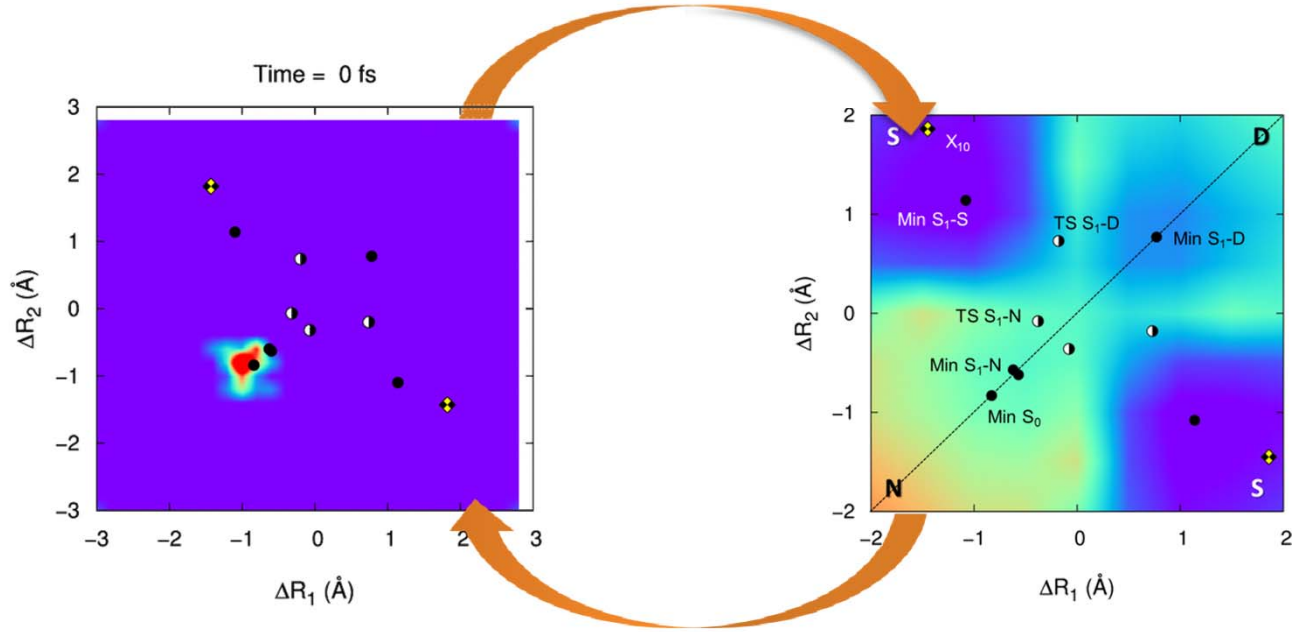
Semiclassical Dynamics:

- All degrees of freedom can be explored
- It reveals features that we would otherwise miss
- However, the computational level must be strongly downgraded



The best we can do is to combine them, reaction paths and dynamics

- Start with reaction paths comparing low/high levels and different methods
- Do low level-dynamics to let the important degrees revel themselves
- Move to high-level reaction paths to check the results
- If things are not consistent, go back, improve dynamics level
- Repeat the steps till self-consistence is achieved



The Five Commandments

I. Thou shalt use dynamics
only for what is really necessary

II. Test thy inputs and outputs before
submitting thy real production jobs

III. Thou shalt NOT let computers running alone
without checking what is going on

IV. Thou shalt NOT start dynamics
without a very careful investigation of the theoretical level

V. Thou art a limited and biased being, therefore,
thou shalt NOT rely on thy eyes to perform analysis

The path to success

- Use automatic approach for data input and analysis.
- Test the results with methods from different families (DFT x CC, for example).
- Improve statistics and compute statistical errors.
- Limit analysis to significant results with the error bar.
- Don’t blindly rely on previous works. Reanalyze their data.
- Be rigorous and honest. Report negative results and failures.