Excited States with
Multi-Reference Self-Consistent Field Methods

Sebastian Mai

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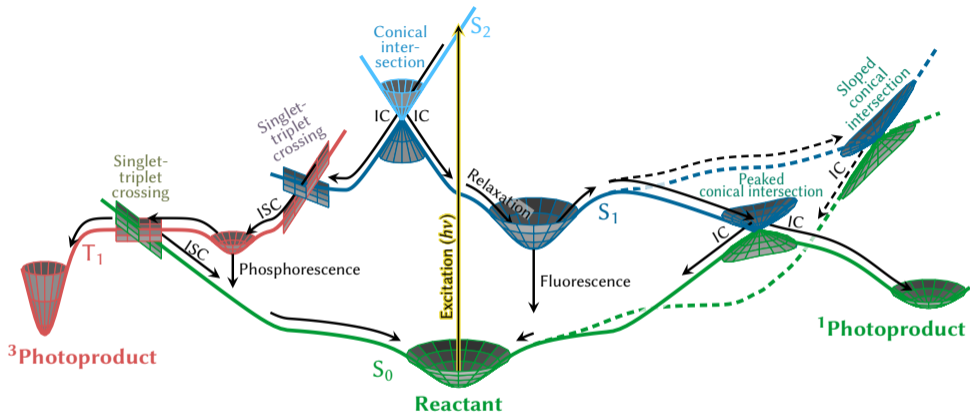
July 7th, 2022

"Excited States and Nonadiabatic Dynamics CyberTraining Workshop 2022" in Buffalo, NY
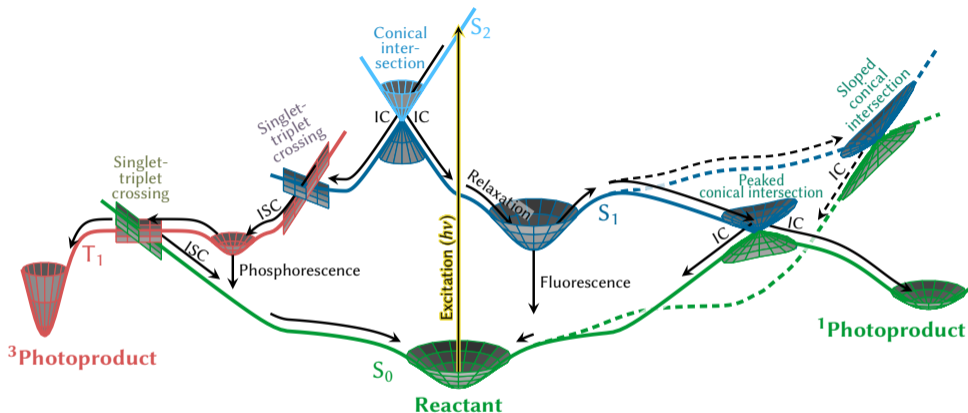
SM, L. González: *Angew. Chem.* 59, 16832, (2019).

- Many things can happen in photochemistry, so electronic structure must be very flexible!
- If ground state is wrong, then excited states will also be wrong.

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Motivation: Difficult situations in quantum chemistry

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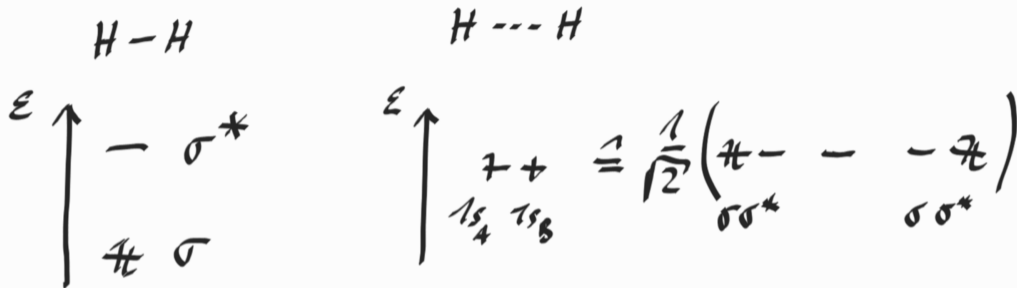
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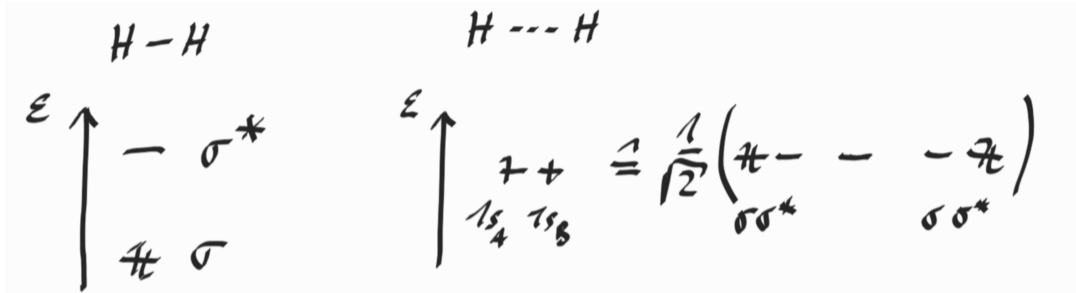
4. Metal complexes

Open shells lead to many near-degenerate electronic configurations.

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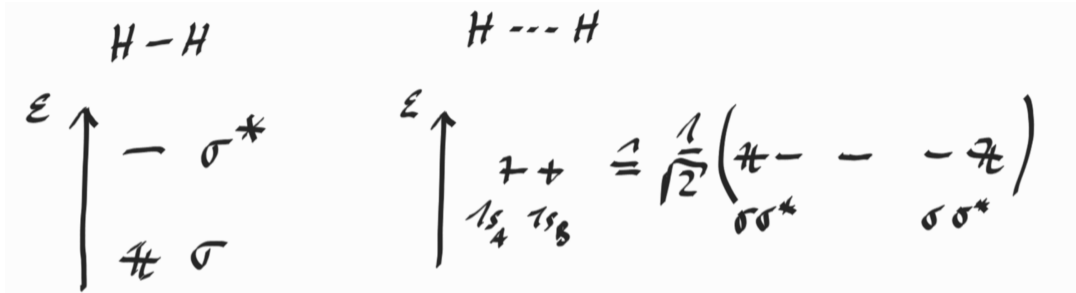

- In molecular H_2, the wave function is well described by the σ^2 configuration
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- $\Rightarrow$ Describing the entire PES consistently requires two configurations.

$$|\mathord{\uparrow}\mathord{\downarrow}\rangle$$

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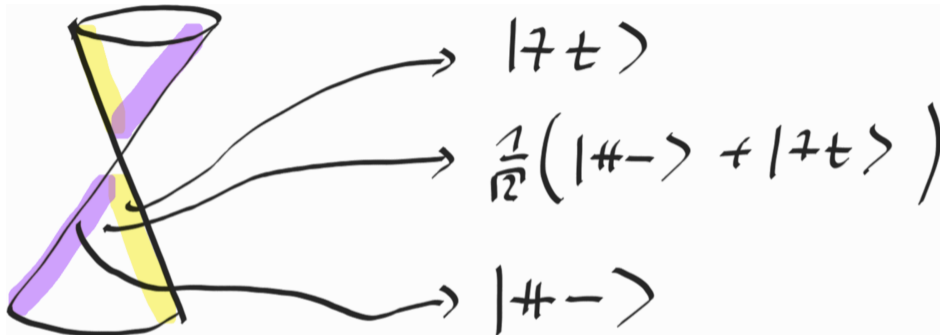$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow-\rangle + |\uparrow\downarrow\rangle\right)$$
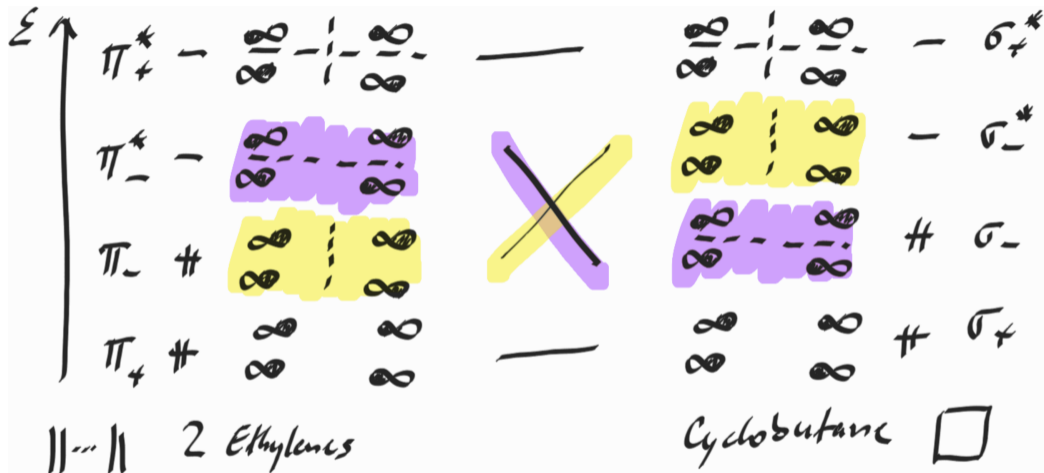
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▶ Depending on where on the lower cone one is, the wave function is either closed shell, open shell, or a linear combination

⟹ With only one configuration for the lower state, the cone cannot be formed.

Example: Transition states

⟹ At the transition state, the wave function is a linear combination of reactant and product configurations.

Example: Metal complexes
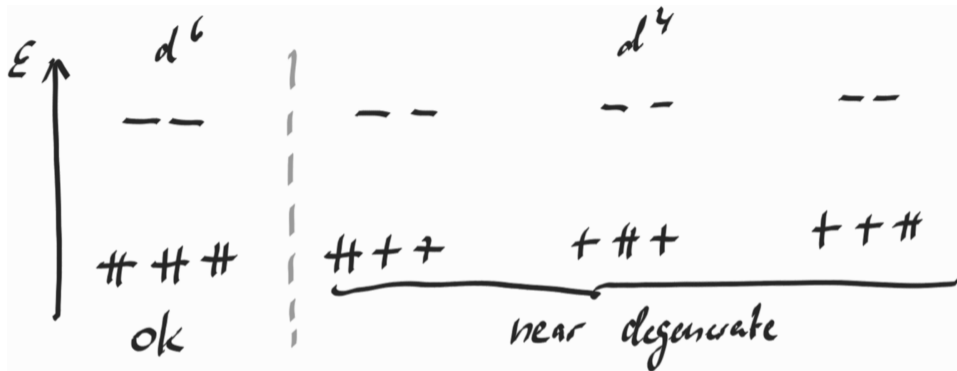
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- Other configurations are prone to be open-shell, like octahedral d^4
- ⟹ Needs to be tested, many metal complexes are open-shell and then require multiple configurations.

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This means:

- Optimize orbitals and CI expansion simultaneously: Multi-configurational SCF (MCSCF)
- To simplify choice of CI expansion: Complete active space SCF (CASSCF)
  (choose important orbitals instead of important configurations)

The CASSCF method
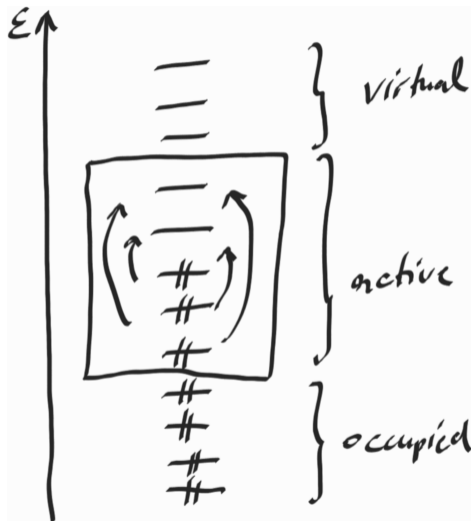
Orbital spaces:

- ▶ Virtual: Empty in all configurations
- ▶ Active: Full CI within these orbitals
- ▶ Occupied: Full in all configurations

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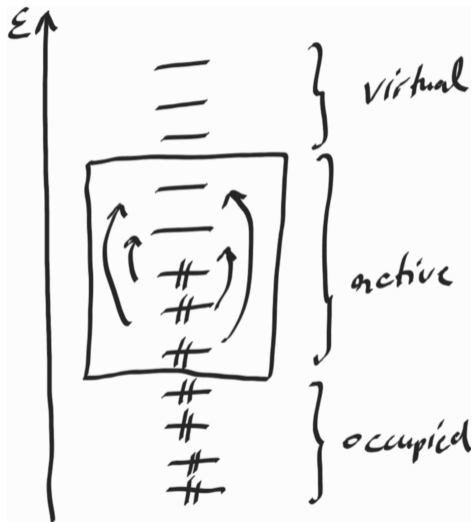
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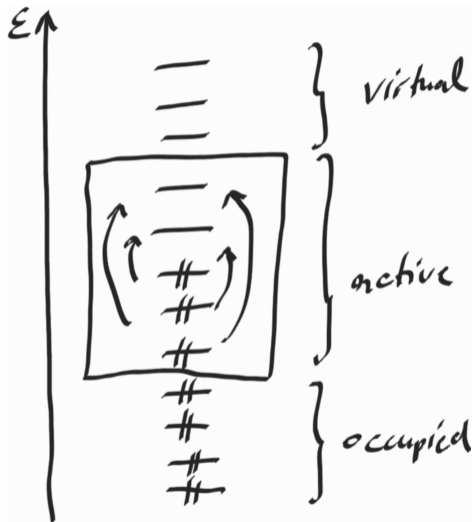
- ▶ CASSCF(N_{el},N_{orb})

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Algorithm:

- Simultaneous optimization of MO and CI coefficients
- MO and CI coefficients not independent
- Many local minima on $E(C_{MO}, C_{CI})$ surface
- Requires good guess and good converger algorithms
- Often manual help needed (swapping orbitals)

The CASSCF method: State–averaging

CASSCF is based on variationally optimizing MO and CI coefficients to give lowest energy.

- ▶ Well defined if only one state required
- ▶ For excited-state calculations, needs **state–averaging**:
    - ▶ CI coefficients are optimized for each state (multiple eigenvalues of the same CI matrix)
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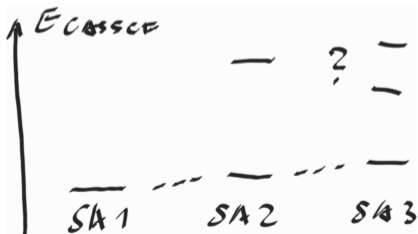CASSCF is based on variationally optimizing MO and CI coefficients to give lowest energy.

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In SA-CASSCF, PESs can be discontinuous if states change character!
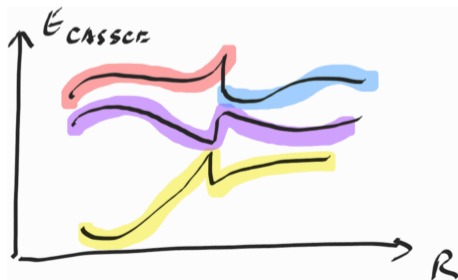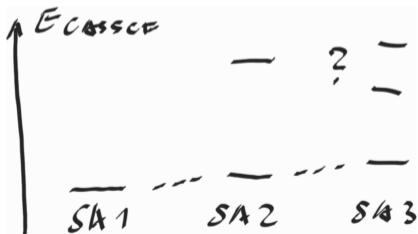
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Number of Slater determinants:

$$N_{\text{dets}} = \frac{2S + 1}{N_{\text{orb}} + 1} \begin{pmatrix} N_{\text{orb}} + 1 \\ N_{\text{el}}/2 - S \end{pmatrix} \begin{pmatrix} N_{\text{orb}} + 1 \\ N_{\text{el}}/2 - S + 1 \end{pmatrix} \tag{1}$$

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For singlet states:

$S = 0$		N_{orb}				
		4	8	12	16	20
N_{el}	4	20	336	1,716	5,440	13,300
	8	1	1,764	70,785	866,320	5,799,465
	12		336	226,512	14,158,144	300,467,520
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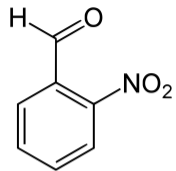- Finding the active space involves trial and error as well as chemical intuition.

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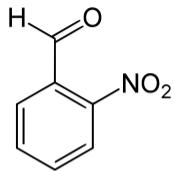It is very easy to reach the limit of 16 active orbitals!   Often requires compromises!

ortho-nitrobenzaldehyde

Courtesy Dóra Vörös

ortho-nitrobenzaldehyde

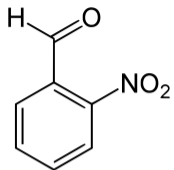What would be a good active space for the excited
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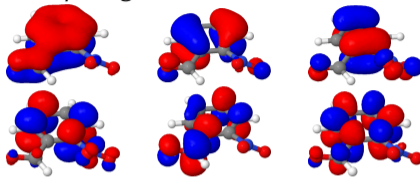
Choice of the active space orbitals: Example

H, O
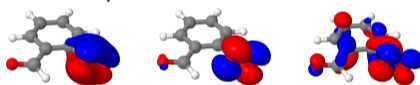
NO$_2$

ortho-nitrobenzaldehyde

What would be a good active space for the excited states?

- ▶ Phenyl ring: 6 π/π^*
- ▶ Carbonyl group: π, π^*, n
- ▶ Nitro group: 3 π/π^*, 2 n

Phenyl ring:

Nitro π system:

Carbonyl π system:

Lone pairs:

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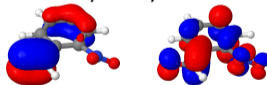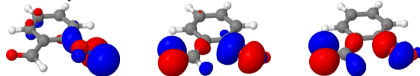
Methods to go to larger active spaces

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Other partition schemes than CASSCF

- ▶ **RASSCF**: restricted active space SCF: active space split into 3 subspaces
- ▶ **GASSCF**: generalied active space SCF: active space split into any number of subspaces
- ▶ Both are very difficult to choose and converge
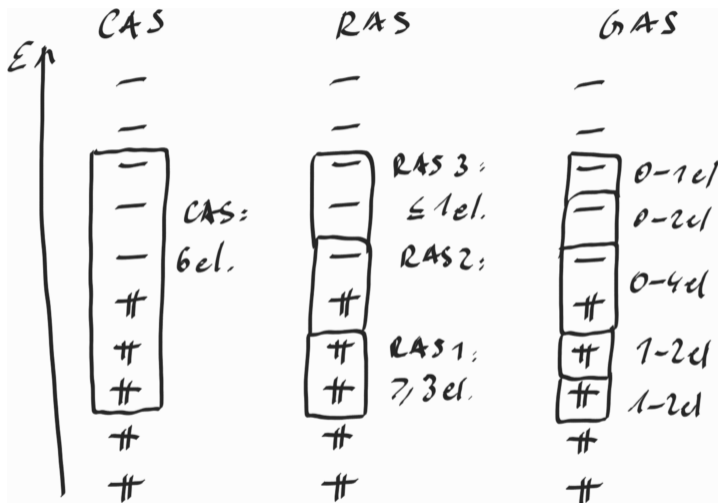
Malmqvist, Rendall, Roos: *JPC* 94, 5477 (1990).
Ma, Li Manni, Gagliardi: *JCP* 135, 044128 (2011).

Pros and Cons of MCSCF and related methods

Advantages:

+ Variational

~ Size consistent/extensive if the active space grows with the system

+ Free of spin contamination, can describe any spin state

+ Full wave function information,
  thus, easy to compute properties (gradients, nonadiabatic couplings, dipole moments, …)

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Disadvantages:

– Includes almost no dynamic correlation,
thus, energies are not very good, accurate results require "post-MCSCF" treatment

Post-MCSCF methods

Multi-reference CISD

- ▶ Variational single+double excitations from occupied+active to active+virtual

Pros/cons:

- \+ Variational
- \+ Gradients, nonadiabatic couplings
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- − Very expensive, limited accuracy for larger molecules

Variants:

- ▶ Uncontracted (COLUMBUS)
- ▶ Contracted (MOLPRO)

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Multi-reference perturbation theory

▸ Perturbative single+double excitations from occupied+active to active+virtual

Pros/cons:

- − Not variational
- − Gradients, nonadiabatic couplings very challenging/expensive
- + Size-consistent
- + Reasonable cost−accuracy balance

Variants:

- ▸ Hamiltonian: CASMP2, MRMP2, CASPT2, NEVPT2, QDPT2, …
- ▸ Multiple states: SS/MS/XMS-CASPT2, QD-NEVPT2, …

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Other details

▶ Has many properties advantageous for nonadiabatic dynamics
▶ Often not accurate enough without a post-MCSCF treatment

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My further thanks goes to: