From pseudopotentials for the chemical environment to challenges in the computational treatment of catalysis

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GDR-NBODY : 8th-10th January 2020

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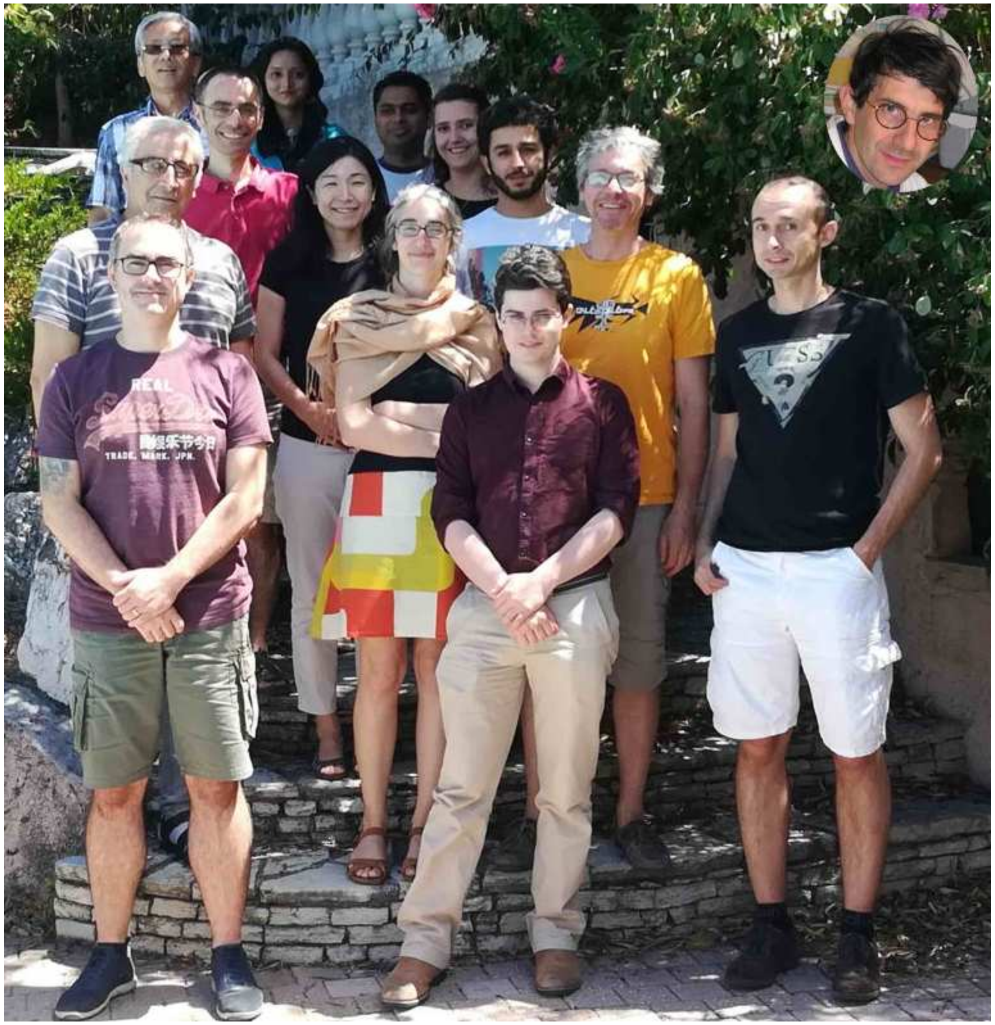


PhD work of

Alexander PUNTER

Molecular Pseudopotentiels

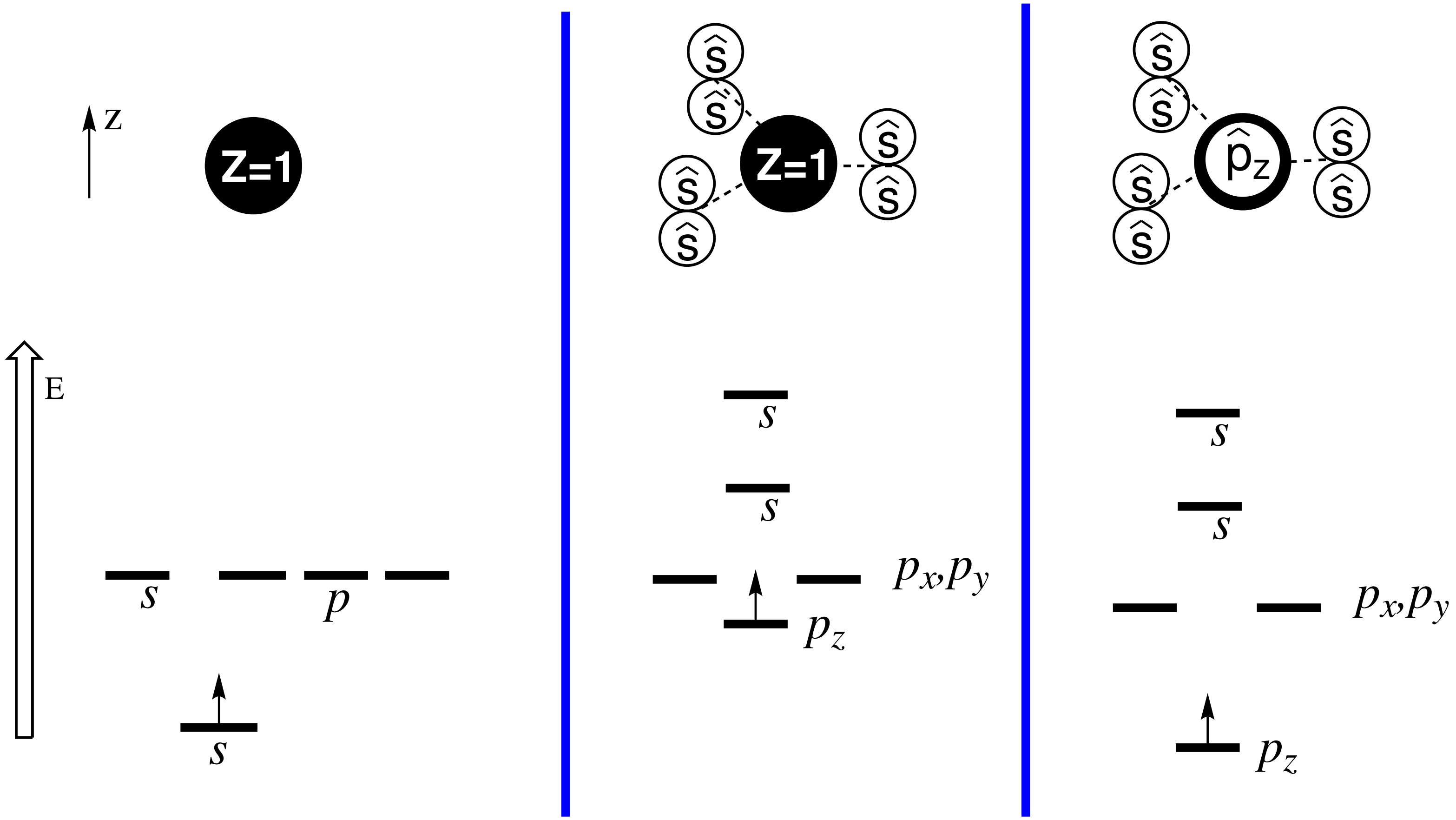
Supervisors :
Yannick CARISSAN
Paola NAVA

A. Punter, P. Nava and Y. Carissan, *Int. J. Quant. Chem.*, **119**, e25914, 2019.

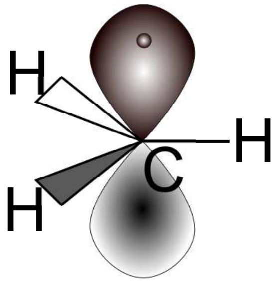
Context and Aims

- Main idea (an old one): separation between active vs. dormant electrons
- Effects of dormant electrons → effective potential
- Unusual (though not unprecedented) elements:
  - not only strictly core electrons are dormant, as well as whole nuclei.
  - Potentials used are not all centered on atoms.
  - Focus: electronic properties.

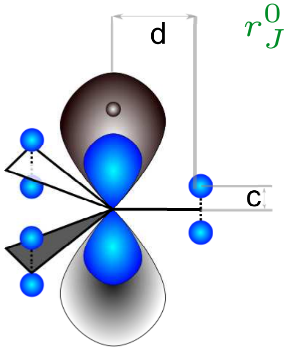
Pseudopotential effect on orbitals – 'Designer' Orbitals



Prototype – the sp^2 carbon fragment



9 protons
9 electrons



1 proton
1 electron

$r_J^0 = \sqrt{d^2 + c^2}$

Idea: ECP formalism (to avoid programming within the codes)

$$\hat{W} = \underbrace{\frac{A}{r}\exp(-\alpha r^2)\sum_m |Y_{1,m}\rangle\langle Y_{1,m}|}_{\text{p projectors}} + \underbrace{\sum_J \frac{C_J}{r - r_J^0}\exp(-\gamma_J (r - r_J^0)^2)\,|Y_{0,0}\rangle\langle Y_{0,0}|}_{\text{s projectors}}$$

Parameters: coefficients: A, C_J

exponents: α, γ_J

position: r_J^0

The Multi-Orbital Optimiser (MOO) program

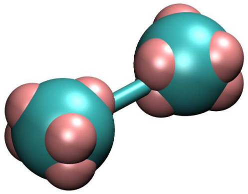
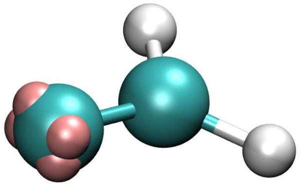
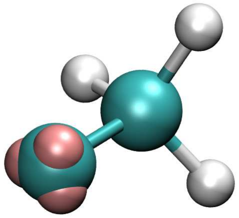
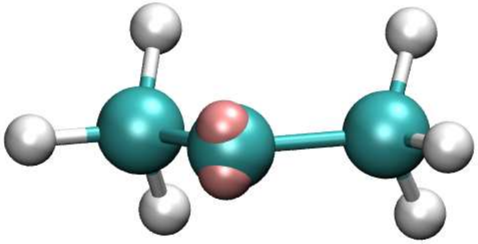
```
alex@Algernon:~/PycharmProjects/chem_scripts$ python3 moo.py
root        : INFO     Logging initialised...

                    ########################################
                     The Multi-Orbital Optimiser   (___)
                                                  <(o o)>______
                              (or MOO)             ../ ` # # \`;
                                                     \ ,___, /
                        A Punter, CTOM group          ||   ||
                      Aix-Marseille Université        ^^   ^^
                    ########################################

MOO file found.
Run optimisation?
1: Start MOO optimisation run.
2: Enter MOO setup.
 >>  2
What would you like to do?
1: Potentialise a molecule.
2: Optimise new potentials.
3. View references.
q: Quit
 >>  2
--------------------------------------------
OPTIMISATION MENU
--------------------------------------------
CURRENT SETTINGS:
ECPs to optimise:        ['c ecp-2 (s-f)']
Orbital Optimisation:    ON (orbitals: [])
Total Gap Optimisation:  OFF (comparison folders: [])
Seeded Optimisation:     OFF (seeds: 1)
Geometry Optimisation:   OFF (carbons of type sp2, indices: [1])
Initial guesses:         [1.0, 2.0]
WARNING: As seeded optimisation is OFF, you will need to supply your own initial guess for potential
parameters.
--------------------------------------------
1. Add ECP functions
2. Toggle MO energy optimisation (currently ON)
3. Molecular Orbital energy criteria
4. Toggle total energy difference optimisation (currently OFF)
5. Total energy difference criteria
6. Semi-random seed options
7. Potential geometry optimisation options
8. Set initial guesses for ECP parameters (only needed if not using semi-random seeds).
9. Run optimisation now
h. Help. Show optimisation guide.
b: Go back
 >>  9
Run optimisation (y/n)?
 >> 
```

- Python program
- It can use several criteria:
  - orbital energies
  - S-T gap
  - IE
  - H-L gap
  - TD-DFT energies
  - Spectral shape fitting

Optimised Pseudofragments

	α	sp^2, 1 electron
	β	sp^2, 2 electrons
	γ	sp^3, 1 electron
	δ	sp^3, 2 electrons

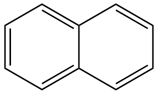
In pink:
position of the non-centered s potentials

Optimisation Protocol

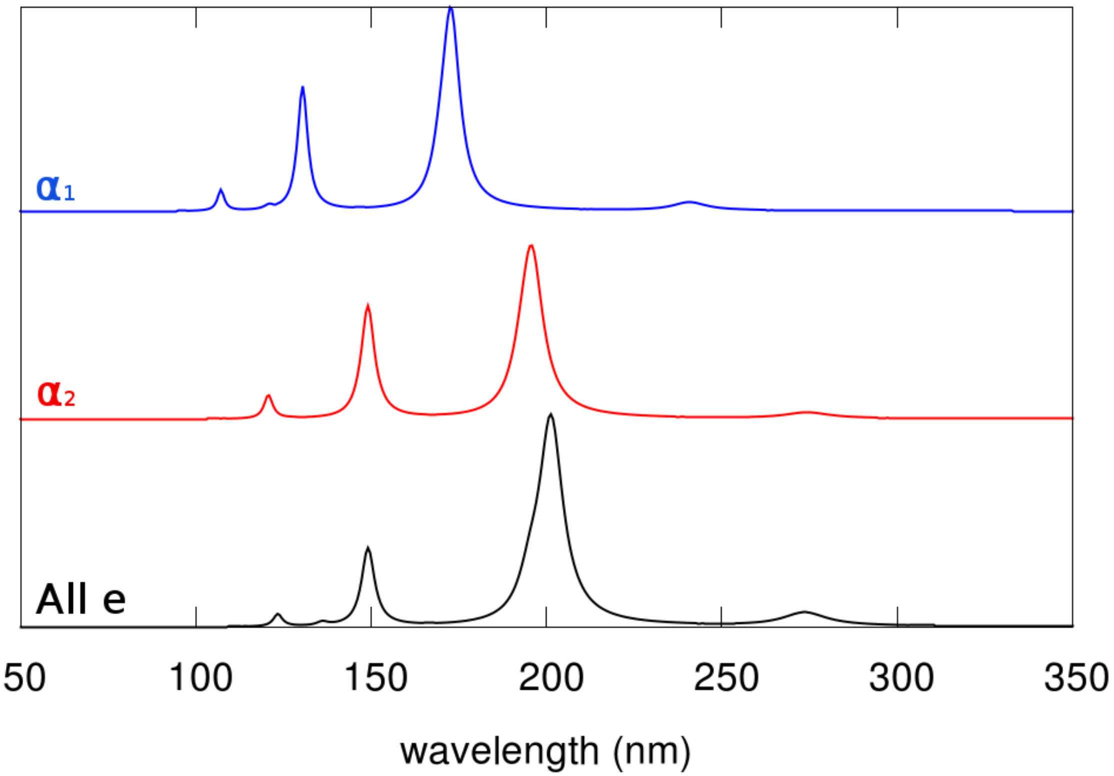
In general:

- extraction is based on reference Hartree-Fock all-electron calculations on small systems
  For α**:** extraction on ethylene
- **tests** to check method transferability: on DFT (CASSCF)
- **tests** are made vs. all-electron calculations

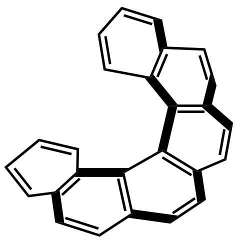
Naphtalene



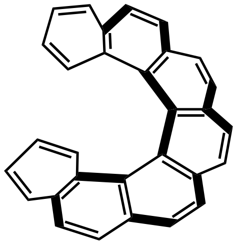
Optimisation Criteria	
α_1	α_2
HOMO	HOMO
IE	LUMO
S-T gap	LUMO+1
Optimisation System	
ethylene	



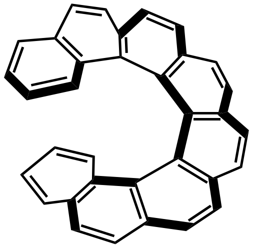
PBE0/def-SV(P)



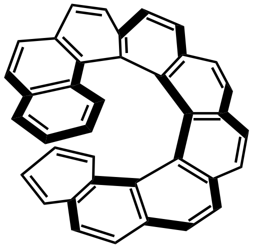
[6]Helicene



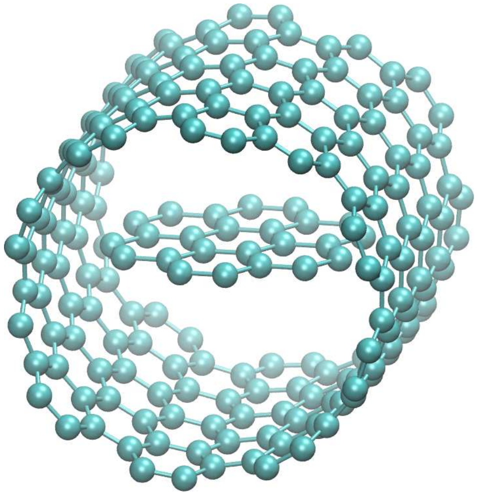
[7]Helicene

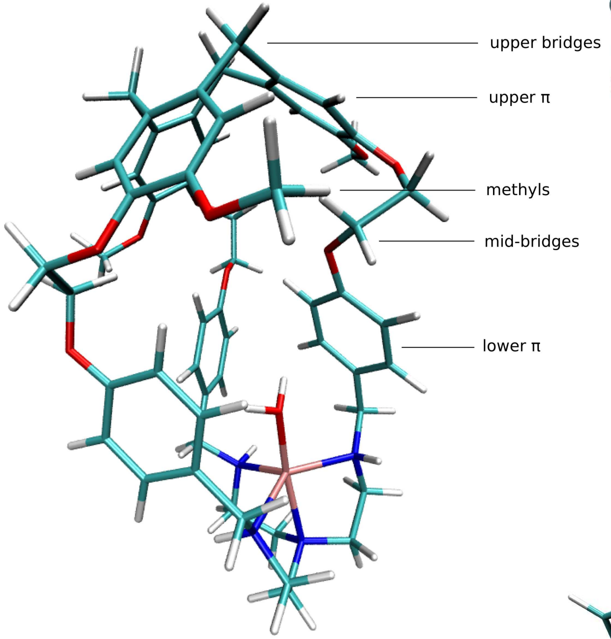


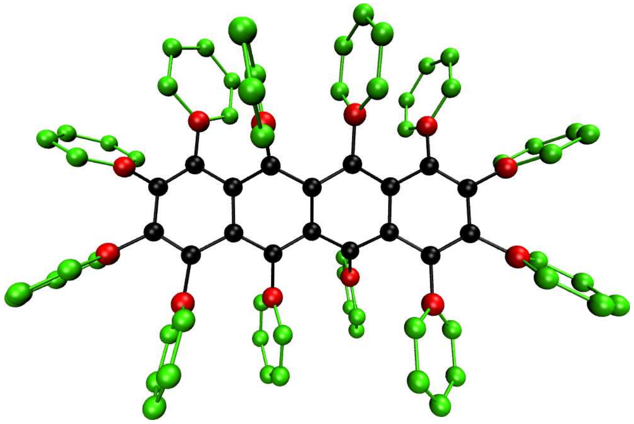
[8]Helicene

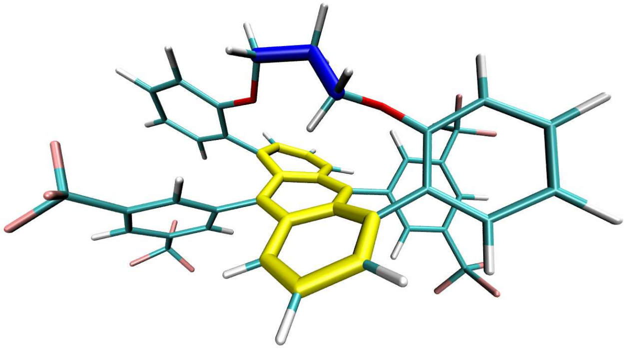


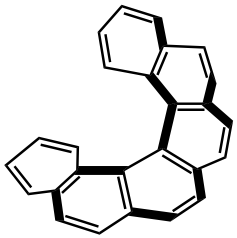
[9]Helicene



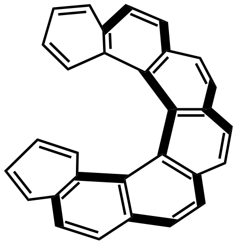




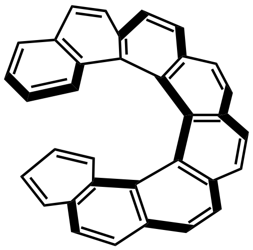




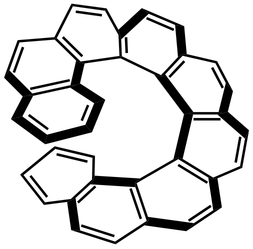
[6]Helicene



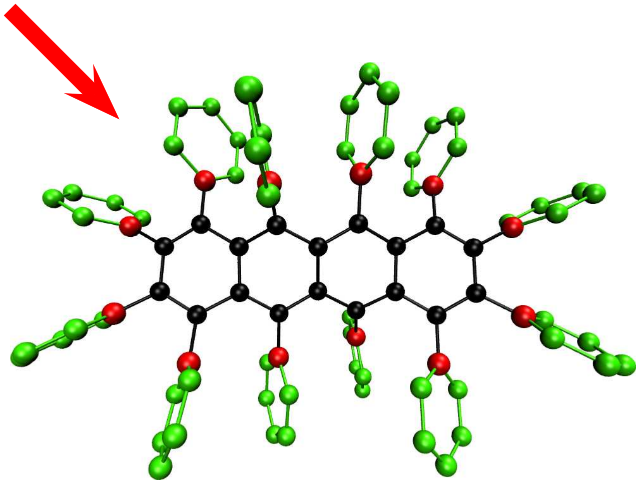
[7]Helicene

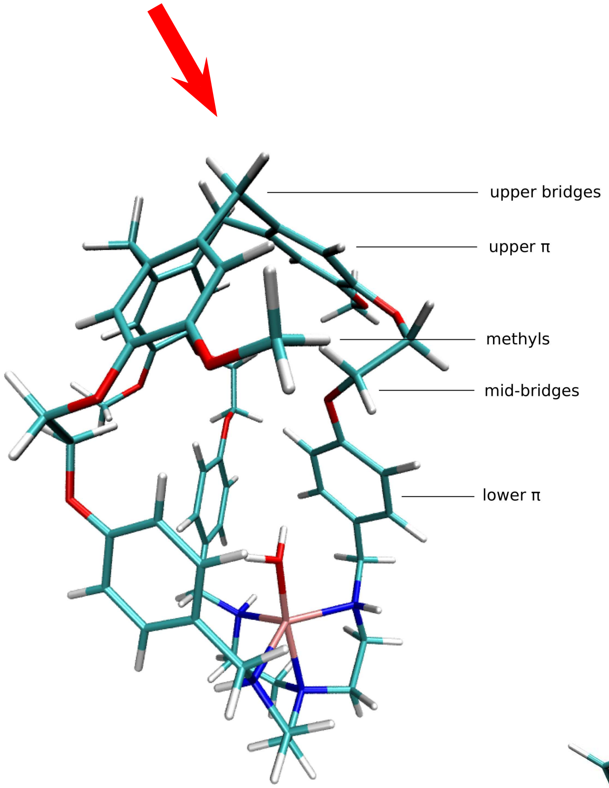


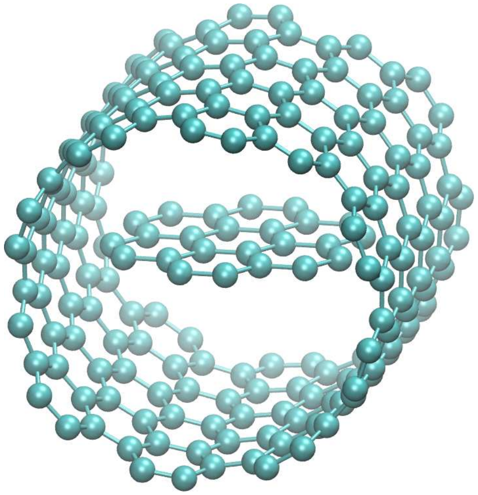
[8]Helicene

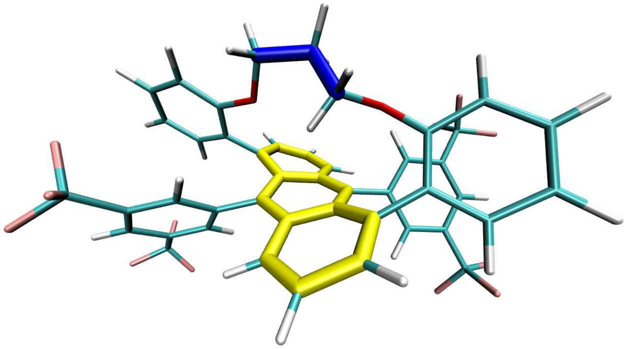


[9]Helicene

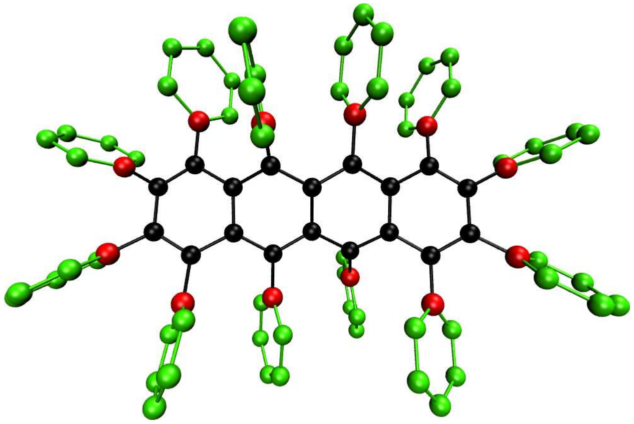






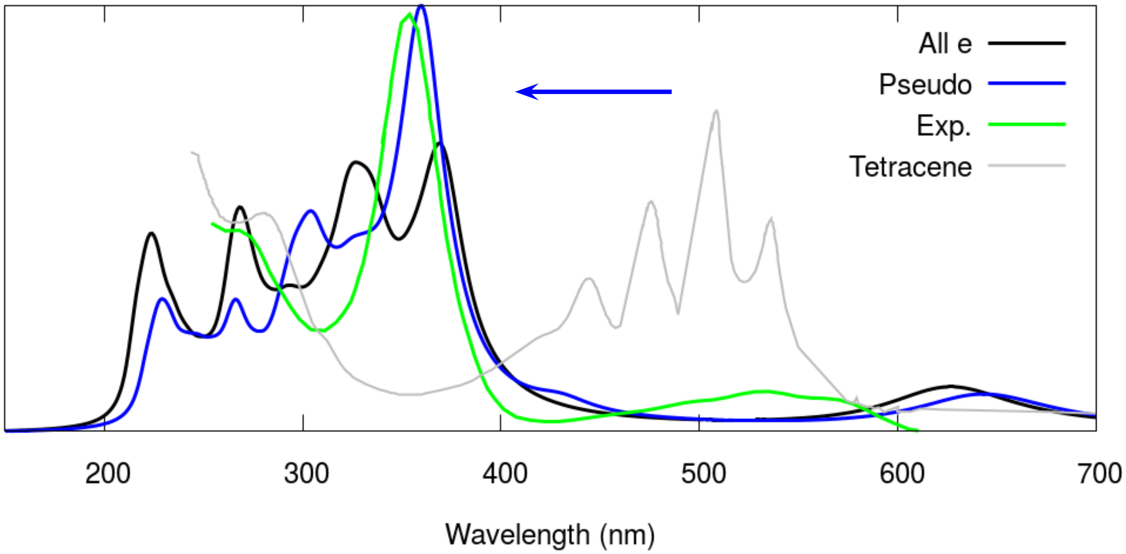


Dodecaphenyltetracene



Green: α potentials
Red: β potentials
Black: all-e carbon

Y. Xiao, J. T. Mague, R. H. Schmehl et al., *Angew. Chem.*, 2019, **58**, 2831-2833.

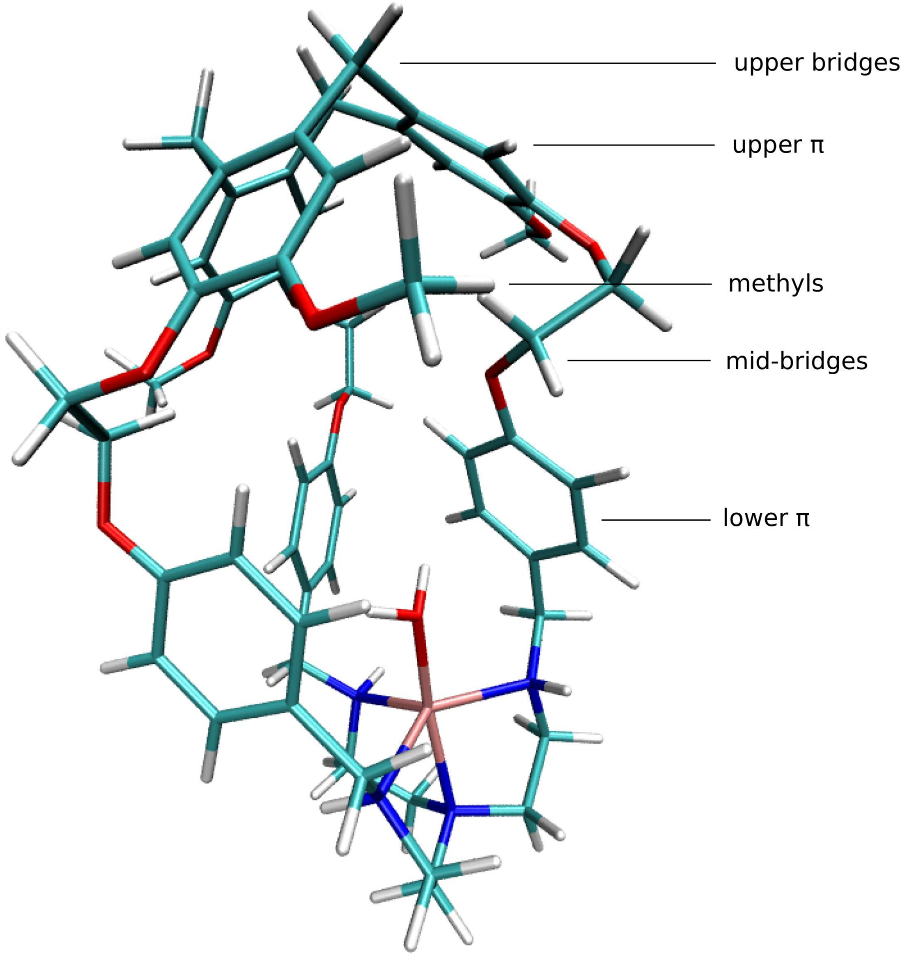


Challenge: Many overlapping and interlocking π rings

Result: well-reproduced blue shift due to the chemical environment

PBE0/def-SV(P)

Cu(II) Hemicryptophane

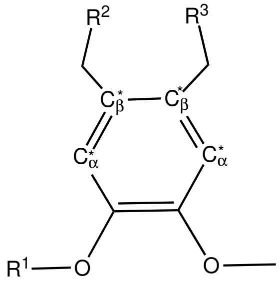


Challenges

- all potential types are used: α, β, γ, δ
- Electronic and ECD spectra

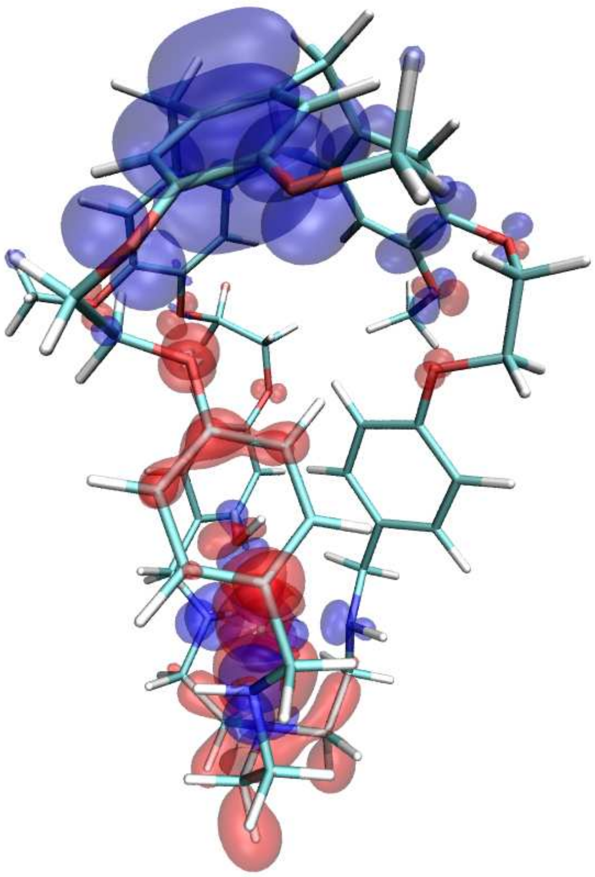
Heterobonding Rule

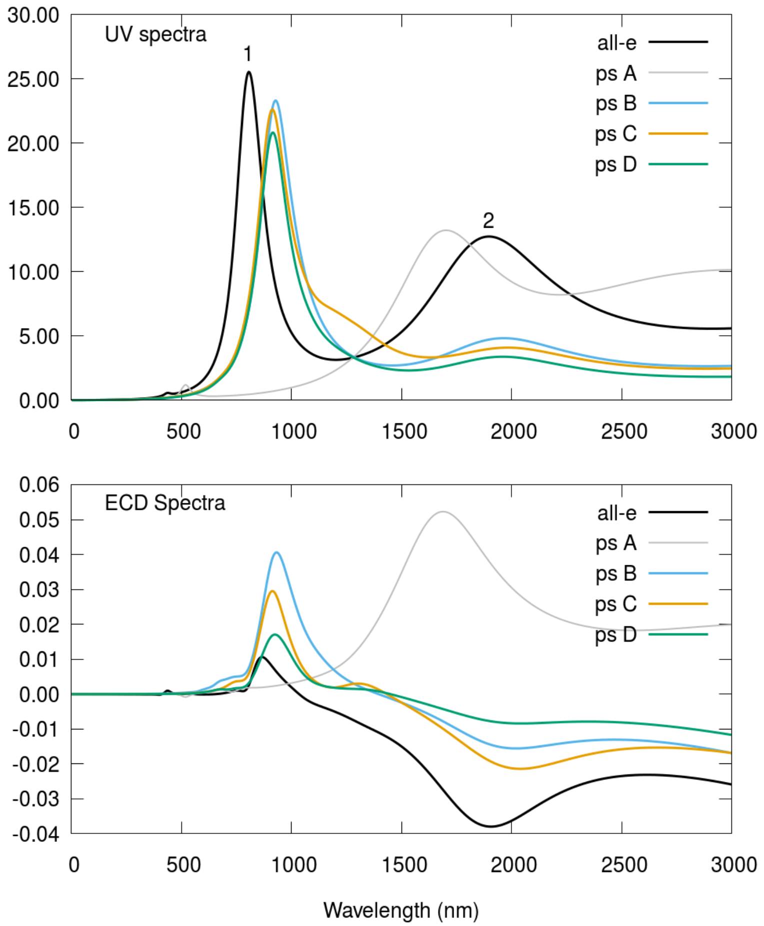
Pseudofragments should be bound to all-e carbon



O. Perraud, J. B. Tommasino, V. Robert, B. Albela, L. Khrouz, L. Bonneviot, J. P. Dutasta, and A. Martinez, *Dalton Trans.*, 2013, **42**, 1530–1535.

Cu(II) Hemicryptophane – Electronic and ECD spectra



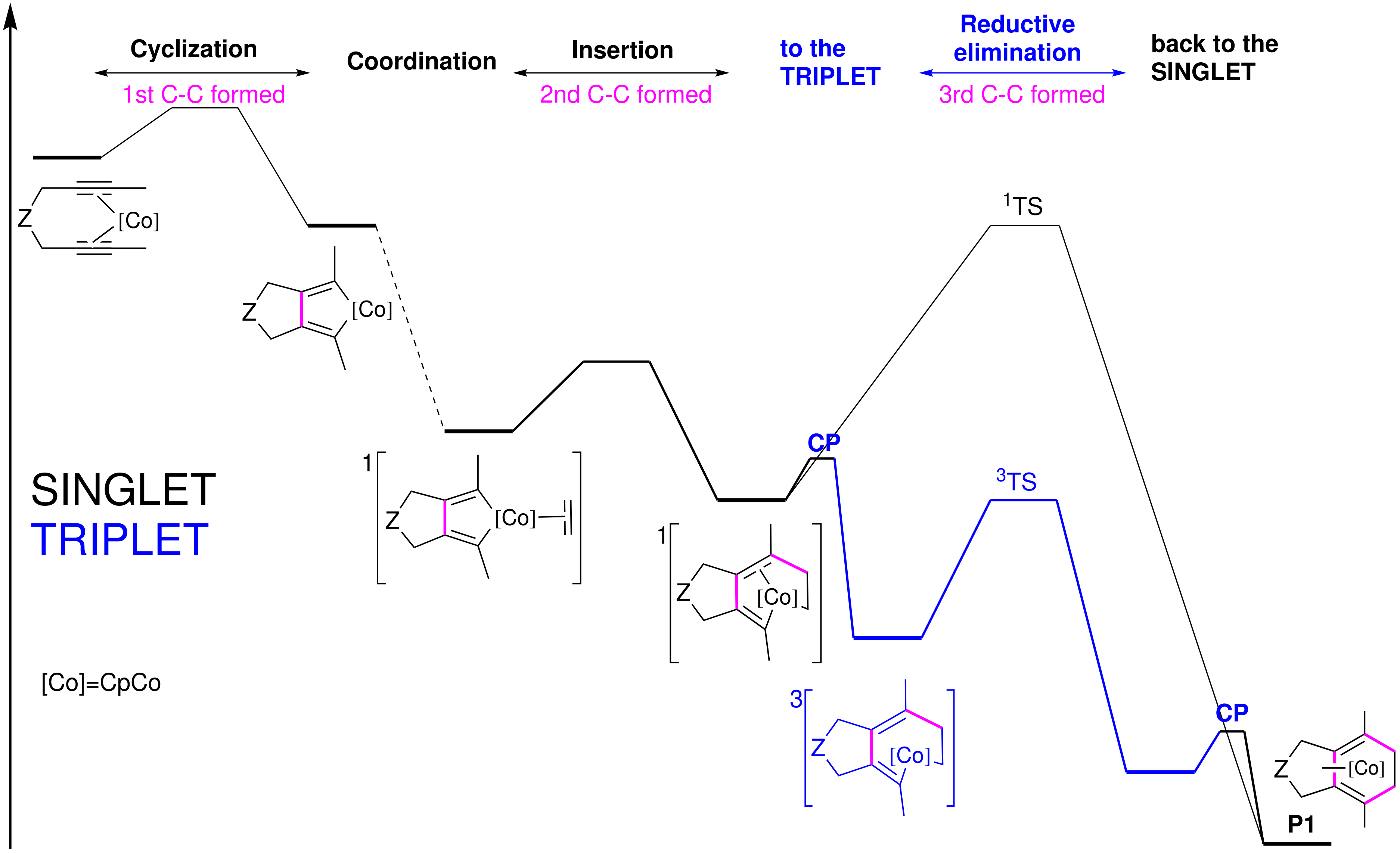


Remplacement scheme A (not following the rule) → no peak 1

B3-LYP/def-SV(P). Electron density decreased in blue and increased in red regions.

Challenges in the computational treatment of catalysis
First-row transition metals

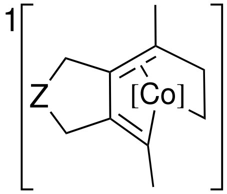
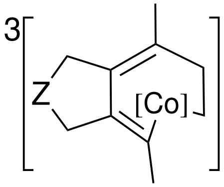
Energetic Profile – Formal [2+2+2] Cycloaddition Reaction



V. Gandon, *et al.*, **JACS**, **2006**, *128*, 8509-8520.

What about the triplet?

We are still working on it (energies in kcal/mol):

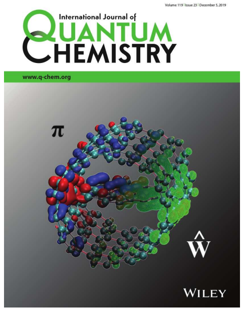
	B3LYP-D3	BP86-D3	F12-CCSD(T)	F12-BCCD(T)
	0.0	0.0	0.0	0.0
	-7.95	12.9	11.0	18.9

[Co]=CpCo

HOWEVER, results need to be confirmed

F12-UCCSD(T) and F12-UBCCD(T) on ROHF, def2-TZVP basis set – B3LYP structures

Acknowledgements



A. Punter, P. Nava and Y. Carissan, *Int. J. Quant. Chem.*, **119**, e25914, 2019.

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Alexander Punter, Yannick Carissan

Denis Hagebaum-Reignier, Stéphane Humbel

stéréO

Jean-Luc Parrain, Muriel Amatore, Laurent Commeiras

THANK YOU FOR YOUR ATTENTION

Aix Marseille université
Initiative d'excellence

Molecular Pseudopotentials for the Study of Chemical Properties

Alexander Punter

Supervisors:
Dr. Yannick Carissan
Dr. Paola Nava

iSm2 Institut des Sciences Moléculaires de Marseille
UMR 7313

Aims

Aims

- Investigate the feasibility of pseudopotential fragments which treat only physically/chemically relevant electrons and nuclei explicitly
- Develop and refine these pseudopotentials, can a general method be found?
- Explore the limits of the technique

Context

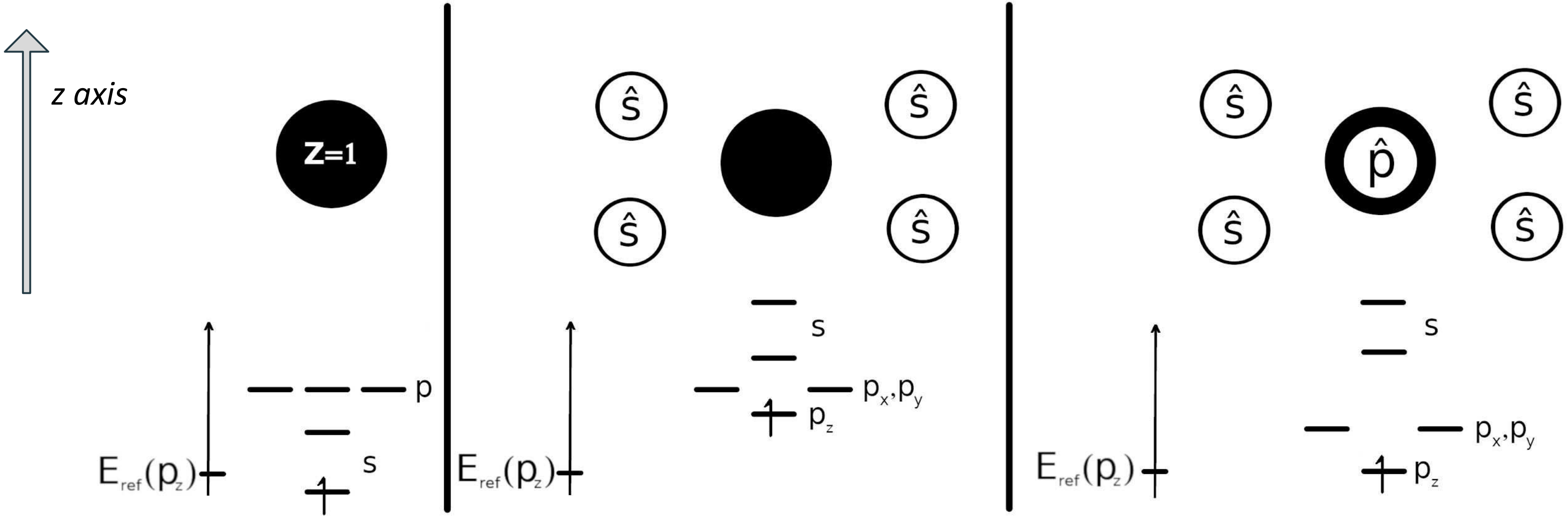
- Pseudopotential theory dates back to the early days of quantum mechanics*.
- Core idea is that electrons can be separated into active and dormant electrons, and the dormant ones treated with a simple potential function rather than calculated explicitly.
- Unusual (though not unprecedented) elements of this work are that:
    - More electrons than normal are included in the dormant region, as well as whole nuclei.
    - Potentials used are not all centered on atoms.

* H. Hellmann, *J. Chem. Phys.*, 1935, 3
P. Gombás, *Z. Phys.*, 1935, 94, 473–488

‘Designer’ Orbitals

To create a custom p_z orbital:

- First make sure the desired orbital is the lowest in energy
- If necessary, break the symmetry of degenerate orbitals, so that the occupation is correct
- Fine-tune the energy



Definition of Pseudopotential

For a monoatomic p$_z$ electron:

$$\hat{W}_i = \underbrace{\frac{A}{r_i}\exp(-\alpha r_i^2)\sum_m |Y_{1,m}\rangle\langle Y_{1,m}|}_{\text{atom-centered potentials}} + \underbrace{\sum_J \frac{C_J}{r_i - r_J^0}\exp(-\gamma_J(r_i - r_J^0)^2)\,|Y_{0,0}\rangle\langle Y_{0,0}|}_{\text{non-atom-centered potentials}}$$

One-electron Hamiltonian:

$$\hat{h}(i) = -\frac{1}{2}\Delta_i - \frac{1}{r_i} + \hat{W}_i$$

Modifying pseudopotential parameters

Multiple parameters that can be modified:

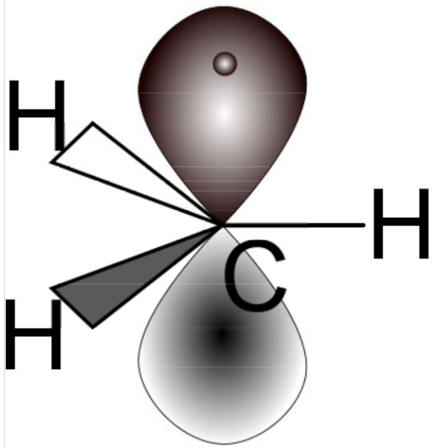
- A: coefficient of atom-centered potential
- α: exponent of atom-centered potential
- C_J: coefficient of non-atom-centered potential J
- γ_J: exponent of non-atom-centered potential J
- r^0_J: distance between non-atomic potentials and nucleus (fixed for early potentials).

$$\hat{W}_i = \underbrace{\frac{A}{r_i}\exp(-\alpha r_i^2)\sum_m |Y_{1,m}\rangle\langle Y_{1,m}|}_{\text{atom-centered potentials}} + \underbrace{\sum_J \frac{C_J}{r_i - r_J^0}\exp(-\gamma_J(r_i - r_J^0)^2)\,|Y_{0,0}\rangle\langle Y_{0,0}|}_{\text{non-atom-centered potentials}}$$

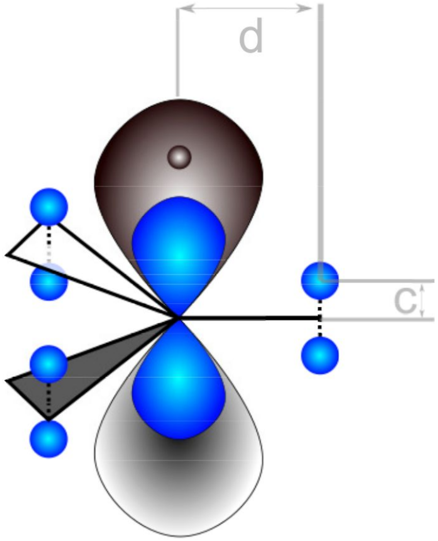
$$r_J^0 = \sqrt{d^2 + c^2}$$

Prototype

- Can we model the electronic structure of a molecular system while keeping only a few chemically-relevant electrons?
- Reducing the complexity of chemical system increases computational efficiency, and tests our understanding of the underlying physics.



9 protons
9 electrons

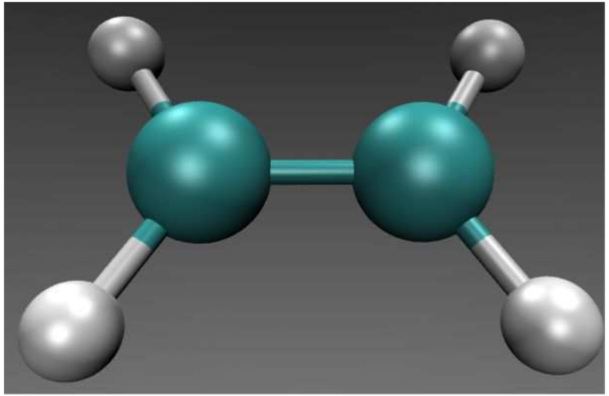


1 proton
1 electron

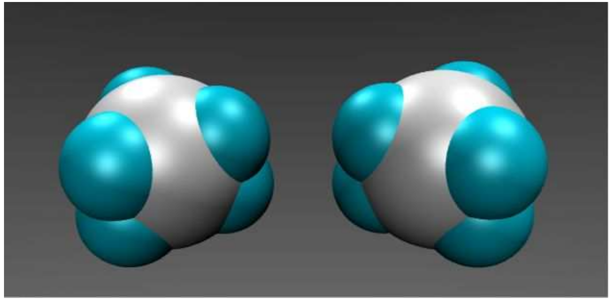
$\widehat{W}$ operator

The first optimisation

- The HOMO, singlet-triplet gap and first ionisation energies of ethylene are used as reference criteria.
- These are chosen in the hope of capturing the underlying physics of the π orbital.
- Optimised on HF in order to keep them unbiased *wrt* correlation.



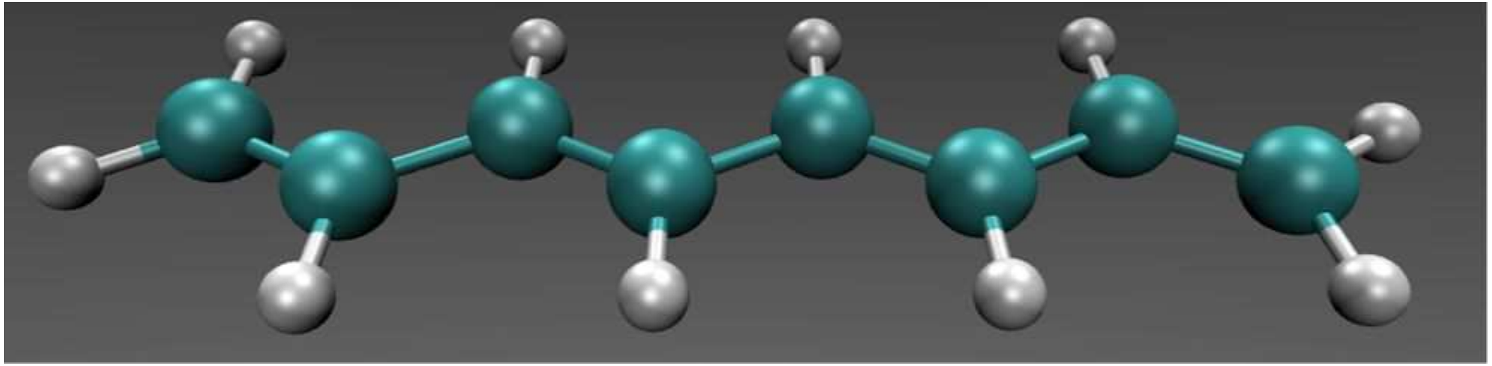
Optimisation Criterion	Reference (eV)	Pseudo-ethylene (eV)
π-π^* gap	+3.533	+3.532
1st ionisation	+9.091	+9.806
HOMO	-10.363	-10.062



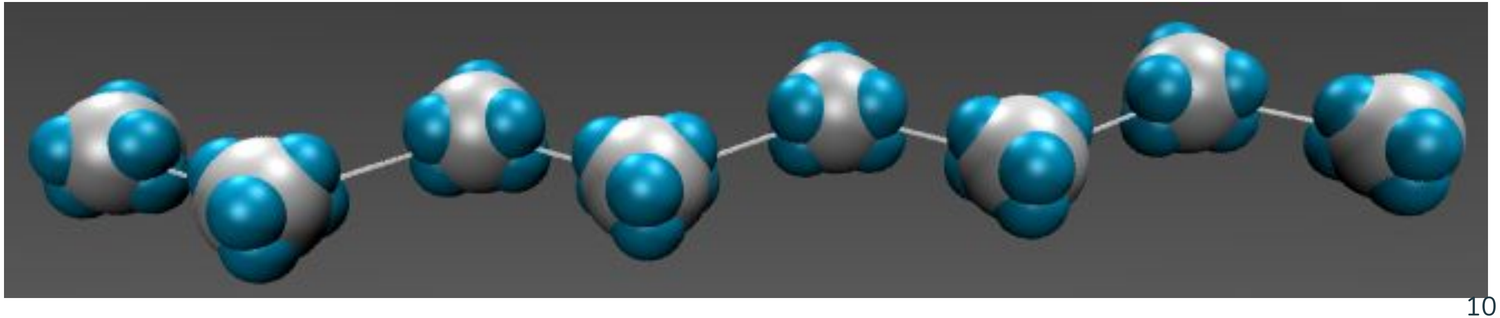
HF/def-SV(P)

All-trans-polyene molecules: pseudo-C_8H_{10}

58 e^-



8 e^-



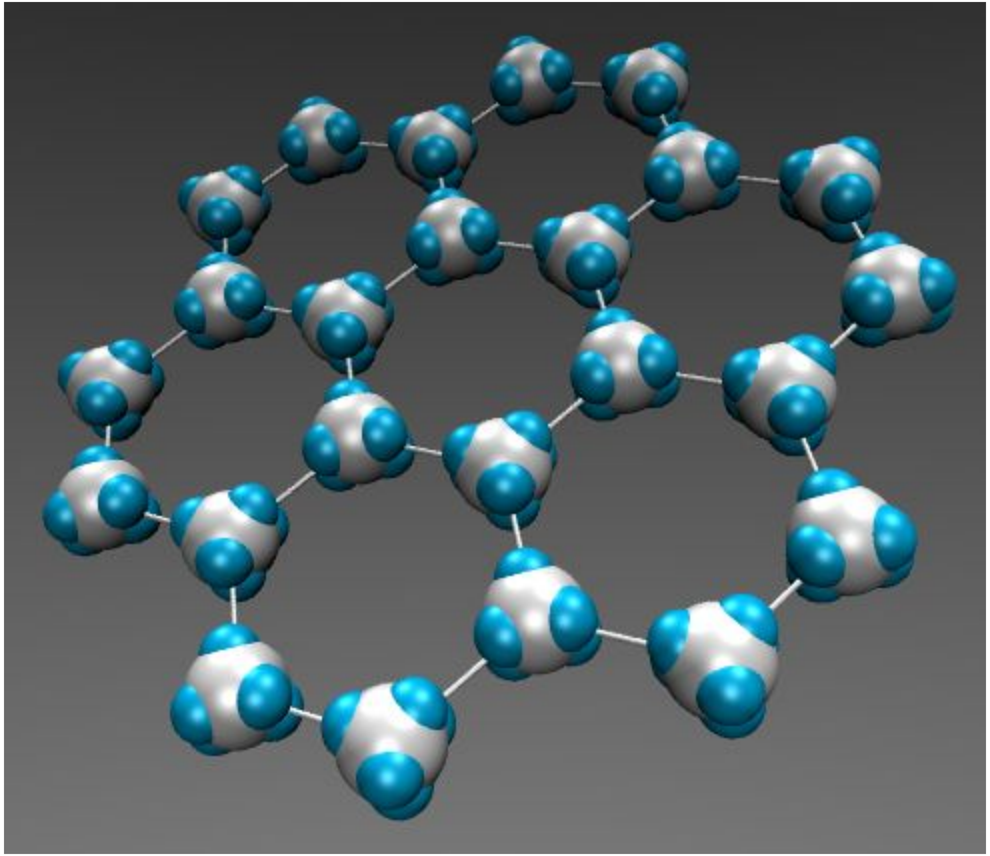
PAH Molecules: Pseudocoronene

All-electron system:

156 e^-

Pseudo-system:

24 e^-



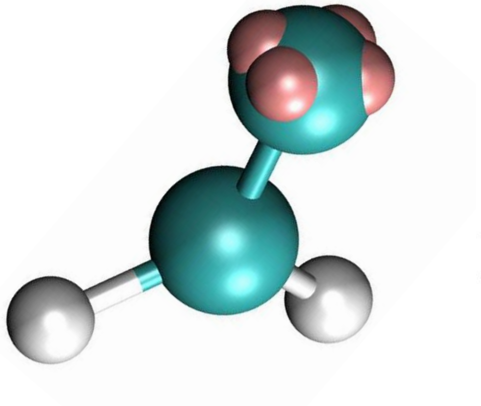
Trans-polyene and PAH Results

	Mean 1st I.E. error	Mean HOMO error	Mean 1st Excitation error (TD-DFT)
trans-polyenes (2 – 12 carbons)	7.0 %	4.2 %	2.6 %
trans-polyenes (20 – 100 carbons)	6.6 %	7.8 %	1.0 %
PAH (1 – 19 hexagonal rings)	12.0 %	11.5 %	4.4 %

PBE0/def-SV(P)

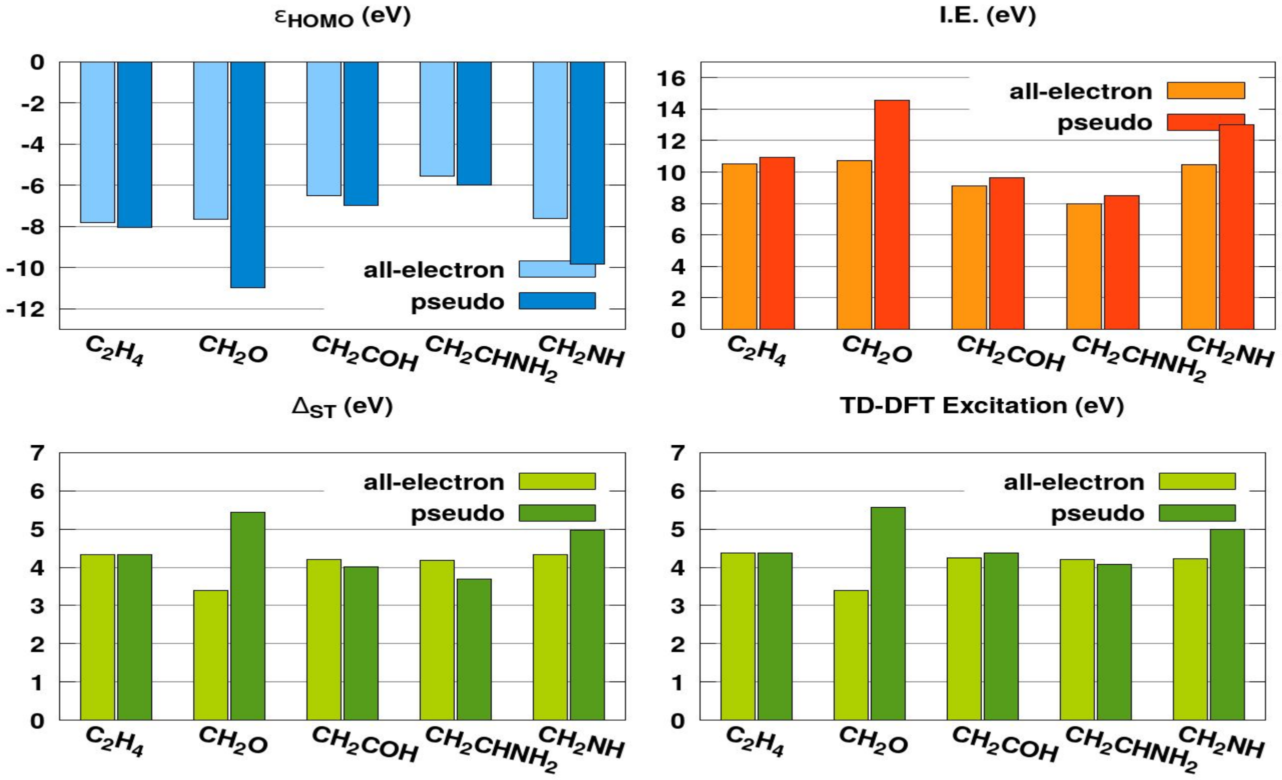
Other Pseudopotential Setups

β potentials: sp^2, two explicit electrons



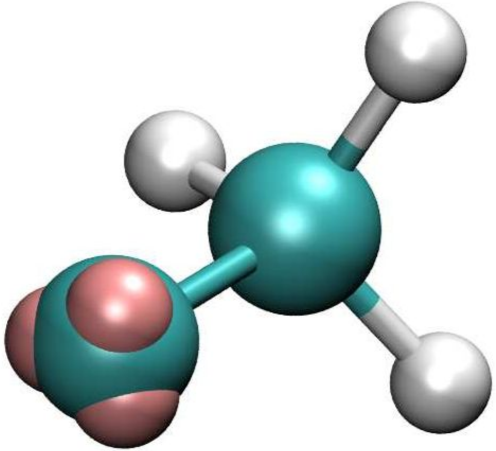
β Optimisation Criteria
HOMO (x3) HOMO-1 HOMO-2

Optimised on ethylene



DFT-PBE0/def-SV(P)

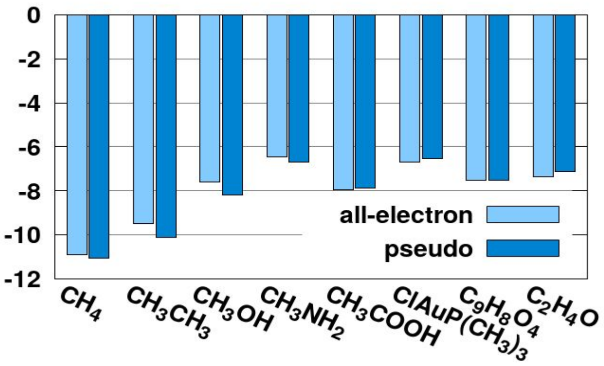
γ potentials: sp^3, one explicit electron



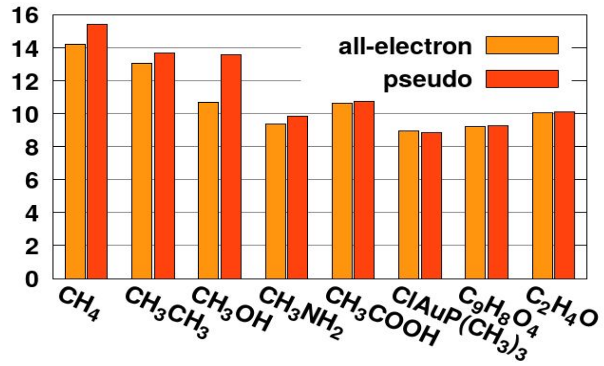
γ Optimisation Criteria
HOMO (x2) HOMO-1

Optimised on ethane

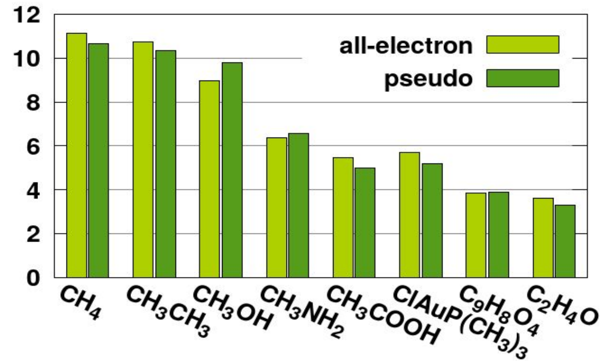
ε_{HOMO} (eV)



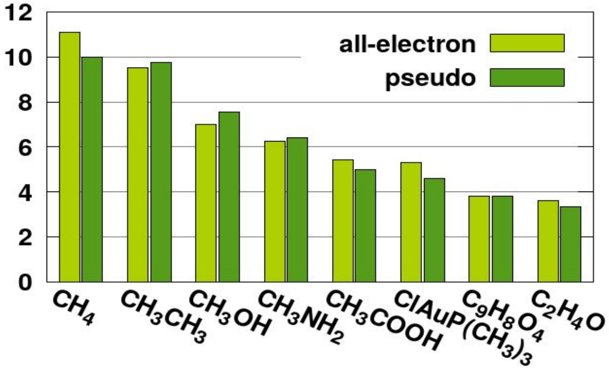
I.E. (eV)



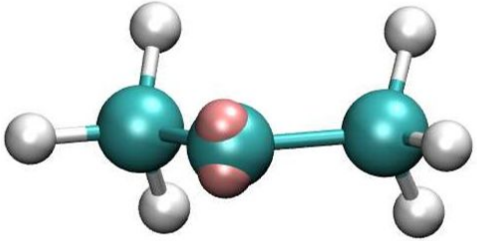
Δ_{ST} (eV)



TD-DFT Excitation (eV)



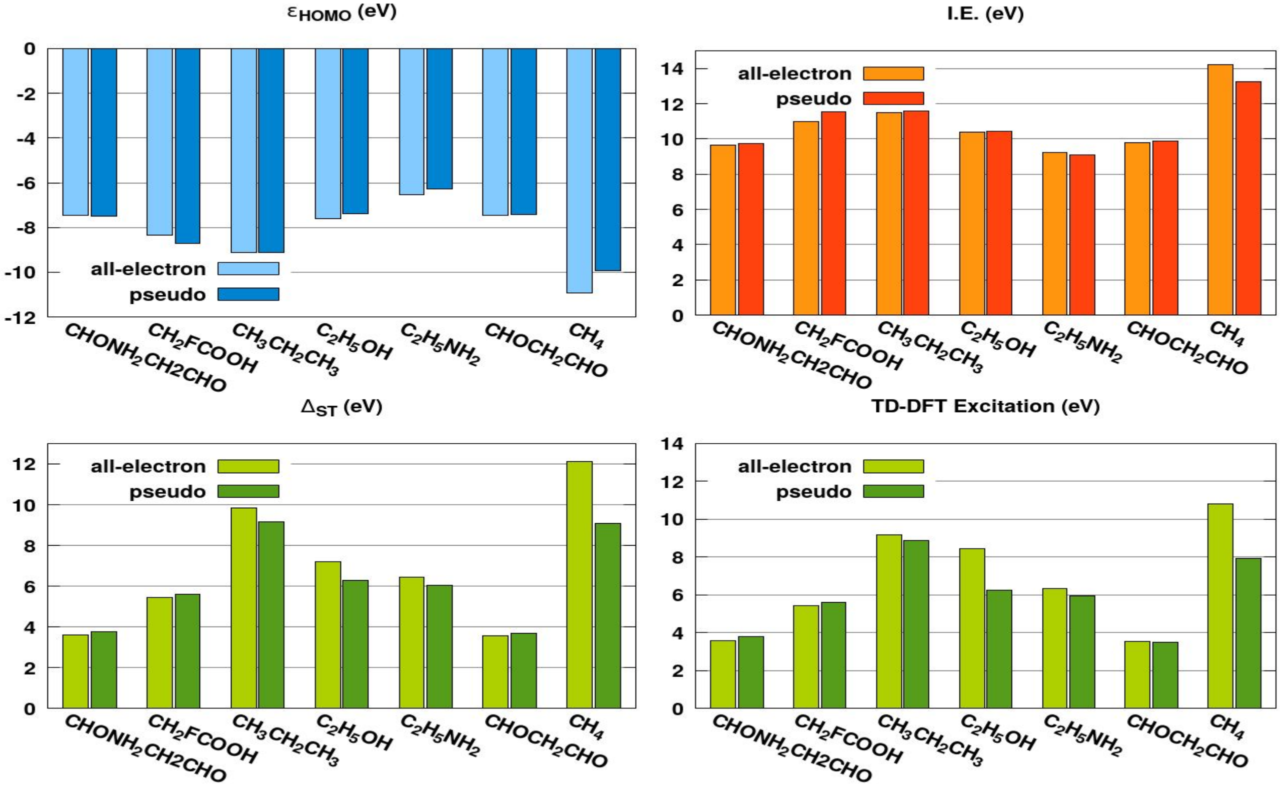
δ potentials: sp^3, two explicit electrons



δ Optimisation Criteria

HOMO
HOMO-1
HOMO-2
HOMO-3
HOMO-4
HOMO-5

Optimised on propane



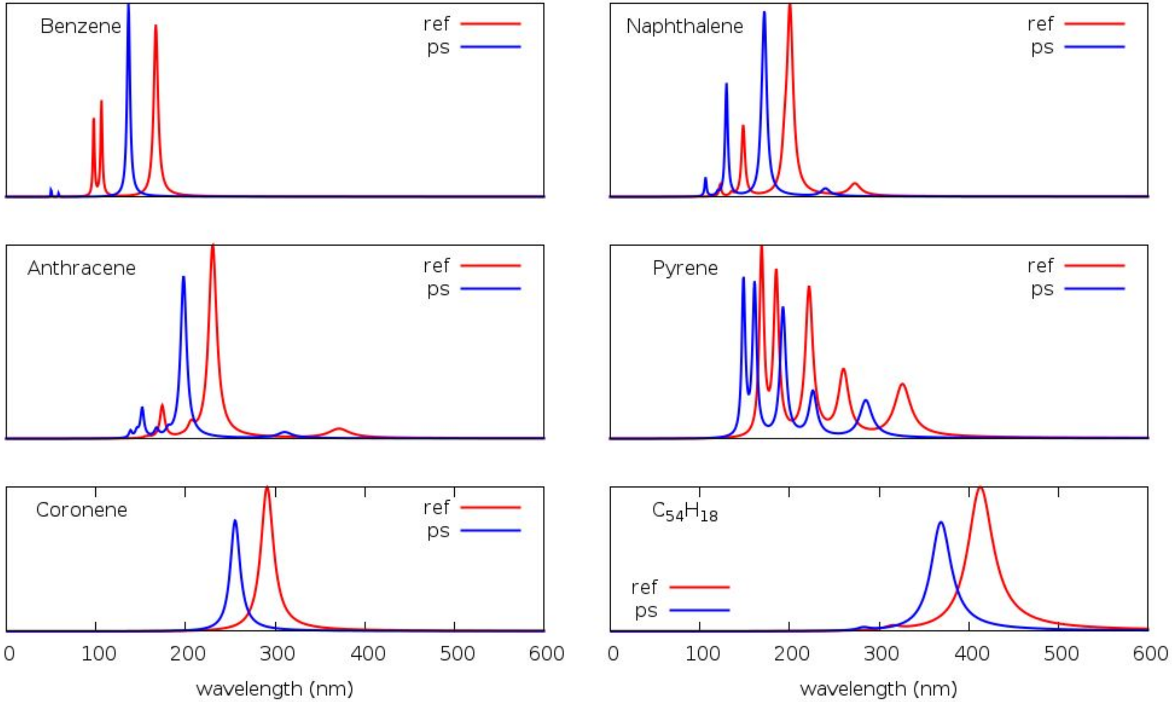
DFT-PBE0/def-SV(P)

Excitation Spectra with Pseudopotentials

Excitation spectra with pseudopotentials

PAH spectra with pseudopotentials:

- All π excitations reproduced
- Intensities correct
- Constant frequency shift, can this be fixed?



TDDFT-PBE0/def-SV(P)

Minimisation of Total Error H_{total}

For each optimisation criterion x_i, we have an error

$$\eta_i = \left| x_{i_{pseudo}} - x_{i_{ref}} \right|$$

and a total error

$$H_{total} = \sum \eta_i \omega_i$$

that we wish to minimise.

Which optimisation criteria can we use?

Over the last 3 years, various criteria have been used:

- Orbital energies
- Singlet-triplet gap
- Ionisation Energies
- HOMO-LUMO gap
- TD-DFT energies
- Spectral shape fitting

The Multi-Orbital Optimiser (MOO) program

1. The user creates a pseudosystem.
2. The user supplies reference optimisation criteria to MOO.
3. MOO tries to minimise the H_{total} by modifying pseudopotential parameters and running calculations via Turbomole.

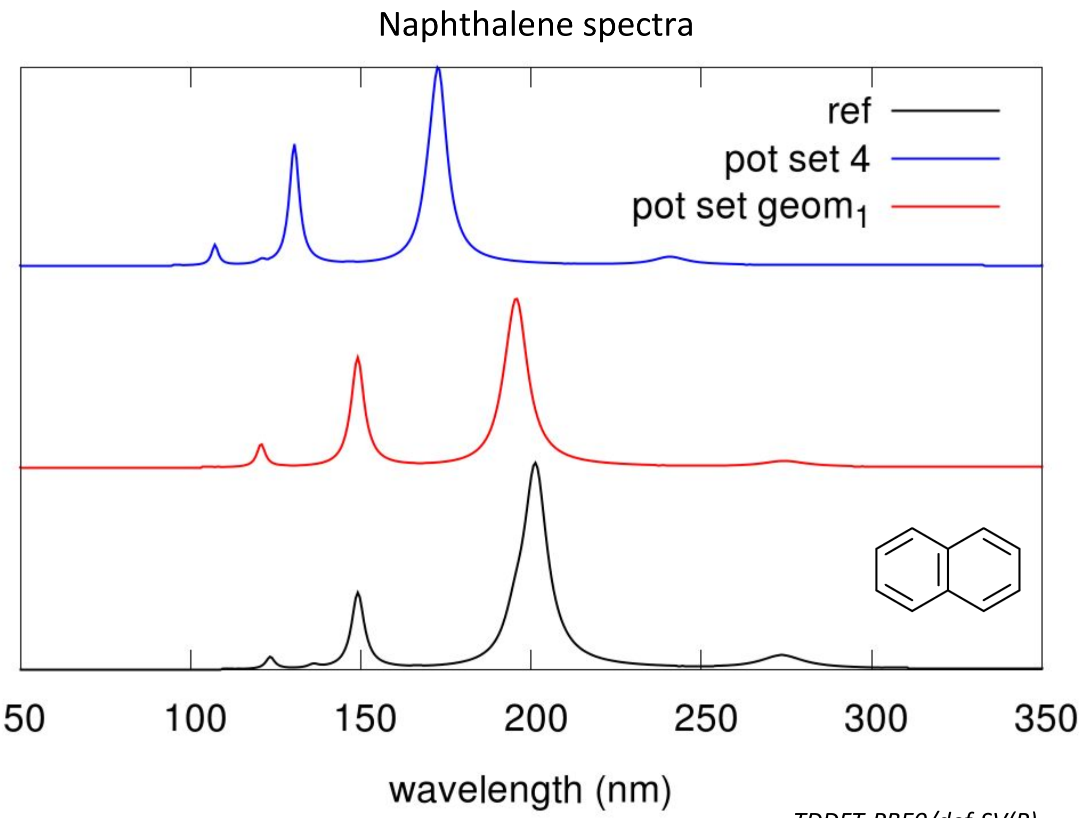
```
alex@Algernon:~/PycharmProjects/chem_scripts$ python3 moo.py
root        : INFO     Logging initialised...

                    #######################################
                     The Multi-Orbital Optimiser   (___)
                                                  <(o o)>______
                              (or MOO)              ../ ` # # \`;
                                                      \ ,___, /
                        A Punter, CTOM group           ||   ||
                      Aix-Marseille Université         ^^   ^^
                    #######################################

MOO file found.
Run optimisation?
1: Start MOO optimisation run.
2: Enter MOO setup.
 >>  2
What would you like to do?
1: Potentialise a molecule.
2: Optimise new potentials.
3. View references.
q: Quit
 >>  2
--------------------------------------------
OPTIMISATION MENU
--------------------------------------------
CURRENT SETTINGS:
ECPs to optimise:        ['c ecp-2 (s-f)']
Orbital Optimisation:    ON (orbitals: [])
Total Gap Optimisation:  OFF (comparison folders: [])
Seeded Optimisation:     OFF (seeds: 1)
Geometry Optimisation:   OFF (carbons of type sp2, indices: [1])
Initial guesses:         [1.0, 2.0]
WARNING: As seeded optimisation is OFF, you will need to supply your own initial guess for potential
parameters.
--------------------------------------------
1. Add ECP functions
2. Toggle MO energy optimisation (currently ON)
3. Molecular Orbital energy criteria
4. Toggle total energy difference optimisation (currently OFF)
5. Total energy difference criteria
6. Semi-random seed options
7. Potential geometry optimisation options
8. Set initial guesses for ECP parameters (only needed if not using semi-random seeds).
9. Run optimisation now
h. Help. Show optimisation guide.
b: Go back
 >>  9
Run optimisation (y/n)?
 >> 
```

Pseudopotential UV Spectra

Optimisation Criteria	
set4	geom_1
HOMO 1st ionisation π-π^* gap	HOMO LUMO LUMO+1
Optimisation System	
ethylene	


Naphthalene spectra

TDDFT-PBE0/def-SV(P)

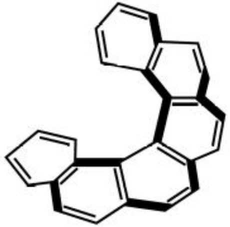
Complex Molecules

ECD: Electronic Circular Dichroism

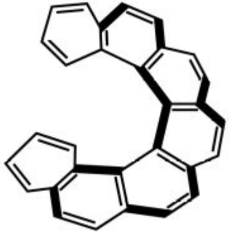
$$\epsilon_{CD} = \epsilon_{LCP} - \epsilon_{RCP}$$

- Difference between absorption of left-circularly-polarised (LCP) and right-circularly-polarised (RCP) EM waves in chiral molecules.
- ECD spectra have a much lower intensity (~10x) than regular absorption spectra.
- This sensitivity means they are a good test of pseudopotential accuracy.

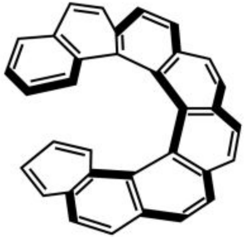
[n]helicenes



[6]Helicene

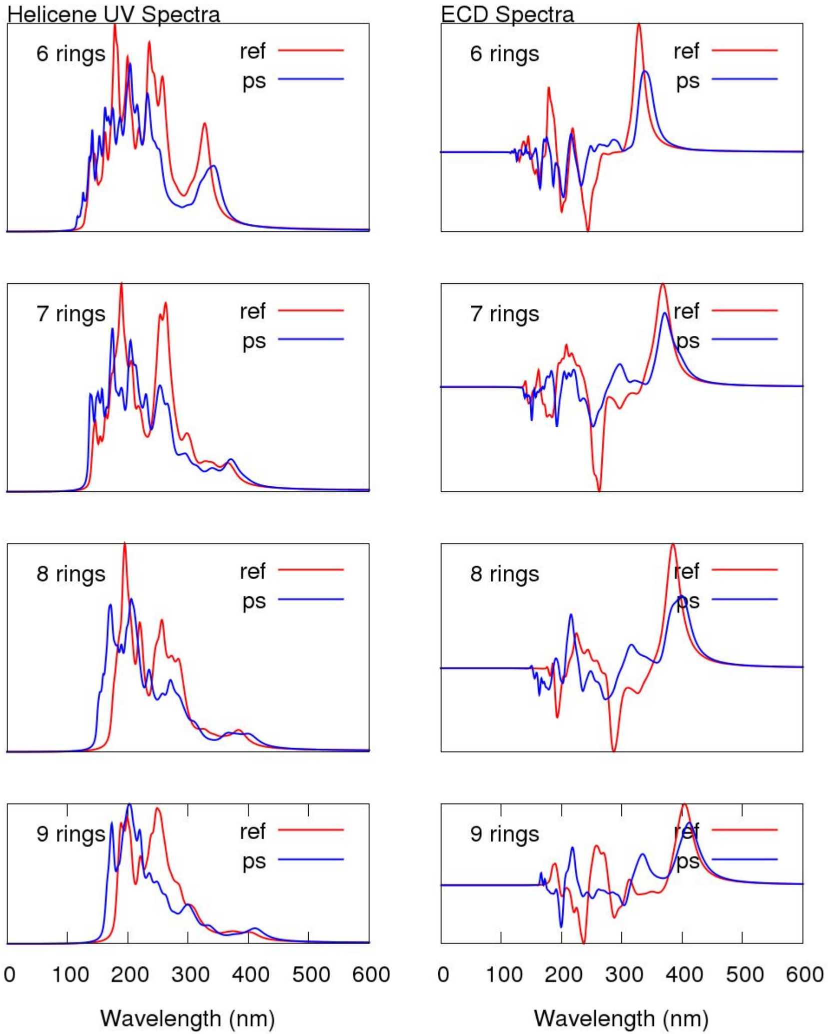


[7]Helicene



[8]Helicene

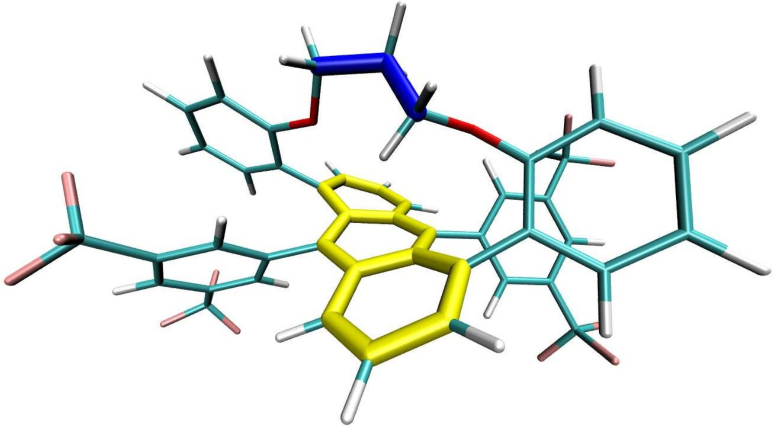
[9]Helicene



Challenges: Distortion of π rings, reproduction of ECD spectra (*P* helicity)

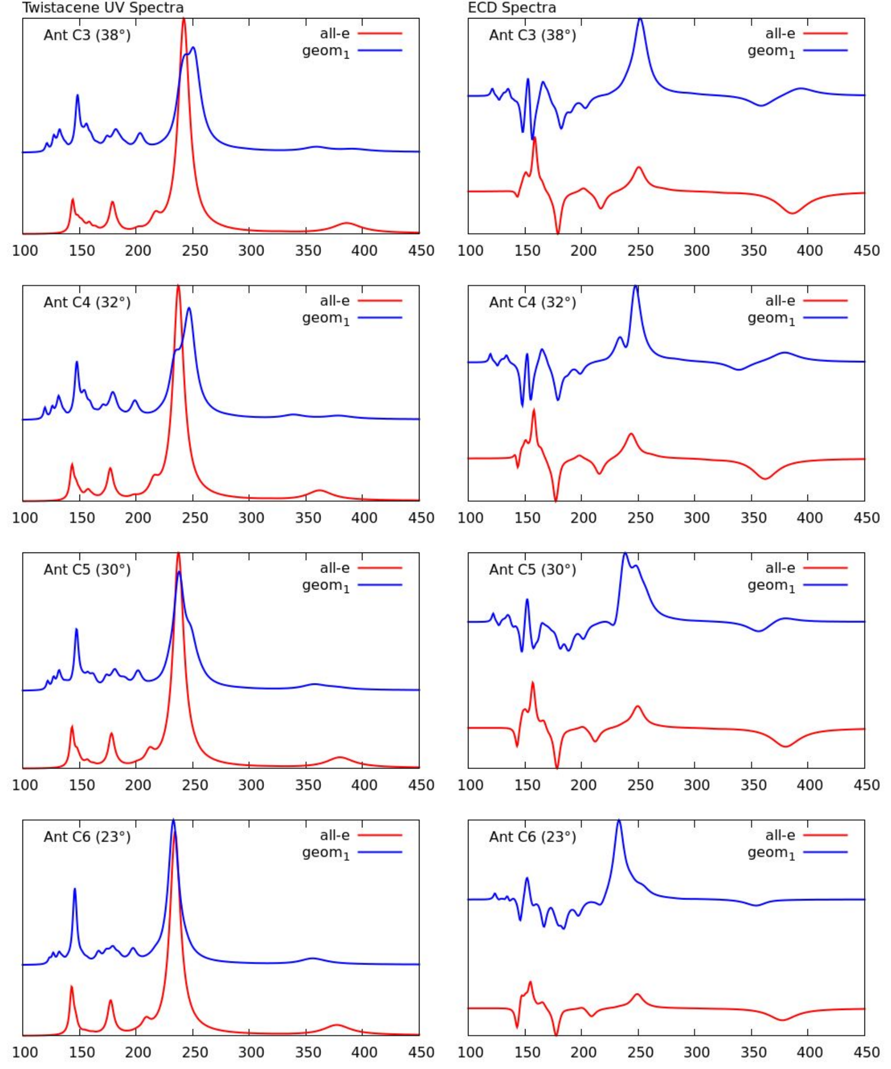
α (geom$_1$) potentials, TDDFT-PBE0/def-SV(P)

Twistacene

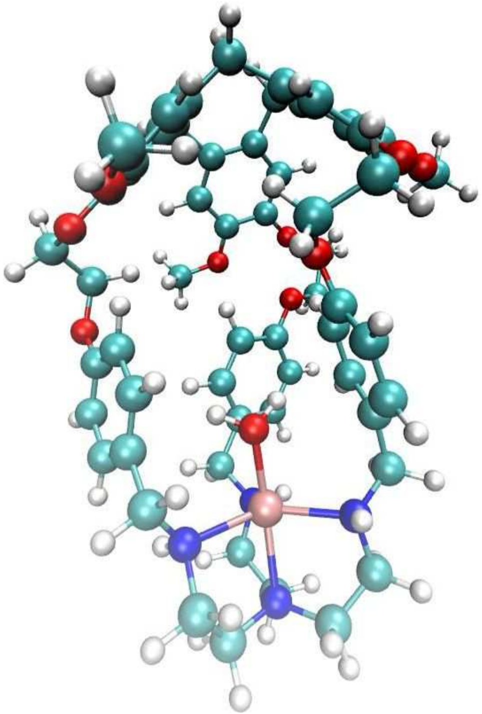


Challenges: Distortion of π rings, reproduction of ECD spectra

A. Bedi, L. J. W. Shimon and O. Gidron,
J. Am. Chem. Soc., 2018, vol 140, p. 8086–8090
α ($geom_1$) potentials, TDDFT-PBE0/def-SV(P)



Cu(II) Hemicryptophane



Molecule produced in collaboration with Chirosciences group at ISM2

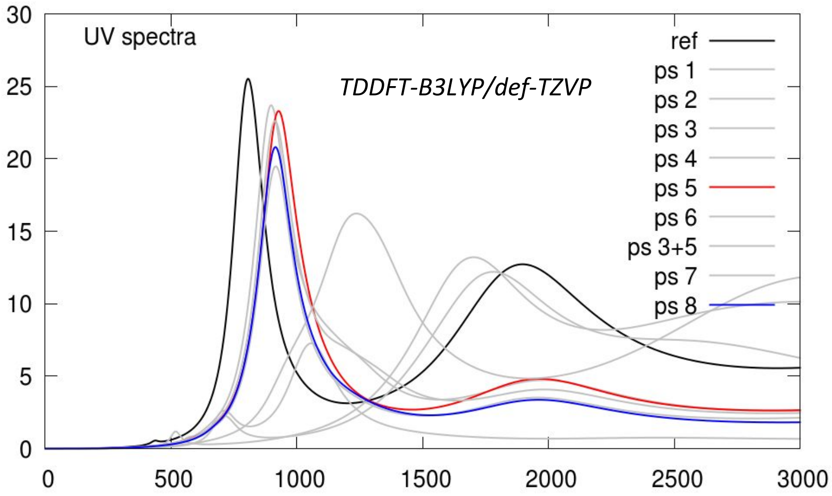
Challenges:

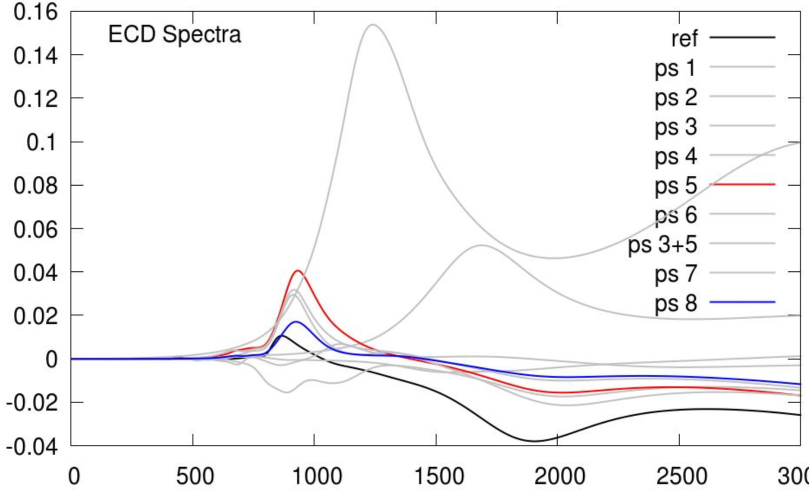
- Contains a metal atom
- Can use all potential types: $\alpha, \beta, \gamma, \delta$
- Reproduction of ECD spectra

System	e^-
--- all-e^-	545
--- ps 5	467
--- ps 8	413

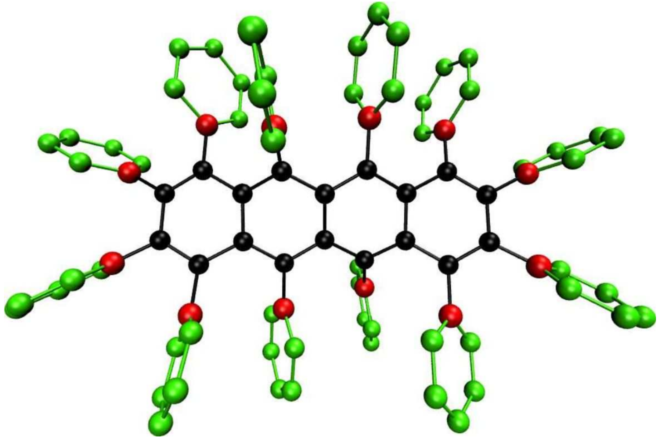
Heterobonding Rule: Pseudofragments should only be bound to all-e carbons:

C*-C-X



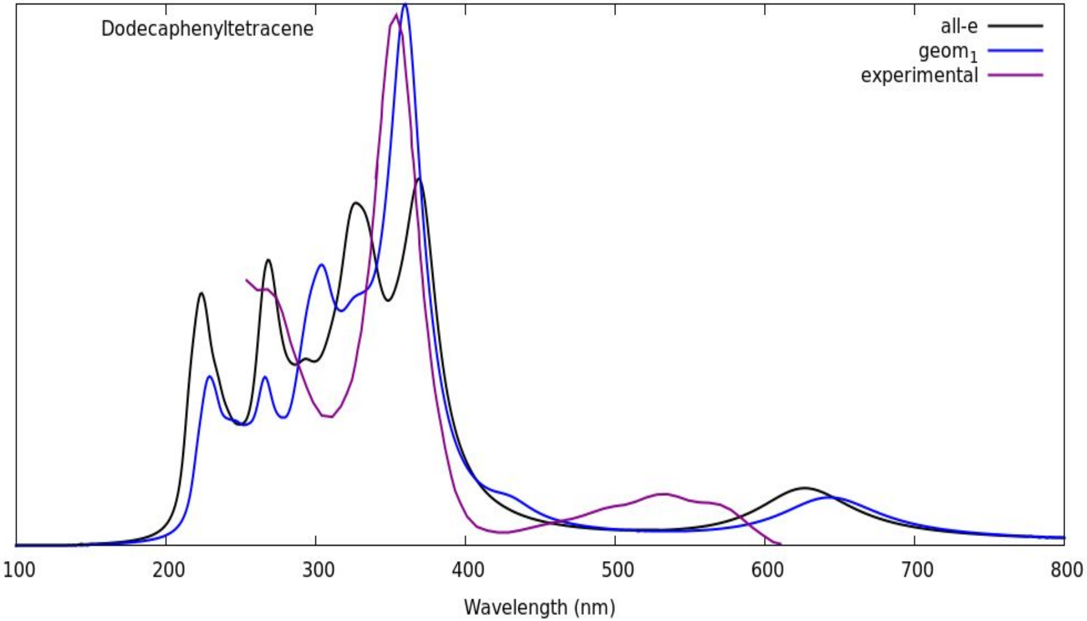


Dodecaphenyltetracene



Green: α potentials
Red: β potentials
Black: all-electron carbon

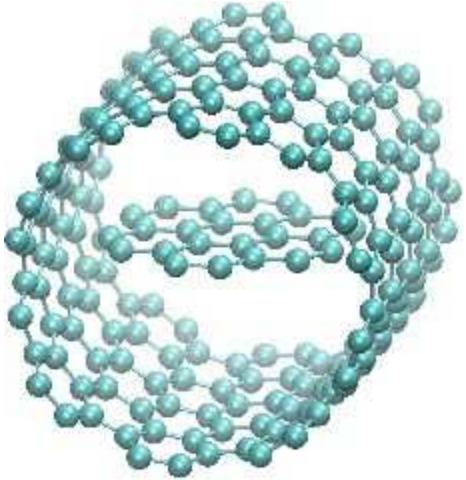
Challenges: Many overlapping and interlocking π rings

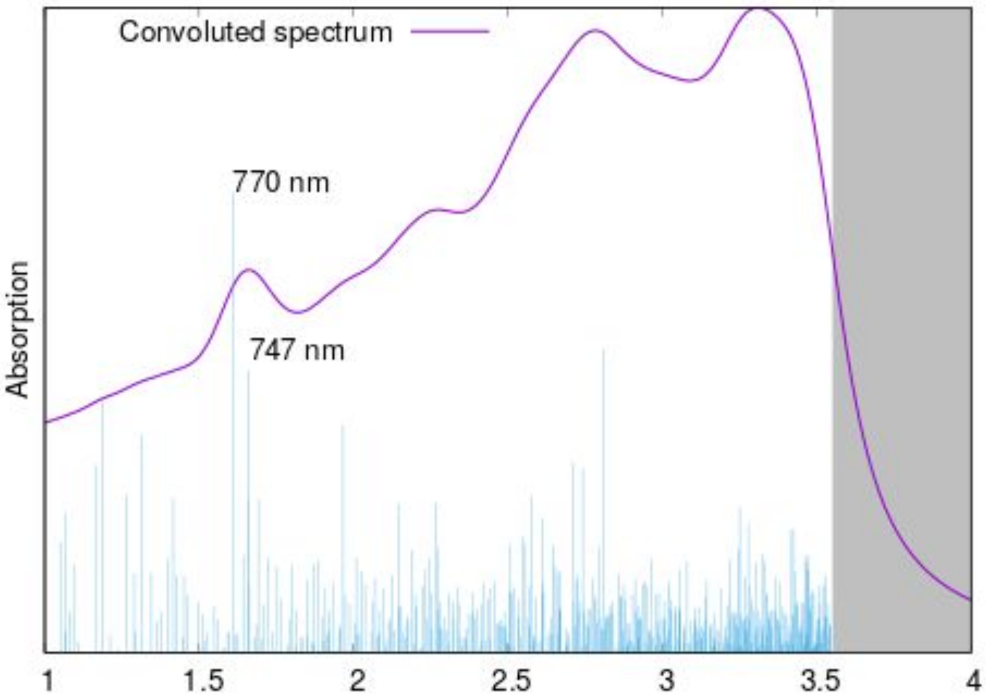


α (geom$_1$) and β potentials, TDDFT-PBE0/def-SV(P)

Y. Xiao, J. T. Mague, R. H. Schmehl et al.,
Angew. Chem, 2019, vol 58, p. 2831–2833

Nanotube-embedded Coronene





α (set4) potentials, TDDFT-PBE0/def-SV(P)

Can we find evidence of electron transfer between polymer and nanotube?

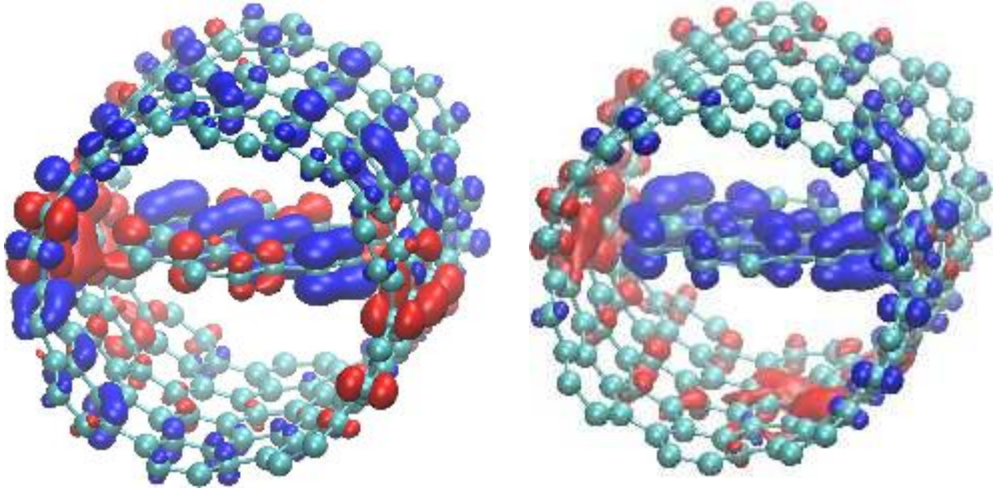
Challenges:

- Distortion of π rings
- Cluster approximation
- Large calculation, 200 excitations

A. Nakamura, K.-i. Yamanaka, K. Miyaura et al., *J. Phys. Chem. C*, 2018, vol 122, p. 16940–16949

Nanotube-embedded Coronene

Electron density transfer both ways between nanotube and coronene.



770nm

747nm

Overall electron density transfer from coronene to nanotube.

Electron density decreased in blue and increased in red regions.

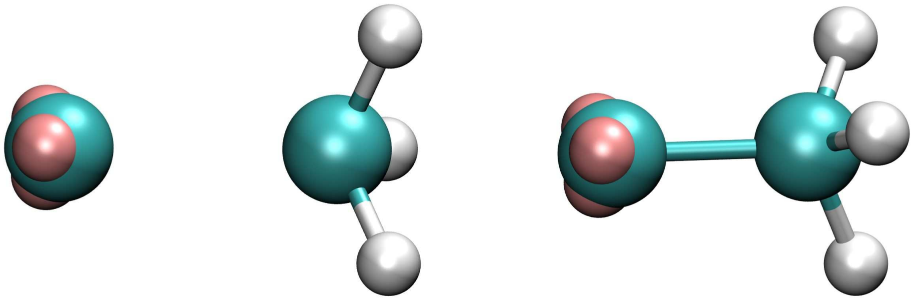
Geometry Optimisation

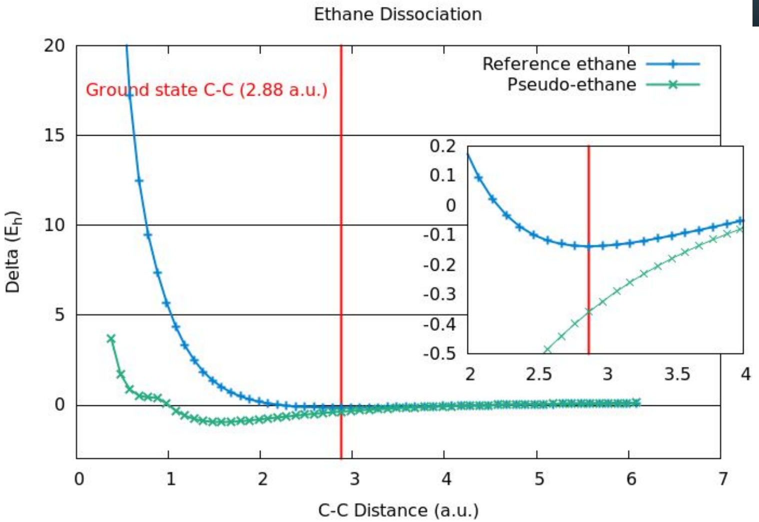
Geometry Optimisation

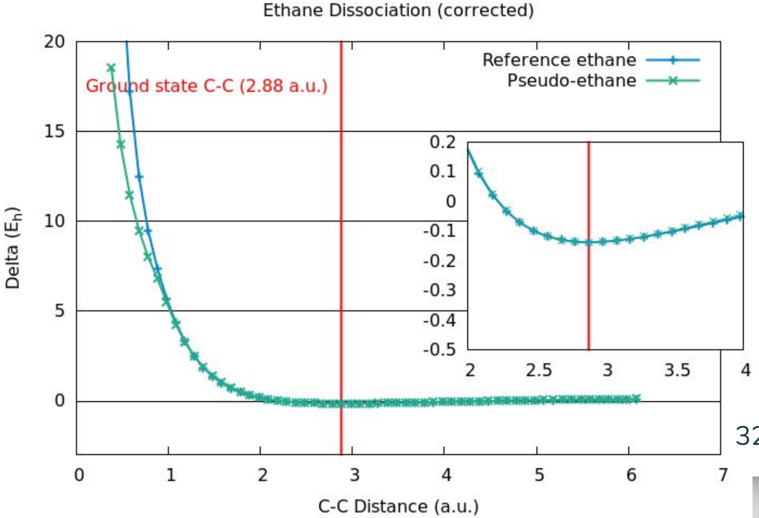
Potential gradients corrected by adding a fitting function of the form

$$g(x) = ae^{-b(x-x_0)}$$

This ensures the potentials fall into the correct geometry.

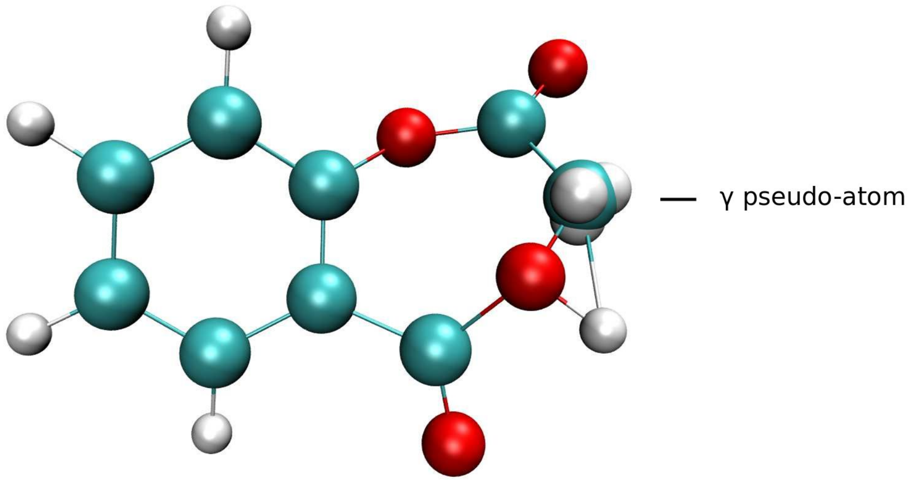



Ethane Dissociation


Ethane Dissociation (corrected)

Geometry Optimisation: Geometric Collapse

- Molecules with more degrees of freedom allow other parts of the molecule to approach the potentials.
- Pseudofragments are ‘sticky’, their atoms can ‘bond’ with them in unphysical ways.
- Pseudopotentials are too attractive at a long range.



A ‘stuck’ aspirin molecule

Timings

- Significant gain in time per iteration across all molecules.
- The gain is particularly improved in molecules with a reduced carbon basis set.
- For some systems (cages), the number of iterations needed for convergence is increased so much as to result in an overall increase in calculation time.
- Gains across all molecules for TDDFT calculation.

SCF Iterations		**Gain**	**Gain / Iteration**	**TDDFT Gain**	**e^- remaining (%)**
All-e^-	**Pseudo**				
Dodecaphenyltetracene					
382	54	42.91	6.07	12.21	49
Ant-c3					
20	30	14.25	21.38	75.82	14
[10]helicene					
31	32	5.37	5.55	1.71	15
Hemicryptophane Cage					
110	434	0.62	2.39	3.15	76

Conclusions

- We can create pseudopotential fragments that recapture most of the electronic behaviour of molecules in spite of removing most of the fragments' electrons and nuclei.
- We have developed a more general method for creating these potentials by considering the different molecular properties we might measure to build up a picture of the underlying physics.
- If used judiciously (i.e. applying the 'heterobonding rule'), these potentials can be used to reproduce some surprisingly complex and sensitive systems and effects.

Further Development

Two major ideas for improvement of pseudopotential accuracy and computational efficiency:

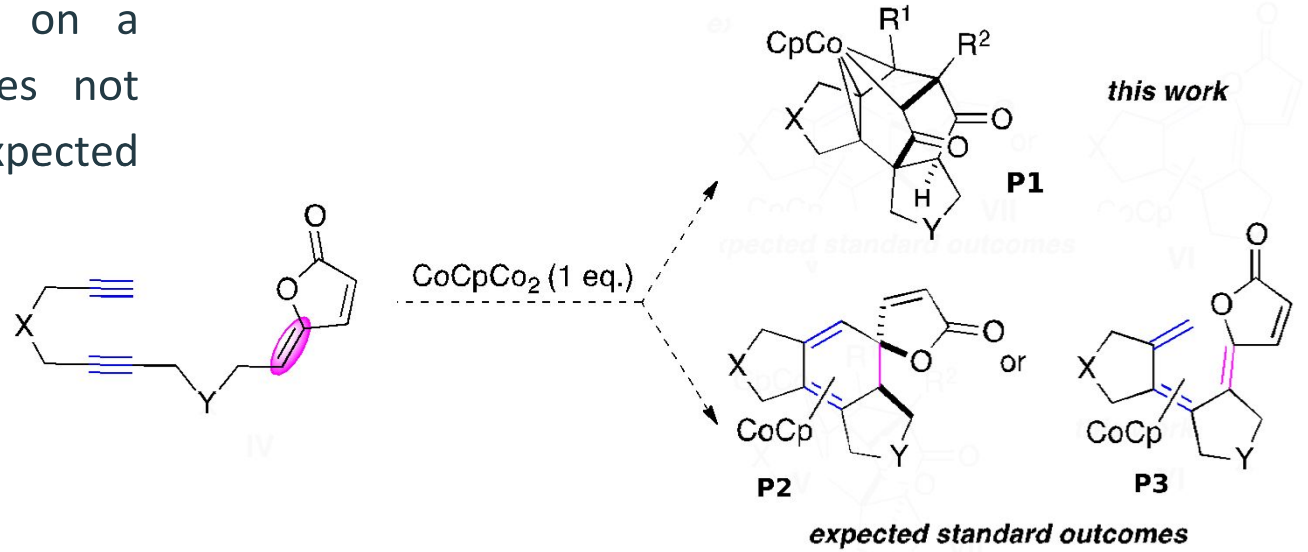
- **Additional pseudopotential functions** - Allows finer tuning of potentials, increasing accuracy
- **Optimisation of custom basis sets** - Can improve accuracy and perhaps reduce the number of basis functions, likely improving speed.

Cobalt-Mediated Cycloaddition

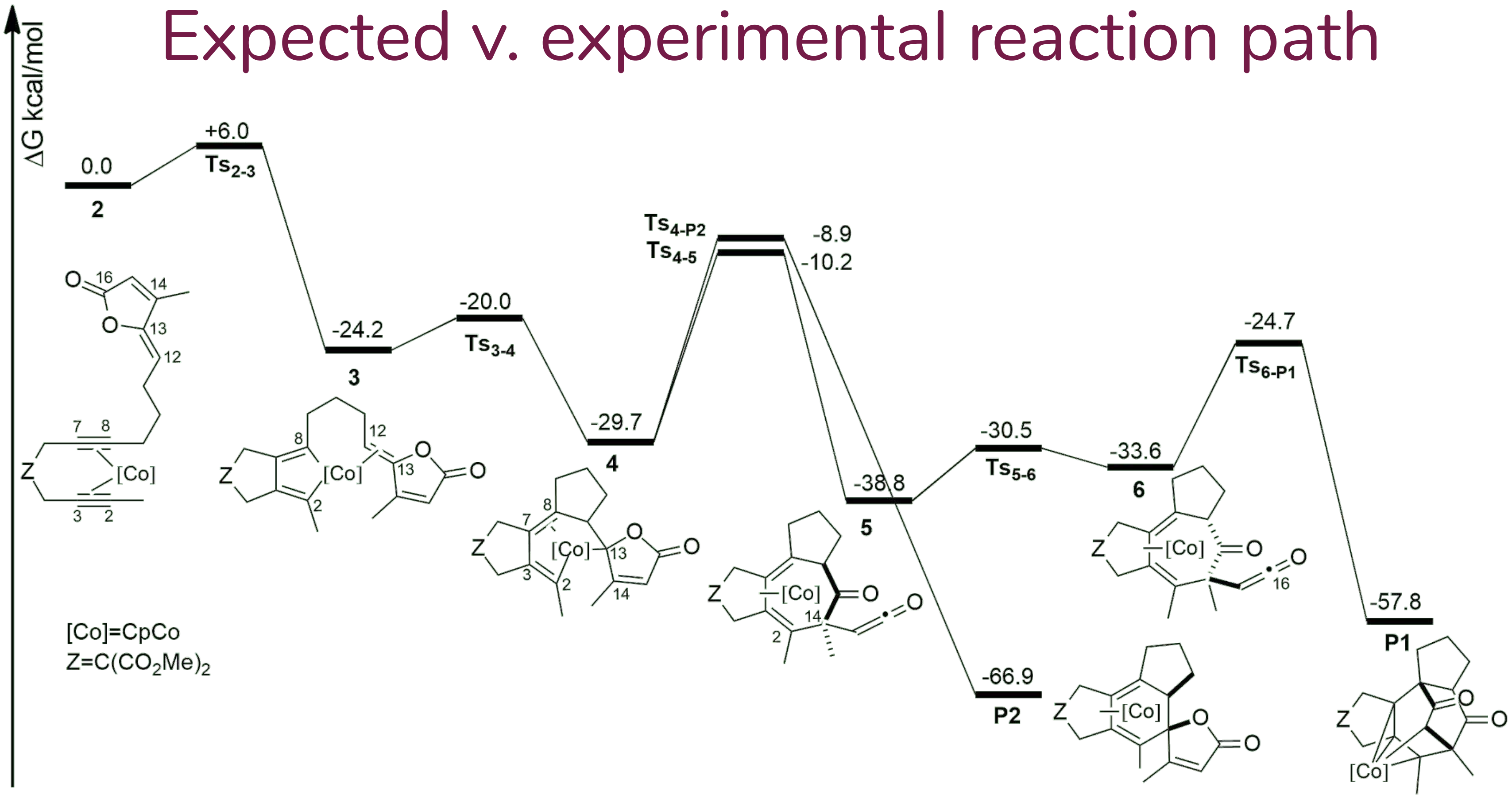
Cobalt-mediated Cycloaddition

A CpCo-mediated (2+2+3) cycloaddition based on a known reaction does not produce the expected results.

Why is this?



Expected v. experimental reaction path



[Co]=CpCo

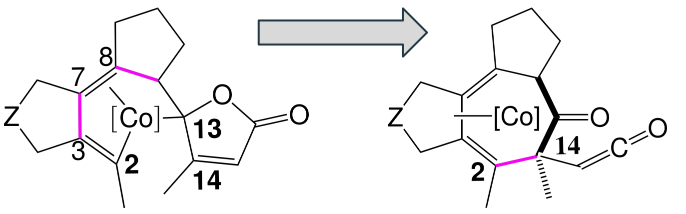
Z=C(CO_2Me)$_2$

BP86-D3/def2-TZVP , COSMO

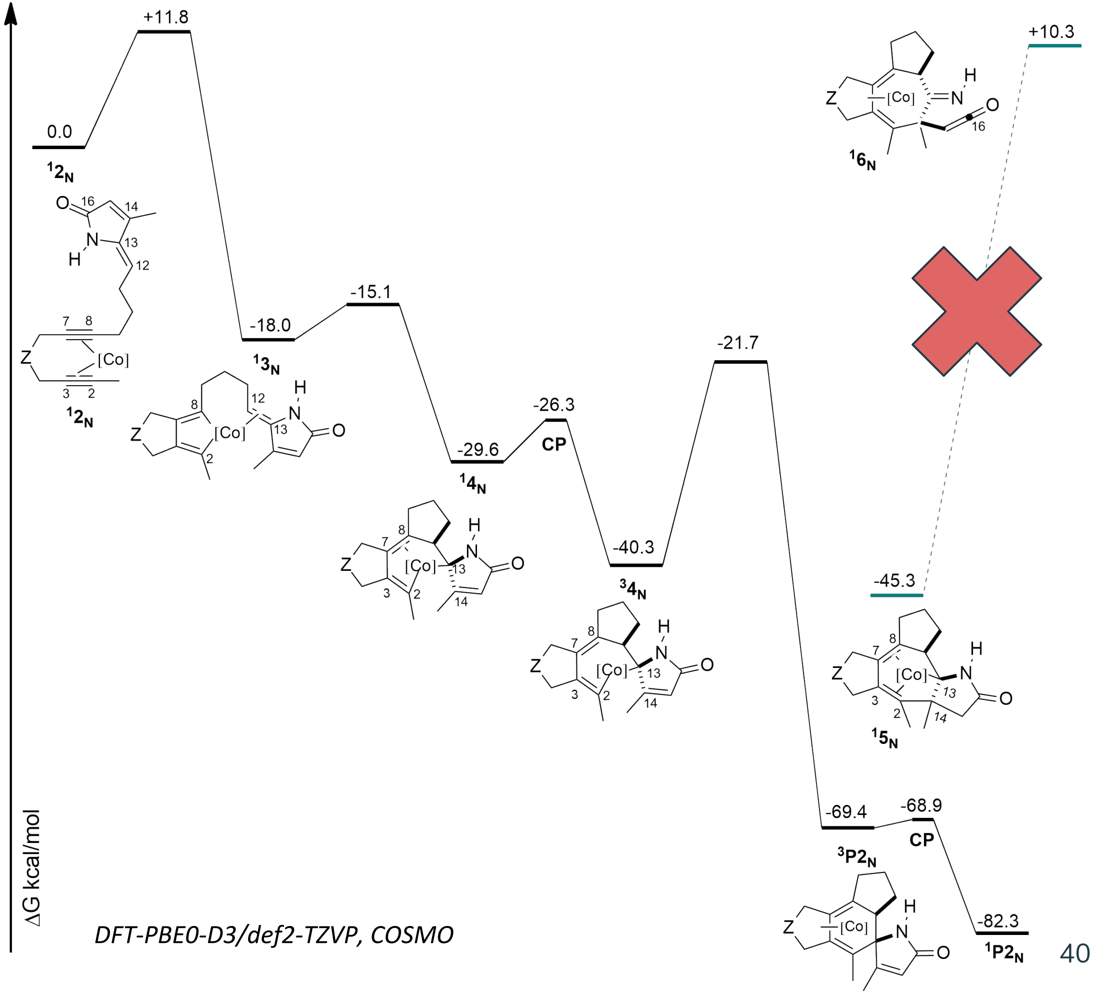
Lactone v. Lactame

With the lactone, the C-O bond breaks at the fourth step, leading to the unexpected result.

With a lactame, the C-N bond does not break, meaning the reaction proceeds as expected.



Lactone



Cobalt Conclusions

- The breaking of the lactone is a crucial step in the reaction.
- Calculations show that with a different functional group (lactame) the C-N bond is unable to break, and the reaction proceeds as expected.
- Work is ongoing to determine fully the mechanism.

Acknowledgements

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Dr. Muriel Amatore

Aix*Marseille
université
Initiative d'excellence

Thank you

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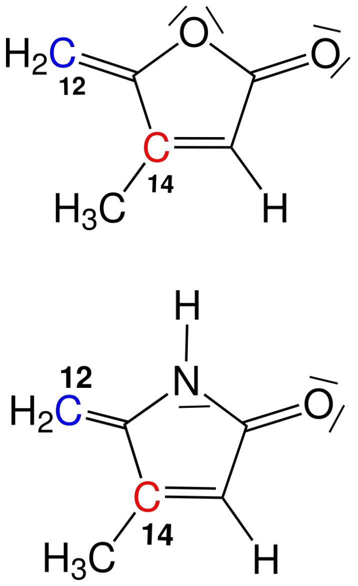
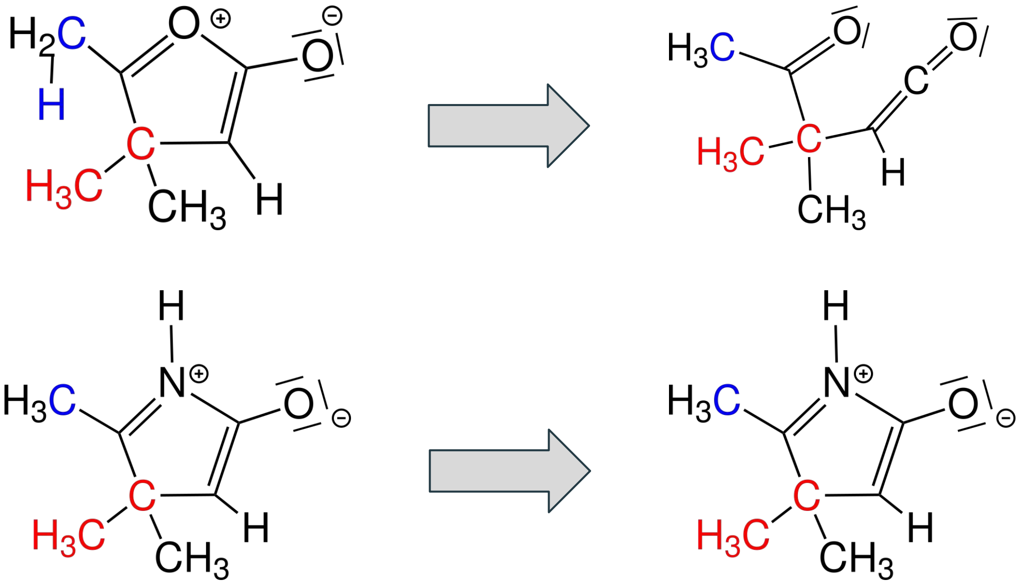
Institut des
Sciences Moléculaires
de Marseille
UMR 7313

Cobalt Extra



Initial molecule



Molecule at diverging step

Molecule after diverging step

LACTONE

LACTAME