

# Molecular Excited States: Multiconfigurational Methods

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# Restricted SCF - why we need to go beyond?

Let's consider the H<sub>2</sub> molecule, the spin-orbital can be express as:

$$\phi_1 = s_A + s_B$$

$$\Psi_{\text{bonding}} = \phi_1 \phi_1 = (s_A + s_B)(s_A + s_B)$$



So, the whole wave function is represented as a single Slater determinant. It is fine for the equilibrium geometry, but when we would like to describe whole potential energy surface (PES) we have problem. The ionic and covalent terms are treated equally in every point of PES!



#### Add one more determinant



$$\phi_2 = s_A - s_B$$
  
$$\Psi_{\text{antibonding}} = \phi_2 \phi_2 = (s_A - s_B)(s_A - s_B) = s_A s_A - s_A s_B - s_A s_B + s_B s_B$$

So the total wave function  $\Psi$  will be:

$$\Psi = c_1 \Psi_{\text{bonding}} + c_2 \Psi_{\text{antibonding}}$$
$$\Psi = c_1 (s_A s_A + s_A s_B + s_A s_B + s_B s_B) + c_2 (s_A s_A - s_A s_B - s_A s_B + s_B s_B)$$
$$\Psi = (c_1 + c_2)(s_A s_A + s_B s_B) + (c_1 - c_2)(s_A s_B + s_B s_A)$$

For  $c_1 = 1$  and  $c_2 = 0$ :

$$\Psi = s_A s_A + s_A s_B + s_A s_B + s_B s_B$$

For  $c_1 = -c_2$ :

$$\Psi = s_A s_B + s_A s_B$$



# Multiconfigurational wave function

$$\Psi = \sum_{i} c_{i} \Psi_{i}$$

To describe **near-degeneracy effects** (situations where multiple electronic configurations have similar energies) it is necessary to go beyond a single Slater determinant. This is achieved by constructing a wavefunction as **a linear combination of several Slater determinants or configuration state functions (CSFs)**, each weighted by a coefficient **c**<sub>i</sub>.



### What are near-degenerated systems?

- Near-degenerate orbitals (like in rotation of  $\pi$  orbitals)
- Bond-breaking (even simple molecule as  $H_2$ )
- Excited states (open-shell singles, mixing states)
- Transition metal complexes (*d*-orbitals can be promoted to other orbitals)
- Biradicals or multiradicals (open-shell singles, mixing states)



#### Let's run some calculations ...



1. Optimization of the CASSCF ground state.

Go to directory: ~/molex2025/MOLEX2025\_TUTORIAL\_FILES/TUTORIAL\_2/01\_GEOM\_RELAX and copy all files.

sbatch submit\_opt.job

2. Single point CASSCF and CASPT2 calculations.

Go to directory: ~/molex2025/MOLEX2025\_TUTORIAL\_FILES/TUTORIAL\_2/02\_SP\_CASSCF\_CASPT2 and copy all files.

sbatch submit\_sp\_casscf\_caspt2.job

3. Single point CASSCF and MSPDFT calculations.

Go to directory: ~/molex2025/MOLEX2025\_TUTORIAL\_FILES/TUTORIAL\_2/03\_SP\_CASSCF\_MCPDFT and copy all files. sbatch submit\_sp\_casscf\_mcpdft.job



Part 1: CASSCF

#### Geometry optimization in OpenMolcas

#### >>> DO WHILE

&SEWARD grid input grid=ultrafine end of grid input

#### &RASSCF

- •
- CiRoot= 5 5 1 RLXRoot = 1

#### &CASPT2

•

RLXRoot= 1

#### **&SLAPAF**

>>> EndDo



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#### Input structure: &GATEWAY section

&GATEWAY

```
Title= Pyrazine_casscf
```

coord = optgeom.xyz -> xyz coordinates in xyz file

```
basis = cc-pVDZ
```

```
group = c1
```

RICD

-> basis set

-> no symmetry; although pyrazine has D2h symmetry, for further MD calculation we do not need it -> atomic Cholesky decomposition approximates two-electron integrals, which significantly seed procedure up



#### Input structure: & SEWARD section

```
>>> EXPORT MOLCAS_MAXITER=1000
&SEWARD
grid input
grid=ultrafine
end of grid input
*>>> If (Iter=1) <<<
*&SCF
*>>> EndIf <<<</pre>
```

-> module handling one- and two-electron integrals

-> guess orbitals Here Hartree-Fock! natural MP2 CASSCF from other calculation



### Input structure: &RASSCF section

```
&RASSCF
```

```
FileOrb = $CurrDir/opt.RasOrb
```

```
Spin= 1
```

```
Nactel= 10 0 0
```

```
Inactive= 16
```

```
Ras2= 8
```

CiRoot= 5 5 1

-> guess orbitals Hartree-Fock natural MP2 CASSCF from other calculation -> singlet state -> number of active electrons -> number of inactive orbitals -> number of active orbitals -> number of states: here ground state and excited states (S1, S2, S3, S4)

Active space CAS(10,8) meaning 10 electrons in 8 orbitals In general CAS(N,n) meaning *N* electrons in *n* orbitals



#### Inactive, Active and Virtual spaces

Restricted Canonical SCF

VIRTUAL Occupation always 0 electrons

OCCUPIED Occupation always 2 electrons CASSCF

VIRTUAL/SECOND ARY/EXTERNAL Occupation always 0 electrons

ACTIVE Occupation from 0 to 2

INACTIVE Occupation always 2 electrons

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#### CASSCF - Complete Active Space SCF

The Complete Active Space is a special case of multiconfigurational methods were:

- Ci coefficients are variationally optimized (CASCI)
- Molecular orbitals are also optimized

Inside active space Full CI procedure is performed, all spin-adapted configuration are considered. Thus, CASSCF is **complete inside active space.** 

So, how big active space can be?

Weyl's formula provides the number of configuration state functions

S - spin quantum number

N- number of electrons

$$K_{n,N,S} = \frac{2S+1}{n+1} \binom{n+1}{N/2-S} \binom{n+1}{N/2+S+1}$$

n - number of orbitals



#### State-average CASSCF

CiRoot= 5 5 1

#### In state-specific CASSCF:

we optimize the orbitals for one specific state for example ground state.

#### In state-average CASSCF:

we optimize the average orbitals for several state averaging them equally or not equally,

minimizing not the energy of specific state but rather the average energy.

The excited states are calculated as orthogonal states to each other, what is not necessary the case for state-specific calculations.



#### Pyrazine - how to choose the active space?

The active space should be chosen according to investigated problem

In our case: we would like to describe the  $n-\pi^*$  and  $\pi-\pi^*$  excitations.

Pyrazine has 3  $\pi$  and 2 lone-pair orbitals - 5 occupied orbitals with 10 electrons.

Since all transitions will involve  $\pi^*$  we need all of them - 3  $\pi^*$ .

This gives CAS(10, 8).

<u>Advice:</u> always check if your orbitals are inside active space.



# CAS space for pyrazine

	π <sub>3</sub>	n <sub>1</sub>
ROOT1	2(1.96)	2(2.00)
ROOT2	2(1.96)	2(1.87)
ROOT3	2(1.87)	2(2.00)
ROOT4	2(1.96)	u(1.25)
ROOT5	2(1.95)	2(1.90)

π <sub>2</sub>
2(1.89)
2(1.89)
2(1.60)
2(1.80)
2(1.90)

n <sub>2</sub>	π <sub>1</sub>	π <sub>1</sub> *	π <sub>2</sub> *
2(2.00)	2(1.90)	0(0.12)	0(0.10)
u(1.13)	2(1.90)	d(1.07)	0(0.11)
2(2.00)	u(1.28)	d(0.74)	0(0.39)
2(1.74)	2(1.88)	d(1.14)	0(0.13)
u(1.10)	2(1.89)	0(0.21)	d(0.97)

ROOT1 - ground state **ROOT2** -  $n_2 - \pi_1^*$ **ROOT3** - π<sub>1</sub>-π<sub>1</sub>\* **ROOT4** - n<sub>1</sub>-π<sub>1</sub>\* **ROOT5** - n<sub>2</sub>-π<sub>2</sub>\*

Natural orbitals: diagonalization of spineless first-order density matrix



 $\pi_{2}^{*}$ 

 $\pi_3^*$ 

0(0.04)

0(0.07)

0(0.12)

0(0.09)

0(0.09)

Part 2: CASPT2



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\*in terms of orbital correlation



CASPT2 is a second-order perturbation theory,

where the second-order correction to energy is calculated,

but this time on a multiconfigurational wave function.

CASPT2 - CASSCF = reminding double but also single(!) excitations, and also from the active space Semi-internal External Internal VIRTUAL ACTIVE VIRTUAL aibt tiuv atuv ijkl abcd t u v xaitu or tiau aibi tiui atbu tiai



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#### XMS-CASPT2 in OpenMolcas

&CASPT2

XMultistate= 5 1 2 3 4 5 >>COPY \$Project.JobMix JOB001

&RASSI

```
Nr of Job=1 5; 1 2 3 4 5
EJob
```

-> the new effective zeroth-order wavefunctions, based on CASSCF states with energies corrected by CASPT2.

#### -> Restricted Active Space State

**Interaction** -> computes matrix elements between different electronic states. Useful to get: excited-state properties like oscillator strengths, lifetimes, non-adiabatic couplings, transition dipole moments, etc.

Toru Shiozaki, Werner Győrffy, Paolo Celani, Hans-Joachim Werner; Communication: Extended multi-state complete active space second-order perturbation theory: Energy and nuclear gradients. *J. Chem. Phys.* 28 August 2011; 135 (8): 081106.



#### CASSCF vs. CASPT2



CAS\_SA5 CASPT2\_SA5



Part 3: MCPDFT



# On-top density-functional energy ( $E_{xc}^{t}[\rho, \Pi]$ ) is computed using **on-top** (**translated**) **DFT functional**. Why translated???

Multiconfiguration Pair-Density Functional Theory, Giovanni Li Manni, Rebecca K. Carlson, Sijie Luo, Dongxia Ma, Jeppe Olsen, Donald G. Truhlar, and Laura Gagliardi, Journal of Chemical Theory and Computation 2014 *10* (9), 3669-3680



# Translated DFT functional

In DFT theory:

- a single Slater determinant, where orbitals have occupation 2 or 0,
- easy to distinguish  $\alpha$  and  $\beta$  electrons and construct  $\rho = \rho_{\alpha} + \rho_{\beta}$
- easy to define spin polarization (m =  $\rho_{\alpha} \rho_{\beta}$ ) and its gradient. Both of them can improve DFT functionals.

However, we have a multiconfigurational wave function!

- Spin polarization undefine, occupation between 0 and 2,
- <u>Solution</u>: on-top **pair density (Π)** -> the probability of finding two electrons at the same point in space, capturing correlation directly.



#### **Final results**



Compressed-State Multistate Pair-Density Functional Theory," J. J. Bao, C. Zhou, Z, D. G. Truhlar. J. Chem. Theory Comput. 2020, 16, 7444-7452 <u>https://comp.chem.umn.edu/openmolcas/attachments/220408%20CMS-PDFT\_for\_MN\_OpenMolcas\_website\_v16.pdf</u>



# Take-home message

Always check your active space.

```
Attach good orbitals FileOrb = $CurrDir/$Project.RasOrb
```

Be minimalistic - you have only 16 orbitals(!).

Listen to your chemical intuition - every problem is different.

Averaging more states can help converging to good results.

Try few active spaces.

CASSCF alone is not sufficient - it almost always misses dynamical correlation.



The end of the tutorial 2! Enjoy the poster session :)