Going beyond Single Reference Methods

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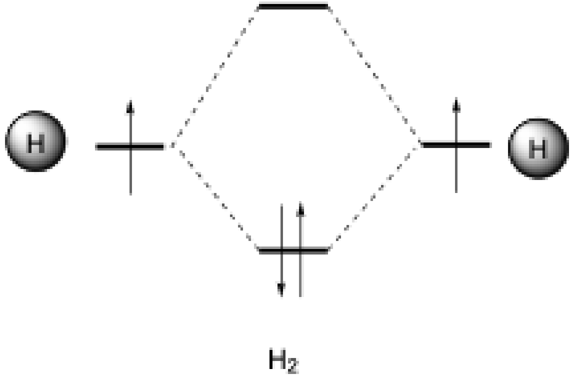
Hartree-Fock and Static Correlation

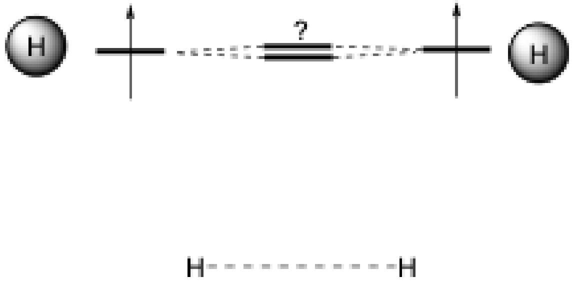
Due to the mean-field nature of Hartree-Fock theory, it fails to capture the instantaneous electron-electron repulsion, leading to its **complete** negligence of correlation energy

$$E_{Corr} = E_{Post-HF} - E_{HF}$$

Static Correlation

Static correlation represents an energy gain coming from including low-energy Slater determinants that arises from a set of degenerate or quasi-degenerate orbitals. Needs more than one Slater determinant as reference (**Multi-reference**)





Dynamic Correlation

The rest of the correlation effect that is not related to degeneracy. This can be added by including more configurations (CISD); perturbation theory (MPn); couple-cluster ansatz (CCSD); or throw it into $E_{XC}[\rho]$ term in Hamiltonian (DFT).

*The distinction between dynamic and static correlation is a bit arbitrary

Multi-reference Nature of Chemical Systems

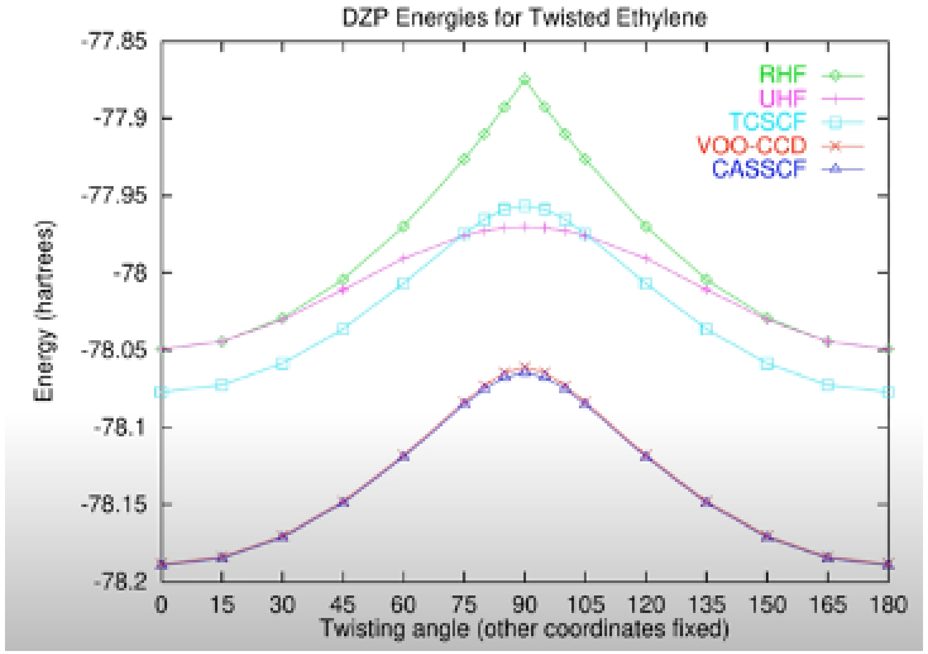
Multi-reference System: System that requires all nearly degenerate electron configurations in starting (reference) wavefunction

Bond dissociation (e.g., H_2 splitting into two atoms, twisting a double bond).

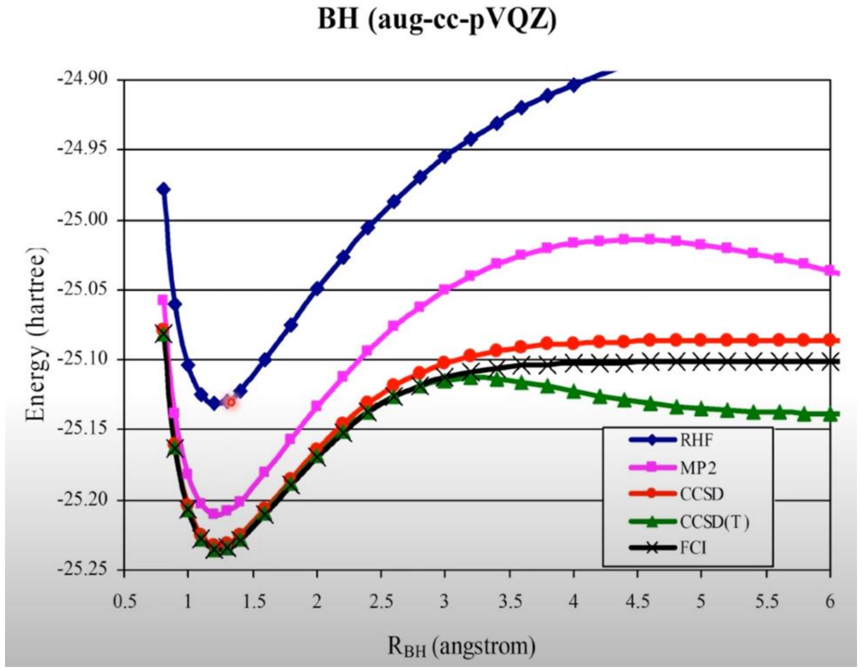
Open-shell systems with degenerate orbitals: (O_2 with a triplet ground state, distant diradicals).

Exicited States

Twisting an ethylene



B-H bond dissociation



Multi-reference Nature of Chemical Systems

Multi-reference vs **Multi-configuration**

Multi-Configuration: The final wavefunction is a sum of multiple Slater determinants

Multi-Reference: The wavefunction starts from a multi-configuration reference.

A multireference method is always multi-configuration, but a multi-configuration method might be single-reference (eg: CISD, CCSD)

Single-Reference, Single-Configuration: DFT, MP2, HF

Single-Reference, Multi-Configuration: CCSD, CISD

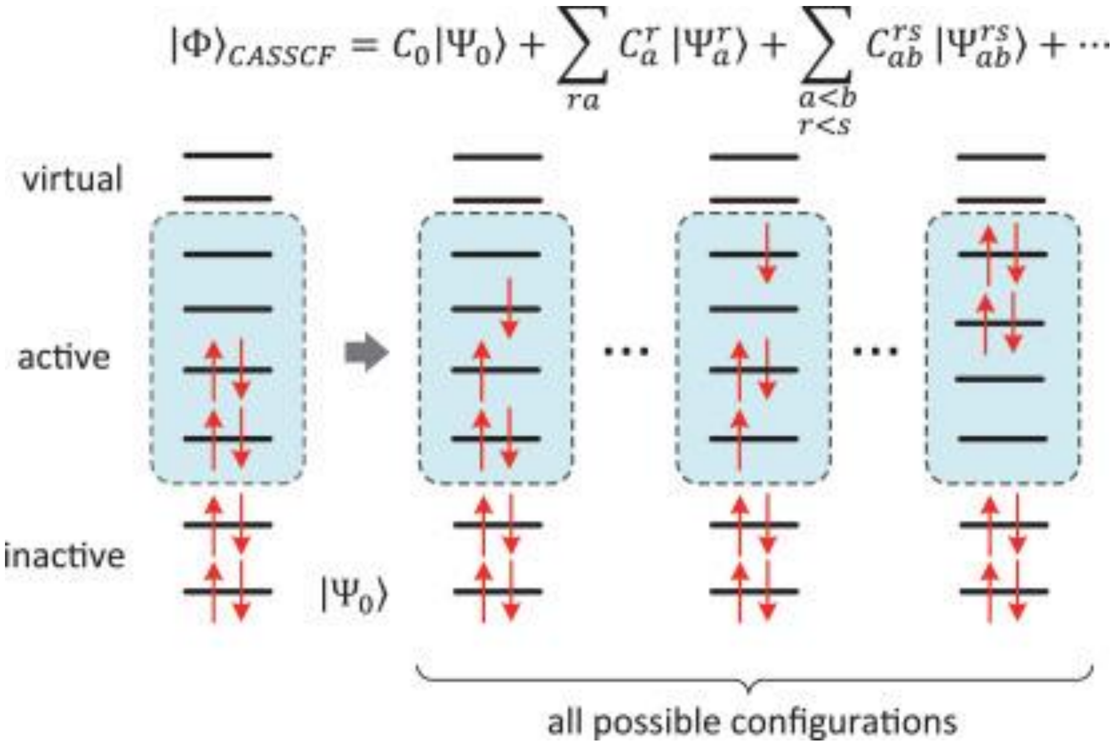
Multi-Reference: CASSCF, MRCI, CASPT2, NEVPT2, MR-CCSD, Full-CI

Unlike DFT, Multi-Reference methods are NOT black box, use it with caution!!!

CASSCF

Multi-Configurational self-consistent field (MCSCF): Include **all nearly degenerate** electron configurations, find orbitals which minimize the energy of the mixture of near-degenerate determinants.

Complete Active Space SCF (CASSCF): linear combination of all CSFs (Full CI) in a restricted active space from a particular number of electrons



$$|\Phi\rangle_{CASSCF} = C_0|\Psi_0\rangle + \sum_{ra} C_a^r\,|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} C_{ab}^{rs}\,|\Psi_{ab}^{rs}\rangle + \cdots$$

Notation: **CASSCF(m,n)**
m: # of active orbitals
n: # of active electrons

Active space: orbitals and electrons important for the multi-reference problem.

Virtual orbitals will remain unoccupied, inactive orbitals will remain doubly-occupied.

Unlike Configuration Interaction, CASSCF will variationally change the orbital coefficient as well

SA-CASSCF

State averaging: Optimize the orbitals not for a single state but for the average of several states.

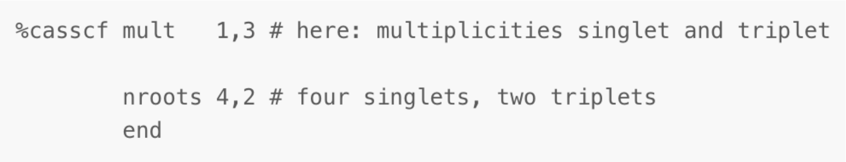
$$E_I\left(\mathbf{c},\mathbf{C}\right)=\sum_{pq}\Gamma_q^{p(I)}h_{pq}+\sum_{pqrs}\Gamma_{qs}^{pr(I)}\left(pq\left|rs\right.\right)$$

The average energy is simply obtained from averaging the density matrices using arbitrary weights.

$$\Gamma_q^{p(av)}=\sum_I w_I\Gamma_q^{p(I)}$$

$$\Gamma_{qs}^{pr(av)}=\sum_I w_I\Gamma_{qs}^{pr(I)}$$

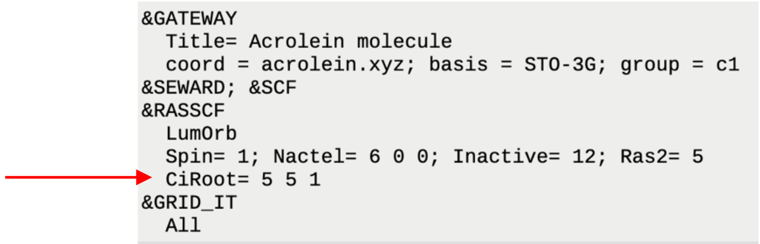
ORCA



```
%casscf mult   1,3 # here: multiplicities singlet and triplet

        nroots 4,2 # four singlets, two triplets
        end
```

MOLCAS



```
&GATEWAY
  Title= Acrolein molecule
  coord = acrolein.xyz; basis = STO-3G; group = c1
&SEWARD; &SCF
&RASSCF
  LumOrb
  Spin= 1; Nactel= 6 0 0; Inactive= 12; Ras2= 5
  CiRoot= 5 5 1
&GRID_IT
  All
```

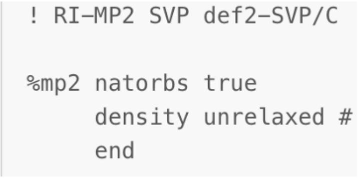
State-averaging is required for excited-state calculations.

Practical Guide for running MCSCF calculation

General workflow

1. Perform a UHF/ROHF/MP2/DFT calculation, save the **natural** orbitals

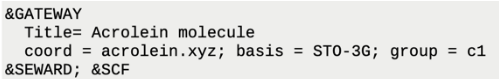
ORCA



```
! RI-MP2 SVP def2-SVP/C

%mp2 natorbs true
     density unrelaxed #
     end
```

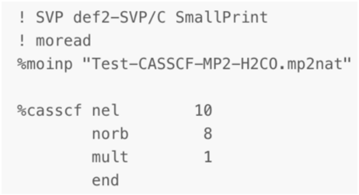
MOLCAS



```
&GATEWAY
  Title= Acrolein molecule
  coord = acrolein.xyz; basis = STO-3G; group = c1
&SEWARD; &SCF
```

2. Read in the orbitals and perform CASSCF

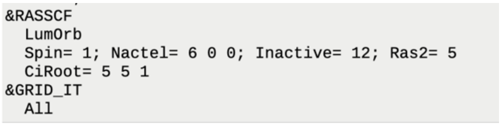
ORCA



```
! SVP def2-SVP/C SmallPrint
! moread
%moinp "Test-CASSCF-MP2-H2CO.mp2nat"

%casscf nel       10
        norb       8
        mult       1
        end
```

MOLCAS

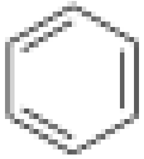


```
&RASSCF
  LumOrb
  Spin= 1; Nactel= 6 0 0; Inactive= 12; Ras2= 5
  CiRoot= 5 5 1
&GRID_IT
  All
```

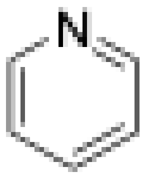
*The maximum active space varies between software.
For ORCA, usually CAS(14,14) is the upper limit
For software designated for MR calculation, the upper limit can be as big as CAS(20,20)

How to select active space?

Method 1: include all and lone-pair electrons

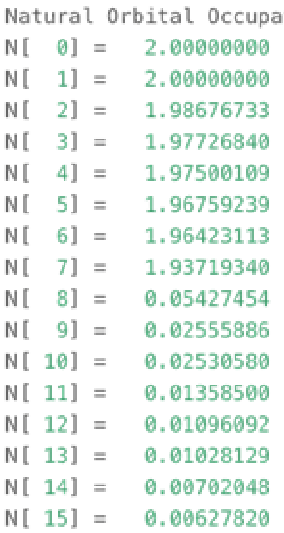


CAS(6,6)

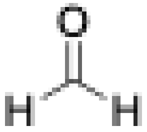


CAS(8,8)

Method 2: Orbital occupation number from MP2



```
Natural Orbital Occupation Numbers:
N[  0] =   2.00000000
N[  1] =   2.00000000
N[  2] =   1.98676733
N[  3] =   1.97726840
N[  4] =   1.97500109
N[  5] =   1.96759239
N[  6] =   1.96423113
N[  7] =   1.93719340
N[  8] =   0.05427454
N[  9] =   0.02555886
N[ 10] =   0.02530580
N[ 11] =   0.01358500
N[ 12] =   0.01096092
N[ 13] =   0.01028129
N[ 14] =   0.00702048
N[ 15] =   0.00627820
```



Pick orbitals and electrons within the range **0.02~1.98** of occupation number

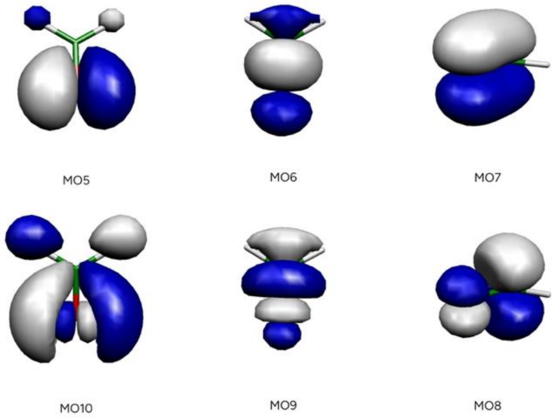
$\mathrm{CAS}(10,8) \longrightarrow \mathrm{CAS}(6,6)$

Adding doubly occupied or empty orbitals will cause convergence issue

Practical Guide for running MCSCF calculation

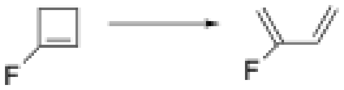
Orbital checking and switching

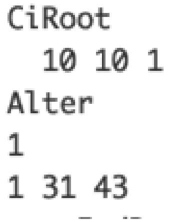
It is always advised to check the orbitals before doing the CASSCF calculation, especially for organometallics.



Sometimes it is necessary to switch orbitals, especially when the orbital of interest is initially not in the active space.

Eg:





```
CiRoot
  10 10 1
Alter
1
1 31 43
```

MOLCAS

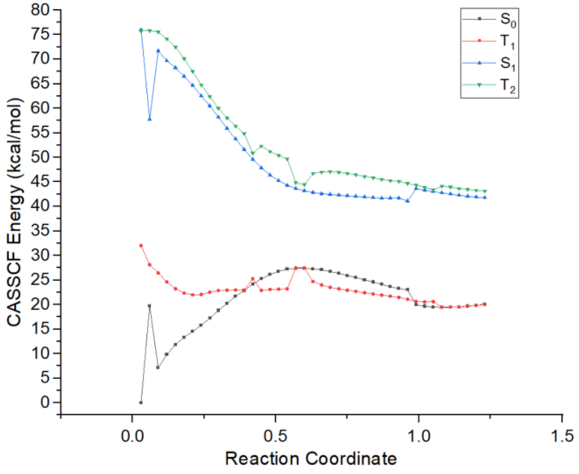
Basis set

MOLCAS has a set of basis set that have been designed to give a balanced description of the atoms in ground, excited, and ionized states, called Atomic Natural Orbital (ANO) basis set.

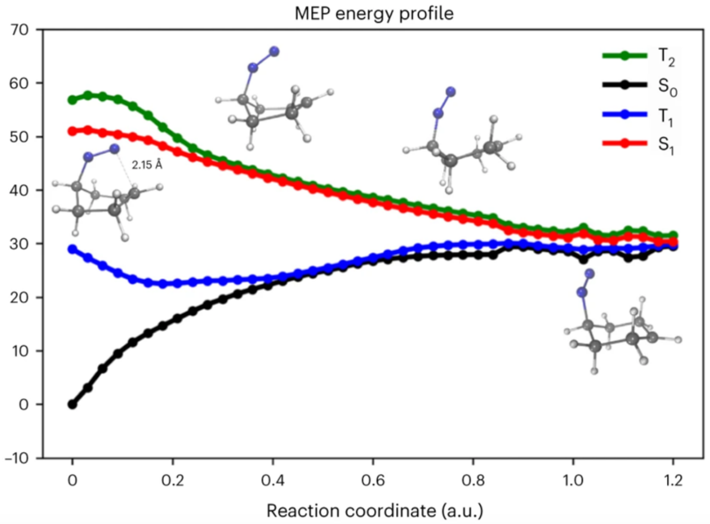
ANO-S-VDZP is the most widely used basis set, similar to 6-31G(d), but larger

Multi-Reference Perturbation Theory

CASSCF still neglects almost all dynamic correlations, giving large error in energy. One way to add dynamic correlation energy is to apply perturbation theory to CASSCF wavefunctions



CASSCF(8,8)/ANO-S-VDZP//revPBE(8,8)/ANO-S-VDZP



CASPT2(8,8)/ANO-S-VDZP//revPBE(8,8)/ANO-S-VDZP

Usually take structure and wavefunction from CASSCF calculation, and calculate energy with **CASPT2** or **NEVPT2** or DCD-CAS

NEVPT2 is in general recommended due to multiple reasons: free from intruder state problem, size-consistency, higher efficiency (strongly contracted).

Adiabatic and Diabatic States

Excited-state calculation is another field that requires multi-reference calculations.

B.O. approximation ⟶ Adiabatic states (eigenstates)

$$\Psi(r;R) = \xi_1(r;R)\phi_1(R) + \xi_2(r;R)\phi_2(R)$$

Incorporating nuclear kinetic energy into Hamiltonian, adiabatic state as basis

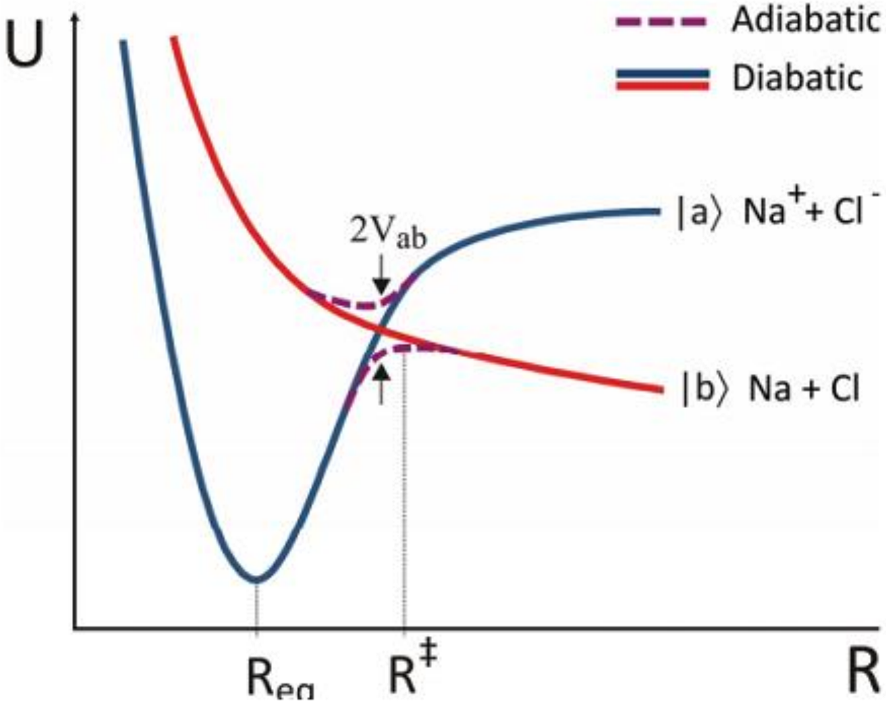
$$\begin{pmatrix} \hat{H}_{11} + \hat{T}_{11} & \hat{T}_{12} \\ \hat{T}_{21} & \hat{H}_{22} + \hat{T}_{22} \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix} = E \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix}$$

To remove the off-diagonal term, we can perform diabatic transformation

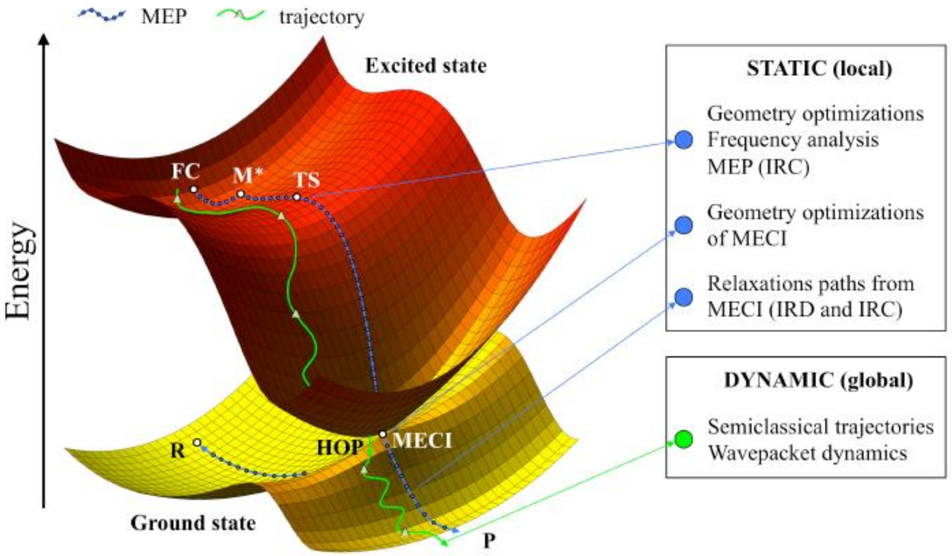
$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} cos\gamma & sin\gamma \\ -sin\gamma & cos\gamma \end{pmatrix} \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix}$$

Diabatic form $\Psi(r;R) = \psi(r;R)_1\tilde{\Phi}(R)_1 + \psi(r;R)_2\tilde{\Phi}(R)_2$

"Physically or Chemically meaningful"



Moldelling Photochemical Reactions

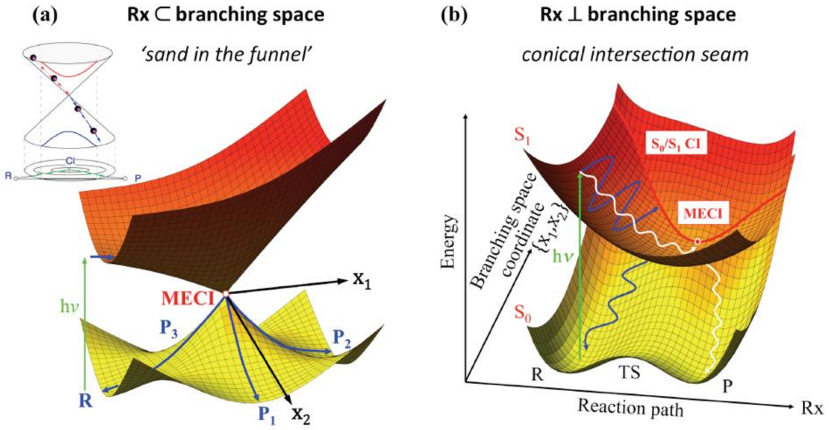


STATIC (local)

- Geometry optimizations
  Frequency analysis
  MEP (IRC)
- Geometry optimizations of MECI
- Relaxations paths from MECI (IRD and IRC)

DYNAMIC (global)

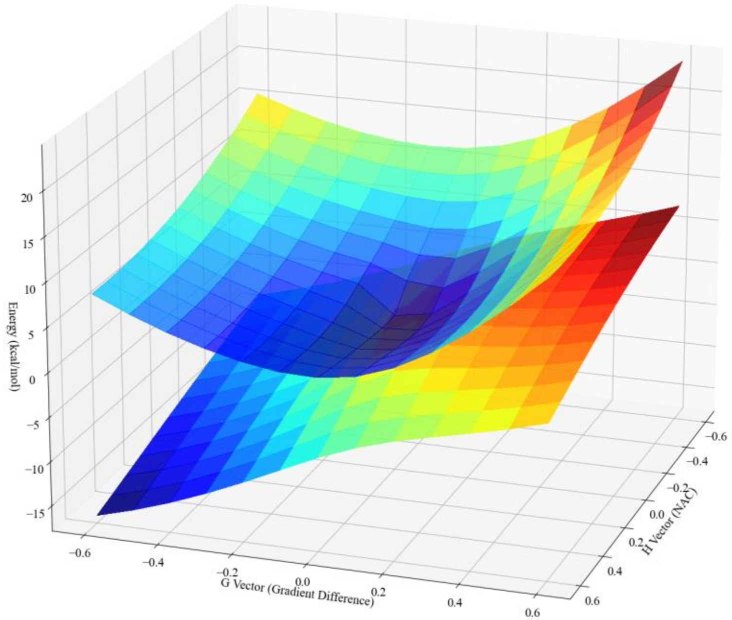
- Semiclassical trajectories
  Wavepacket dynamics

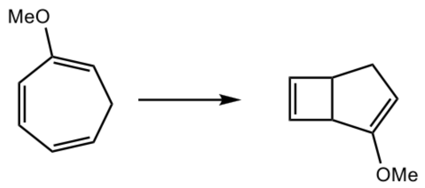

(a) Rx ⊂ branching space

'sand in the funnel'

(b) Rx ⊥ branching space

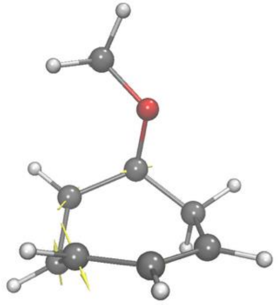
conical intersection seam



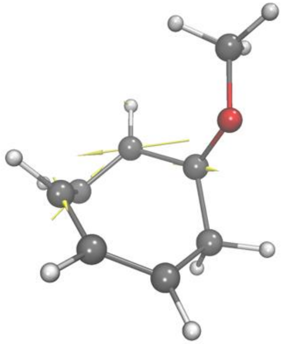


Gradient Difference vector

$$\mathbf{x_1} = \frac{\partial(E_1 - E_2)}{\partial R}$$



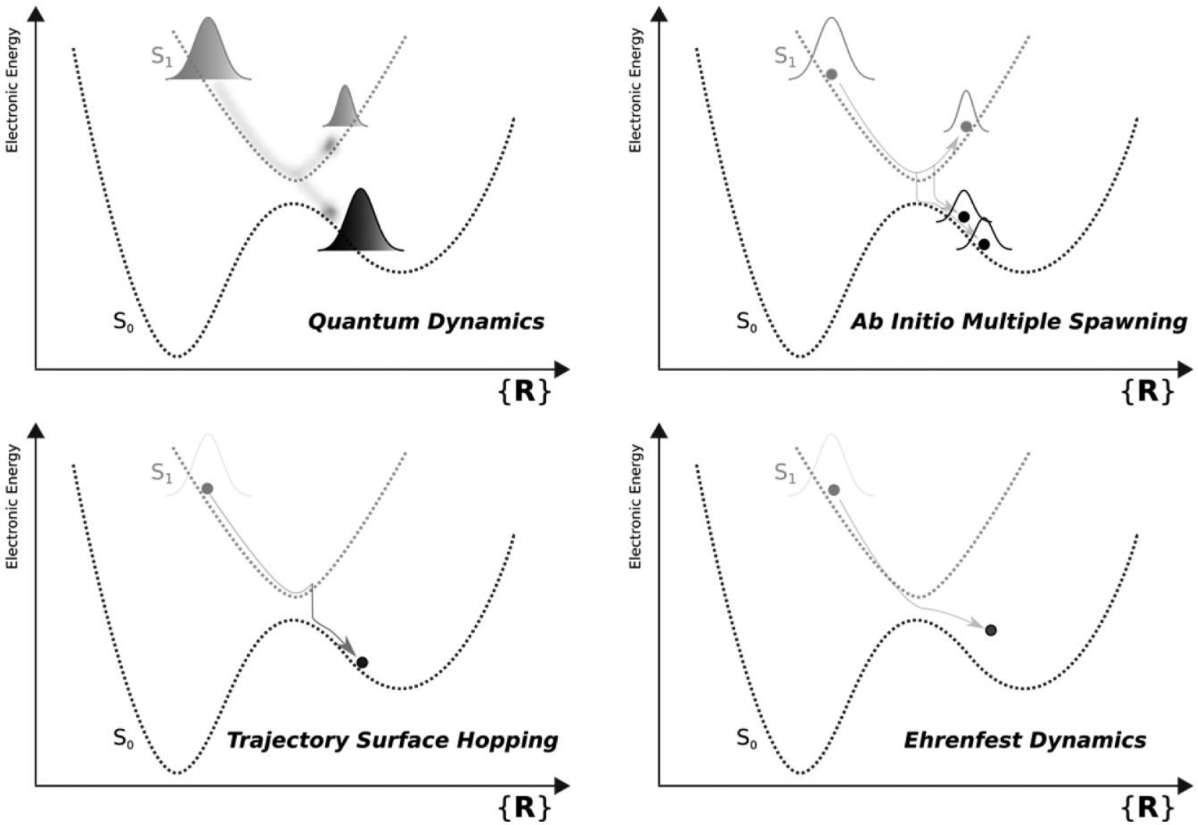
Coupling Vector



$$\mathbf{x_2} = \left\langle \psi_1 \middle| \frac{\partial \hat{H}^{el}}{\partial R} \middle| \psi_2 \right\rangle$$

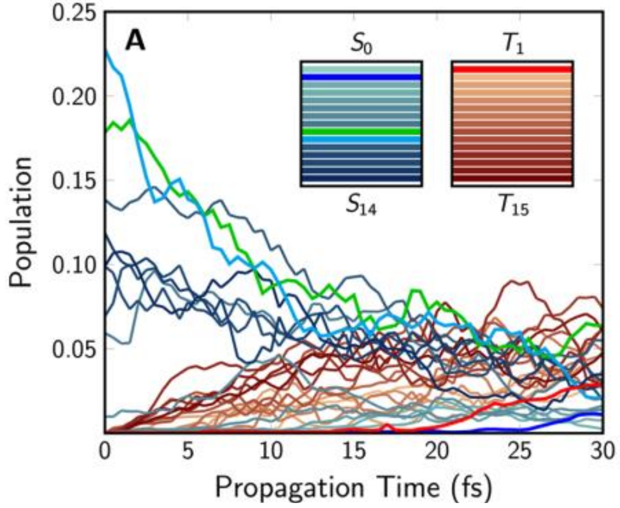
Martial Boggio-Pasqua. Computational mechanistic photochemistry: The central role of conical intersections. Theoretical and/or physical chemistry. Université Toulouse III, 2015. tel-01184241

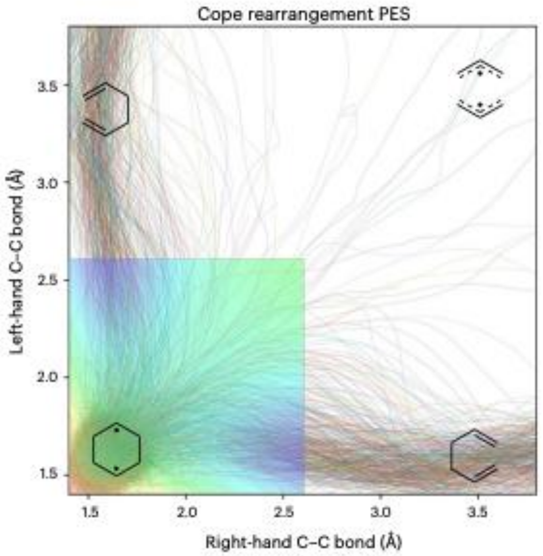
Non-adiabatic Molecular Dynamics



$$P_{\alpha\to\beta} = \frac{2Rel\{c^*_\beta(t)c_\alpha(t)[\frac{i}{\hbar}\boldsymbol{H}_{\beta\alpha} + \boldsymbol{K}_{\beta\alpha}]\}}{c^*_\beta(t)c_\beta(t)}$$

$Ru(bpy)_3{}^{2+}$





J. Chem. Theo. Comp. **2011**, 7 (5), 1253–1258
J. Phys. Chem. Lett. **2012**, 3 (21), 3090–3095.
Chem. Rev. **2018**, 118, 3305-3336.