

Multiconfigurational methods in MOLCAS

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Overview

- What is correlation?
- CASPT2 theory
 - (we will skip math, but it is kept for your convenience)
- CASPT2 variants and implementations
- Some practical issues

Correlation

Schrödinger equation: $\hat{H}\Psi = E\Psi$

Correct wave-function:

$$\Psi(r_1, r_2, \dots, r_n)$$

Hartree product (no correlation):

$$\Psi = \phi(r_1) * \phi(r_2) * \dots * \phi(r_n)$$

Without spin correlation electrons behaves as bosons,
and so no Pauli exclusion principle, no chemistry at all!

Spin correlation gives us Hartree-Fock theory.
HF theory describes one electronic configuration.

Hartree-Fock theory and the ground state

For the ground state HF reproduces 99% of the energy

Total energy for benzene molecule (in kcal/mol)

Hartree-Fock	-144791.5
CASSCF (6 orbitals)	-144837.4
CCSD(T)	-144843.8

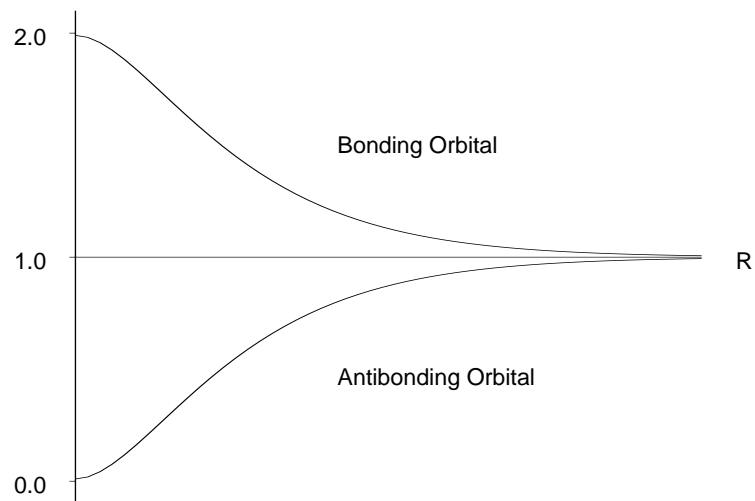
Cases where HF gives a wrong description of the ground state are exotic:

- molecules created from closed shell atoms, e.g. Be_2
- low and high spin states in transition metal complexes, e.g. $[Co(CO)_6]^{+3}$
- ...

So, what is wrong with Hartree-Fock?

If we consider of a pair of orbitals: bonding and anti-bonding, Hartree-Fock will predict the same population: 2 and 0 independently on the distance between atoms.

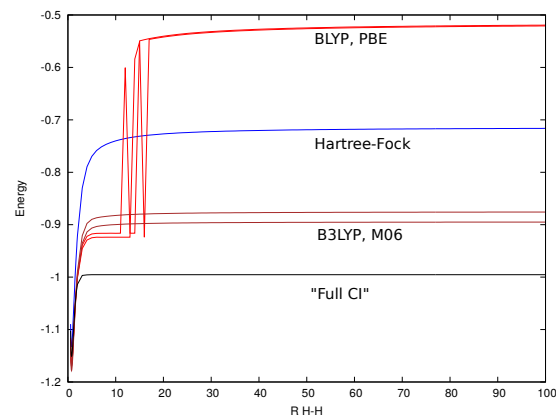
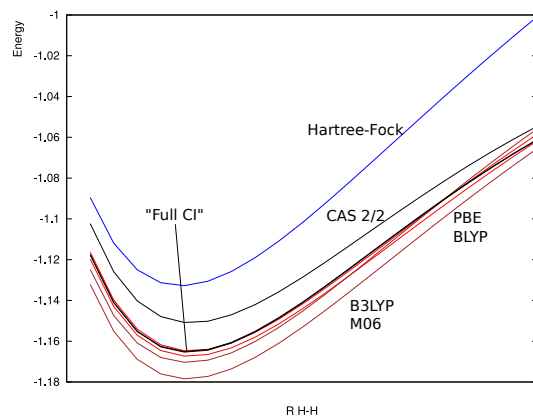
More realistic dependence of occupation numbers on inter-atomic distance:



The result is well known: completely wrong dissociation limit (if symmetry is preserved)

Why can't we use DFT?

H_2 molecule dissociation



DFT is doing a very good job to describe ground state energies at equilibrium geometries. To break/create bonds, especially multiple bonds, multiconfigurational theory is desired.



Full CI

Full CI (with unlimited basis set) is exact

$$\Psi = \sum_K C_K \Phi_K,$$

where Φ_K is antisymmetric N-electron function.
But how large is this sum?

Number of orbitals: n

Number of electrons N

Spin quantum number S

Weyl's formula for the number of configuration state functions (CSF)

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

Is it expensive?

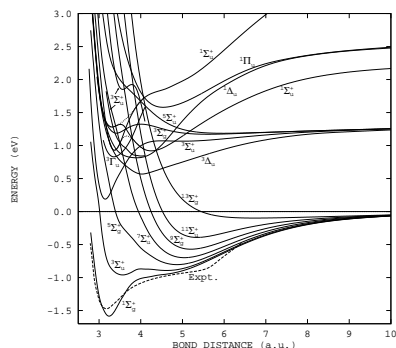
number of CSF for N electrons on n orbital

2	3
4	20
6	175
8	1764
10	19404
12	226512
14	2760615
16	34763300
18	449141836
20	5924217936
22	79483257308
24	1081724803600
...	
48	81528782754899118132297728
50	1205564663340194413152305152
...	
100	39526543784136344338113583654697013219610000000000000000

The main challenge in correlation theory

Do we need all these configurations?

Maybe.. there are so many small contributions..



NO! many configurations have almost zero weight.
But we *don't know* how to find all needles in a haystack.



Approximate methods

Variational methods

$$\hat{H}\Psi^{trial} = E\Psi^{trial}, \text{ for any } \Psi^{trial}, E \leq E^{exact}$$

We can get more and more closer to the exact solution.

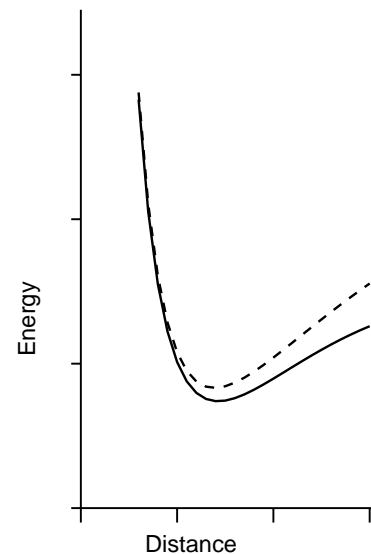
These are white-collar methods.

They are controllable and can be gradually improved.

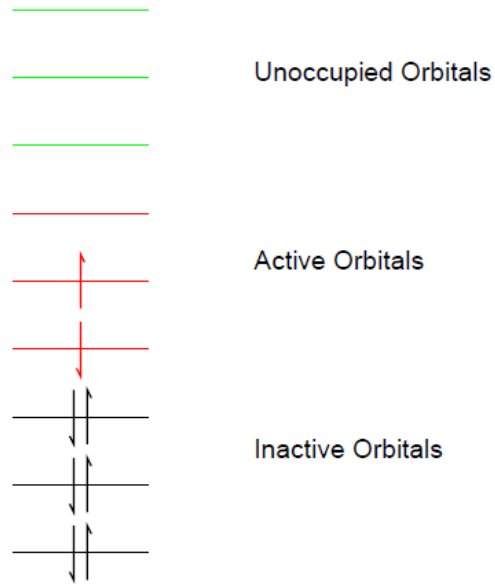
Examples

(skipping the details):

- Hartree-Fock
- CASSCF
- RASSCF
- MRCI
- DMRG

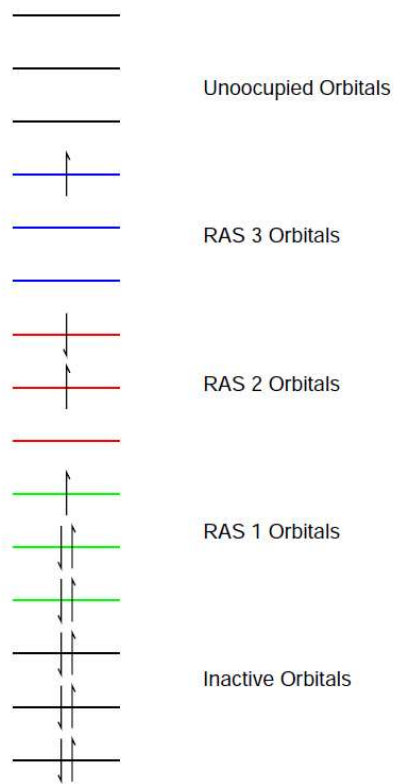


Multiconfigurational approach



CASSCF = Full CI on a limited set of orbitals

Possible improvement



RASSCF = Full CI on a limited set of orbitals +
SD for limited set of orbitals

Selection of active space

"Sometimes trivial, sometimes more difficult, sometimes impossible"
(Björn Roos)

- depends on the problem
 - ◆ π orbitals for organic molecules
 - ◆ but can be σ orbital for dissociation
 - ◆ d orbitals for transition metals
 - ◆ sometime with double d shell

- Weyl formula








$$N_{\text{CAS}} = \frac{2S+1}{n+1} \binom{n+1}{N/2 - S} \binom{n+1}{N/2 + S + 1}$$

- can not exceed about 16 orbitals for CASSCF
- can not exceed about 40 orbitals for RASSCF

Atom base selection

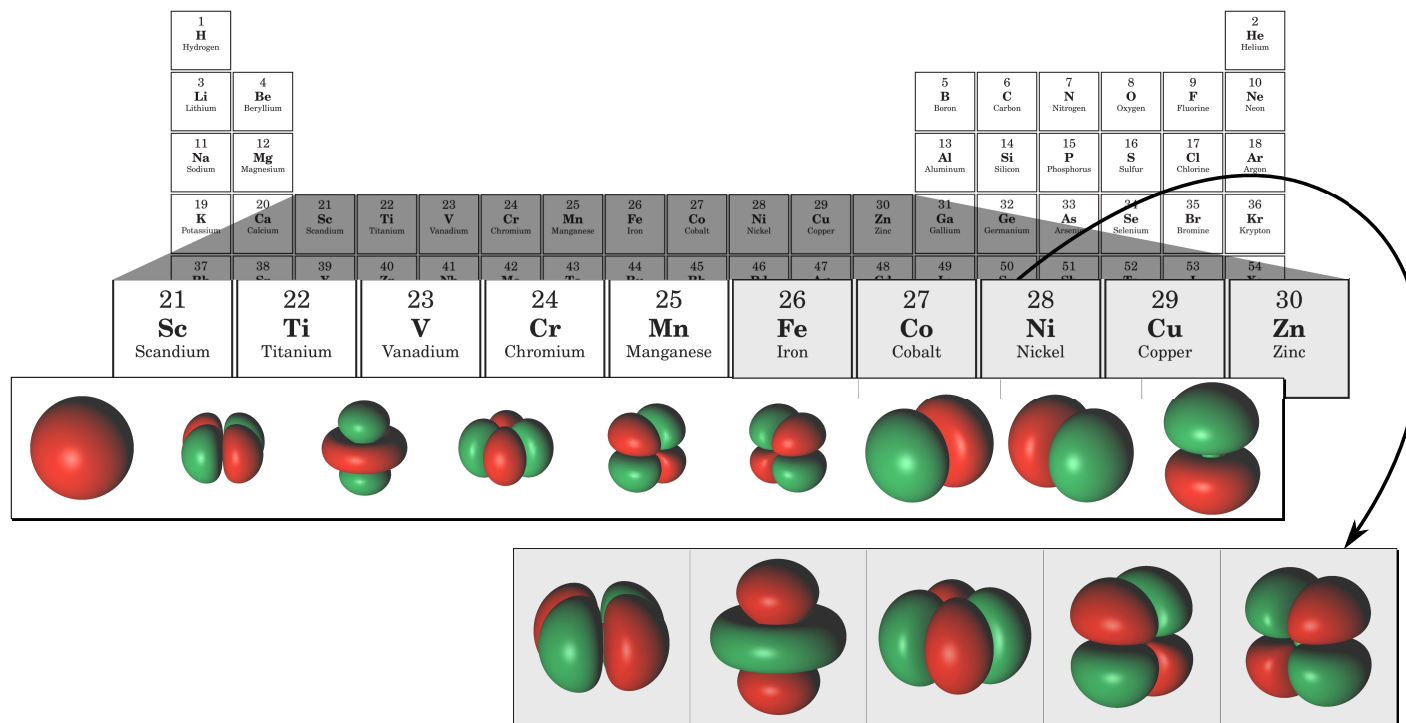
Li-C: 2s, 2p; N-F: 2p

PERIODIC TABLE OF THE ELEMENTS

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	3 Li Lithium		4 Be Beryllium		5 B Boron		6 C Carbon		7 N Nitrogen		8 O Oxygen		9 F Fluorine		53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium															79 Au Gold	111 Rg Roentgenium
87 Fr Francium	88 Ra Radium																

Transition metals

PERIODIC TABLE OF THE ELEMENTS



The size does matter!!

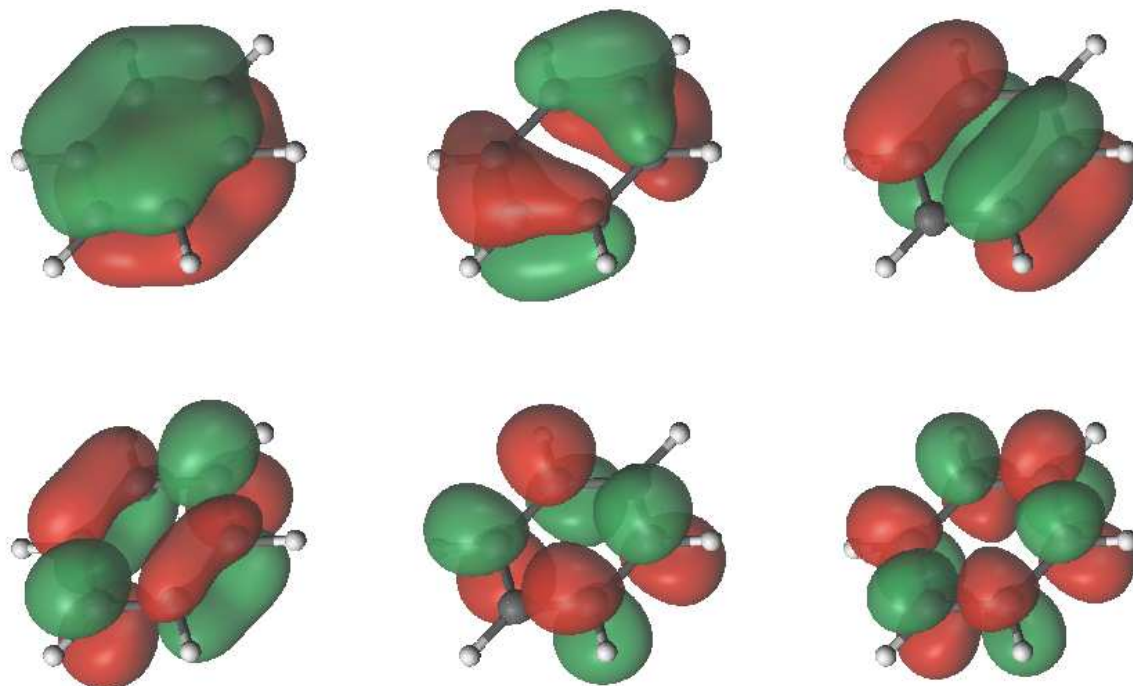
For real systems the number of potential active orbitals is too high.

- several transition metals, or lanthanides/actinides
- one transition metal with ligands
- many conjugated bonds
- complex ligands

We need to find a compromise !!

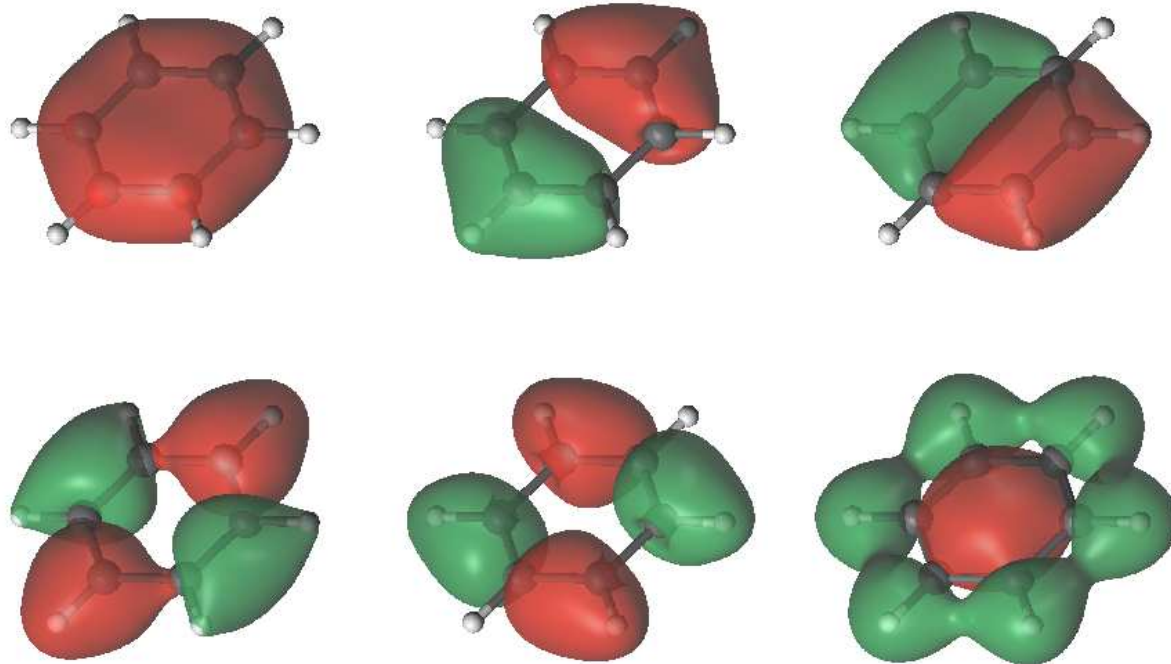
Benzene molecule

π - orbitals: 3 occupied and 3 virtual

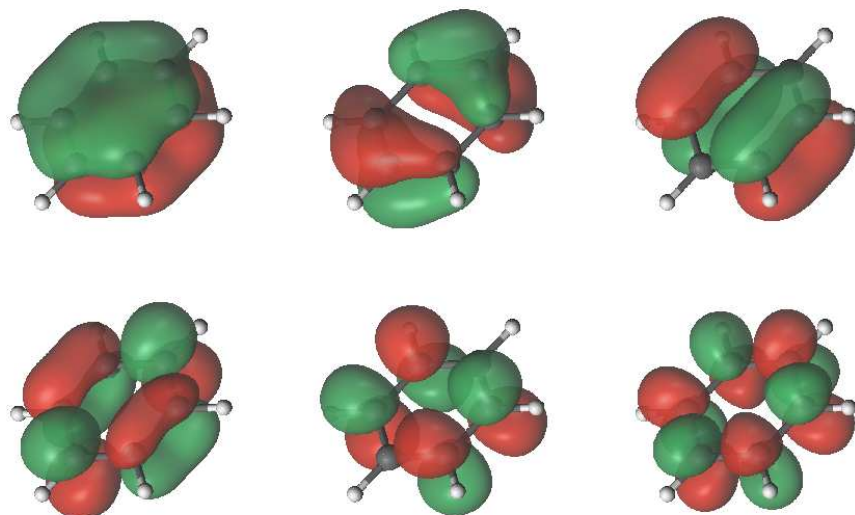


Benzene molecule

σ – orbitals



Orbitals around HOMO-LUMO



HOMO-4, HOMO-2, HOMO, LUMO, LUMO+1, LUMO+2

Q: What a program will do if we include into active space HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 ? Will it magically rotate orbitals, and tune the active space?

A "failure" of MCSCF approach

- far away from experiment (yes, we need dynamic correlation!)
- intruder states in CASPT2
- selection of active space is an ART

The majority of the 'failure' cases are due to:
small or wrong active space.

Avoid "We used 4-by-4 active space":

- too small active space
- unclear how it was selected

Perturbation theory

Unperturbed equation $\hat{H}\Psi = E\Psi$

We can now solve Schrödinger equation in parametrized form

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1 + \lambda^2\hat{H}_2 + \dots$$

$$\Psi = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \dots$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots$$

since the solution is independent on λ , chain equations can be derived:

$$\hat{H}_0\Psi_0 = E_0\Psi_0$$

$$\left(\hat{H}_0 - E_0\right)\Psi_1 = \left(E_1 - \hat{H}_1\right)\Psi_0$$

etc.

Second order perturbation theory

In second order we solve:

$$\left(\hat{H}_0 - E_0\right) \Psi_1 = \hat{V}\Psi_0$$

Presenting first-order WF as a linear combination of zero-order functions:

$$\Psi_1 = \sum_n c_n \Psi_{0,n}$$

finally, we get second-order correction to energy

$$E_2 = \langle 0 | \hat{H}_2 | 0 \rangle + \sum_{n \neq 0} \frac{|\langle 0 | \hat{H}_1 | n \rangle|^2}{E_0 - E_{0,n}}$$

since $E_{0,n} > E_0$, $E_2 < E_0$

Properties of PT2

- The energy is always goes down (not the case for odd orders!)
- In contrary to variational methods, the energy can go below E_0
- Might have singularities (if $E_{0,n}$ is close to E_0)
- The result depends on the reference (H_0)
- Works better if correction is small (reference is close enough to the correct solution)

Excitation operators

Spin-free excitation operators:

a single excitation from orbital p to q

$$\hat{E}_{pq} = \sum_{\sigma=\alpha,\beta} \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma}$$

a double from p and r to s and q :

$$\hat{E}_{pqrs} = \sum_{\sigma,\mu} \hat{a}_{p\sigma}^{\dagger} \hat{a}_{r\mu}^{\dagger} \hat{a}_{s\mu} \hat{a}_{q\sigma}$$

$$\hat{E}_{pp} |m\rangle = n_p |m\rangle,$$

where n_p is an occupation number of orbital p

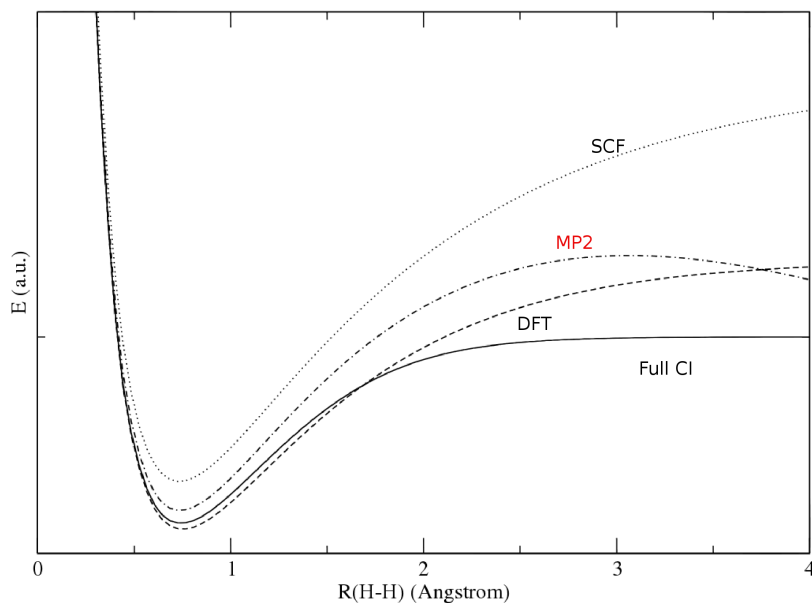
MP2 theory

We apply single excitations to HF wavefunction
(from occupied to virtual orbitals)

H_0 hamiltonian can be selected as one-electron operator $\sum_p \epsilon_p \hat{E}_{pp}$

MP2 works for the same cases as HF.

But it can not improve problems with dissociation of H_2 .

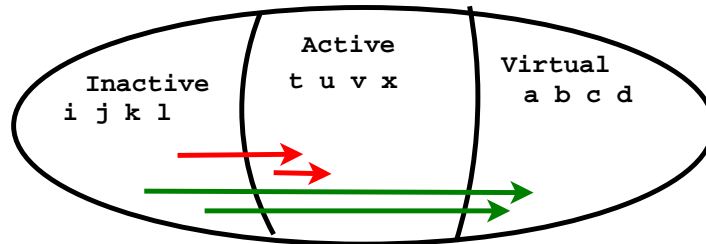


CASSCF as a reference function

We have Full CI on limited active space..

So, what do we miss? Actually, a lot (so-called dynamic correlation):

$$FullCI - CAS = S + D + TQ....$$



Excitation types in CASPT2:

Internal	Semi-internal	External
$\hat{E}_{tiu\upsilon}$	$\hat{E}_{atu\upsilon}$	\hat{E}_{atbu}
$\hat{E}_{tiu\jmath}$	\hat{E}_{aitu} or \hat{E}_{tiau}	\hat{E}_{aibt}
	$\hat{E}_{tia\jmath}$	$\hat{E}_{aib\jmath}$

(some examples of missing (in CAS) double excitations)

Zeroth-Order Hamiltonian for CASPT2

\hat{H}_0 should be

- relatively simple
- include single and double excitations
- preferably convert to MP2 for no active space

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \hat{P}_{TQ} \hat{F} \hat{P}_{TQ}$$

Where \hat{P}_0 is a projector into CAS space, \hat{P}_{SD} - projector into SD space
Now we have to choose F, the generalized Fock operator:

$$\hat{F} = \sum_{p,q} F_{pq} \hat{E}_{pq}$$

$$F_{pq} = h_{pq} + \sum_{rs} \left((pq|rs) - \frac{1}{2} (ps|rq) \right) D_{rs}$$

CASPT2 equation

Summing up, CASPT2 equation in a matrix form:

$$(\mathbf{F} - E_0\mathbf{S})\mathbf{c} = -\mathbf{R}$$

ϵ_i	F_{ia}	F_{iv}
F_{ai}	ϵ_a	F_{av}
F_{vi}	F_{va}	ϵ_v

Gray areas: Non-zero matrix elements.

The solution of CASPT2 equation includes the following steps:

- construction of the matrices
- iterative diagonalization (using preconditioned conjugate gradient method)

Modifications and improvements

Trying to improve H_0

$$F_{ii} = -(IP)_i \text{ (ionization potential for inactive)}$$

$$F_{aa} = -(EA)_a \text{ (electron affinity for virtual)}$$

thus, for active orbitals

$$\text{it should in between.. } F_{tt} = -\frac{1}{2}((IP)_t + (EA)_t)$$



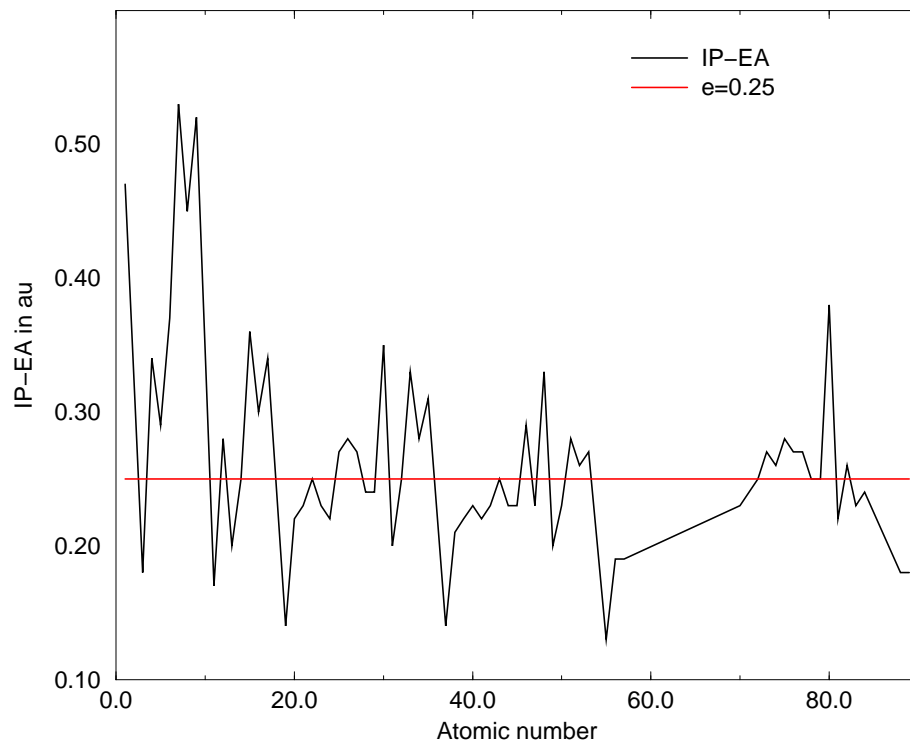
So, we can correct the diagonal of F to make it consistent.

The correction for excitation into active orbital $\frac{1}{2}D_{tt}((IP)_t - (EA)_t)$

and for exciting out $-\frac{1}{2}(2 - D_{tt})((IP)_t - (EA)_t)$

IPEA shift

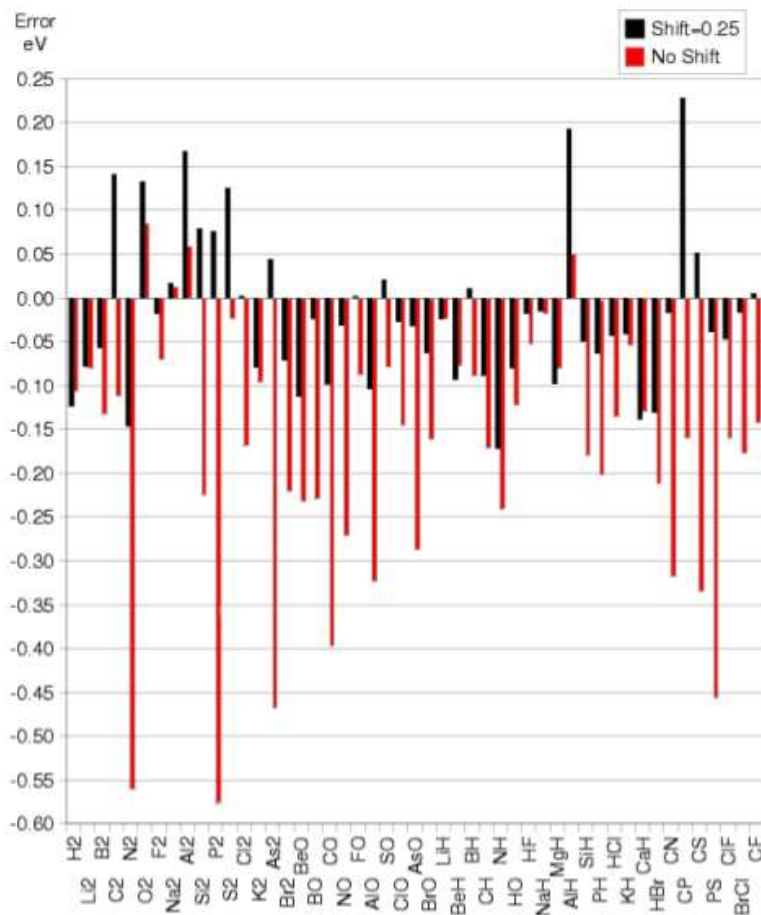
Now we consider $\epsilon = (IP)_t - (EA)_t$ as a constant.
We set ϵ to 0.25, as an average value for atoms:



an empirical correction, if you wish...

Is it accurate now?

Dissociation energies for two-atomic molecules.
(Error bars are red for the standard CASPT2 and black for IPEA shift)



Intruder states

Symptoms:

A state from SD space with energy close or even below the reference energy.

Causes:

Intrinsic for PT2 theory, but rather seldom in MP2 due to large separation in energy of occupied and virtual spaces.

Strong intruder state - insufficient active space, so PT2 theory is not any longer valid

Weak intruder state - due to small difference between inactive and virtual orbitals.

Diagnosis:

Large difference between reference (CASSCF) and the final (CASPT2) energies.

Small (almost zero!) reference weight.

Historical:

It was very common in the early days of CASPT2

How to deal with intruders?

The treatment:

IPEA (side effect), level shift technique, or imaginary shift ε :

$$(\hat{H}_0 - E_0 - \varepsilon)\Psi_1 = (E_1 - \hat{H}_1)\Psi_0$$

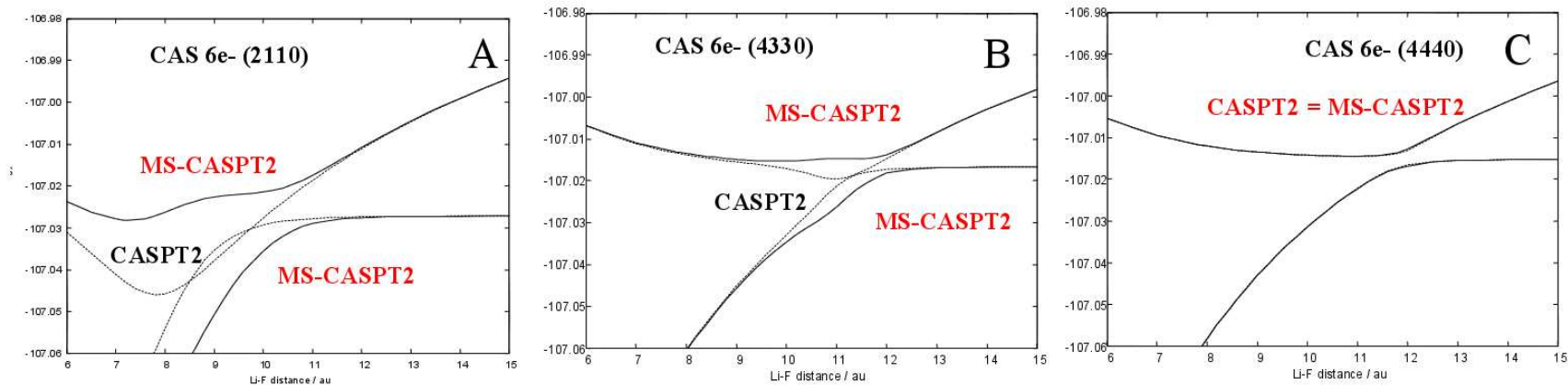
To simulate an intruder state we set up a "CAS" calculation for H_2 molecule (with H-H distance= 20Å) as containing 1(!) active orbital, and 2 electrons.

CAS energy	= -0.726970
CASPT2 energy	= -1.9131454
Reference weight	= 0.04376
if we include imaginary shift:	
CASPT2 energy	= -0.9045727
Reference weight	=0.89060

Multistate CASPT2

PT2 can be applied to multistate CAS function
An example from L.Serrano-Andrés JCP (2005).

Avoiding crossing $^1\Sigma_g^+$ state for dissociation of LiF.



MS-CASPT2 allows to get realistic picture even for minimal active space (A), increasing active space makes CASPT2 and MS-CASPT2 identical (C).

RASPT2

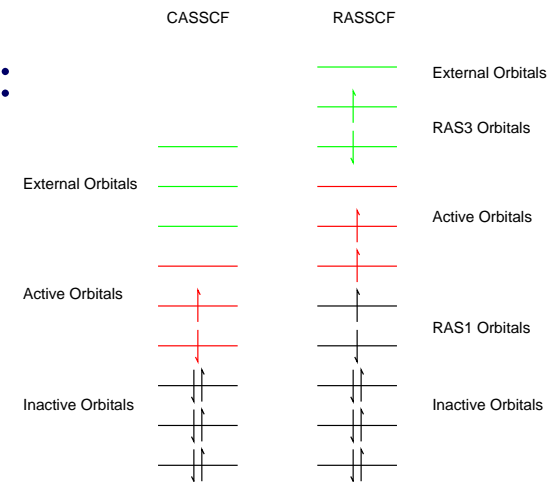
Reference function can have a form of RASSCF:

- RAS1
(not more than n holes are allowed)
- RAS2 (full CI)
- RAS3
(not more than n electrons are allowed)

Same H_0 , but more subspaces.

From the practical point of view RASPT2 method is more "heavy".

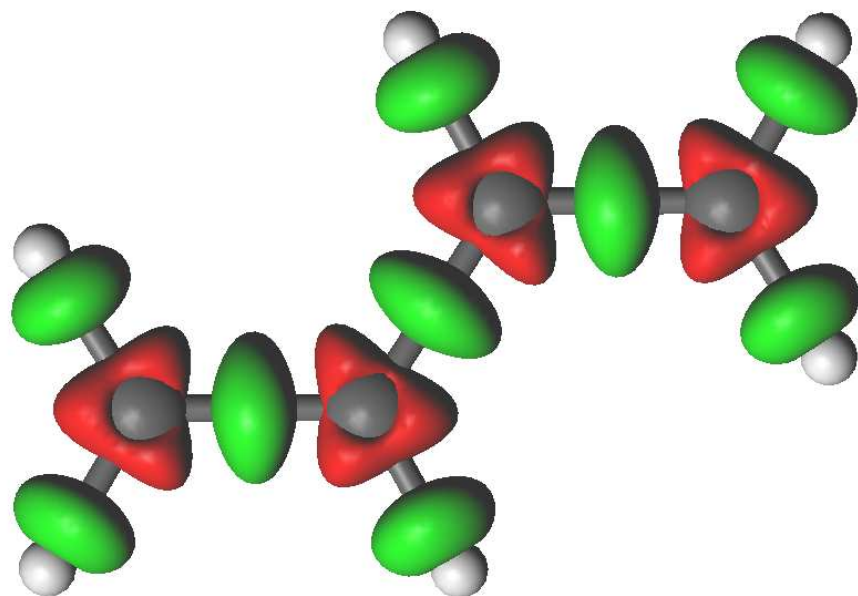
Computation time is increased (due to slower convergence for RASSCF, and memory requirements in RASPT2 part.)



CASSCF vs. CASPT2

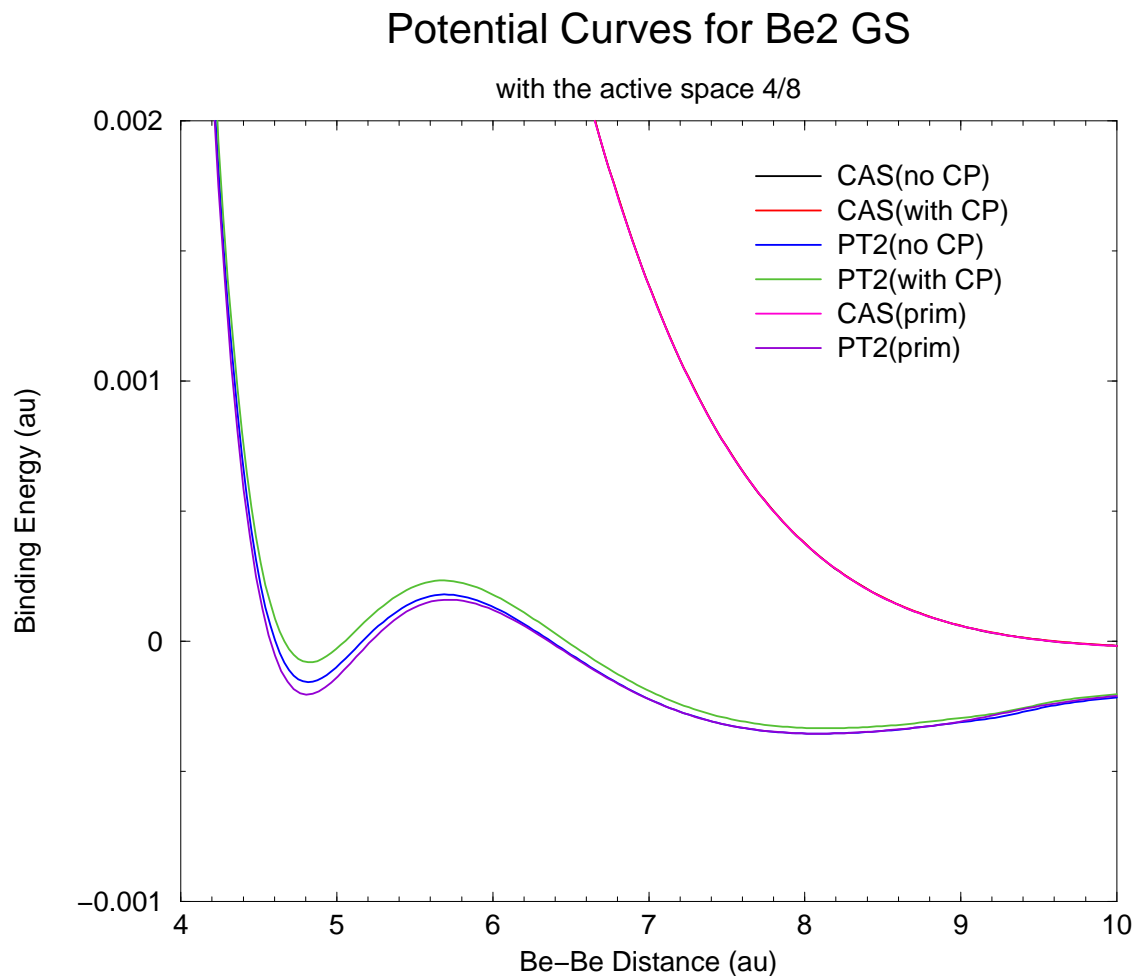
Usually, the only visible difference is the energy.

The difference between electron density, computed with CASSCF and CASPT2 for butadiene molecule is negligible (the difference is shown for iso-electron level 0.001(!) a.u.)



Can CASPT2 do magic?

Ground state of Be_2 molecule is repulsive in HF and in small CAS.
But CASPT2 shows a minimum!

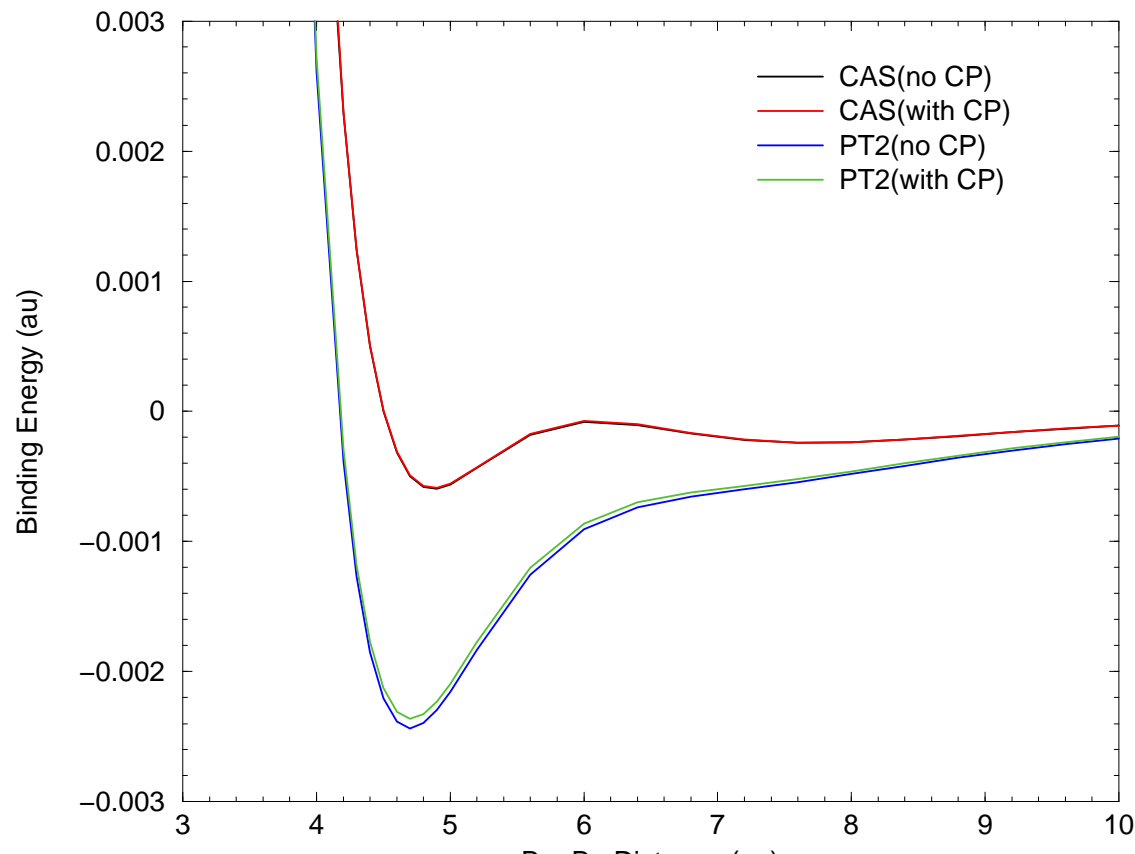


increasing CAS..

CASPT2 was trying to recover some missing correlation. Same effect can be achieved by increasing the active space in CASSCF (to 16 orbitals).

Potential Curves for Be₂ GS

Calculation with 16 active orbitals



Software, examples..

Software for CASPT2 calculations

Due to my ignorance I will focus on MOLCAS software



No hardcoded limit, but limited by the hardware limits and time:
A typical CASSCF/CASPT2 calculation 12-on-12 or 14-on-14.
(from hours to days on average PC/laptop)
Large CASPT2 calculation 16-on-16 (no symmetry!)
Large RASPT2 calculation up to 40 orbitals (might require special hardware)
Basis set size up to 2000 basis functions.
CASPT2 in the next version of MOLCAS will efficiently use GPUs and multicores.

What about CASPT2 input?

You may select in the CASPT2/RASPT2 input:

- H_0 type - **not recommended**
- change IPEA shift - **not recommended**
- Shift (Imaginary) - **only** if you have a weak intruder state
- change default set of frozen orbitals - **not recommended**
- multistate (for MS-CASPT2)

This module works [mostly] as a a black box.

Practicalities...

- set up the system
 - ◆ select the basis set
 - ◆ select the symmetry
- compute CAS wavefunction
 - ◆ choose the active space
- solve CASPT2 equations

The hardest part is marked with red..

But, let's go step-by-step...

Basis set

We rarely pay attention to the basis set selection.

For CASPT2 calculations ANO (Atomic Natural Orbitals) basis set is the right choice.

Remember that Pople's basis sets were constructed for the GS!

Example: Nitric oxide, CASPT2 (CAS 8).

basis set	IP, eV	EA, eV
STO-3G	6.9	6.3
6-31G	9.3	0.6
6-31G*	9.1	1.0
6-31G**	9.1	1.0
ANO-S-VDZP	9.1	0.04
ANO-L-VTZP	9.4	0.03
experiment	9.3	0.03

Symmetry

Symmetry (often) simplifies the selection of active space. Input can be set up just by indication of the sizes of subspaces (number of inactive orbitals).

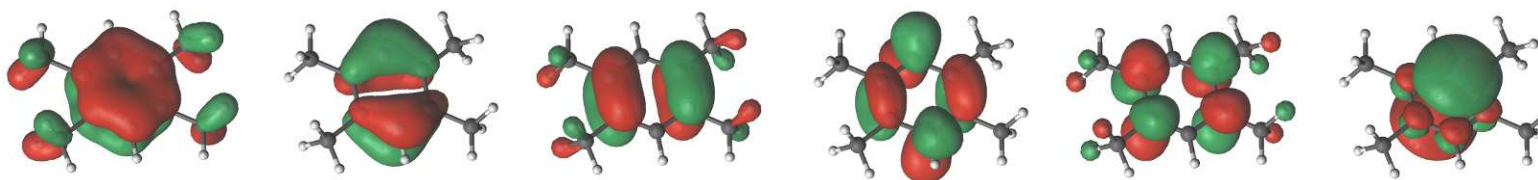
Although some symmetry analysis is needed, most interesting orbitals (to be placed into the active space) are located in 'obvious' places.

Orbitals of trans-1,3-butadiene separated by irrep of C_{2h} point group. Symmetry can easily spot π orbitals..

irrep	a_g	b_u	b_g	a_u
$(1s)_C$	2	2	0	0
$(\sigma)_{CC}$	2	1	0	0
$(\sigma)_{CH}$	3	3	0	0
$(\pi)_{CC}$	0	0	1	1
$(\pi^*)_{CC}$	0	0	1	1
$(\sigma^*)_{CC}$	2	1	0	0
$(\sigma^*)_{CH}$	3	3	0	0

somewhere around HOMO-LUMO..

For benzene molecule we know the active space - 6 π orbitals.
So, same should be valid for durene - 1,2,4,5-tetramethylbenzene...



For virtuals (with large basis set):

π^* orbitals are: **LUMO+14, LUMO+15, LUMO+43**

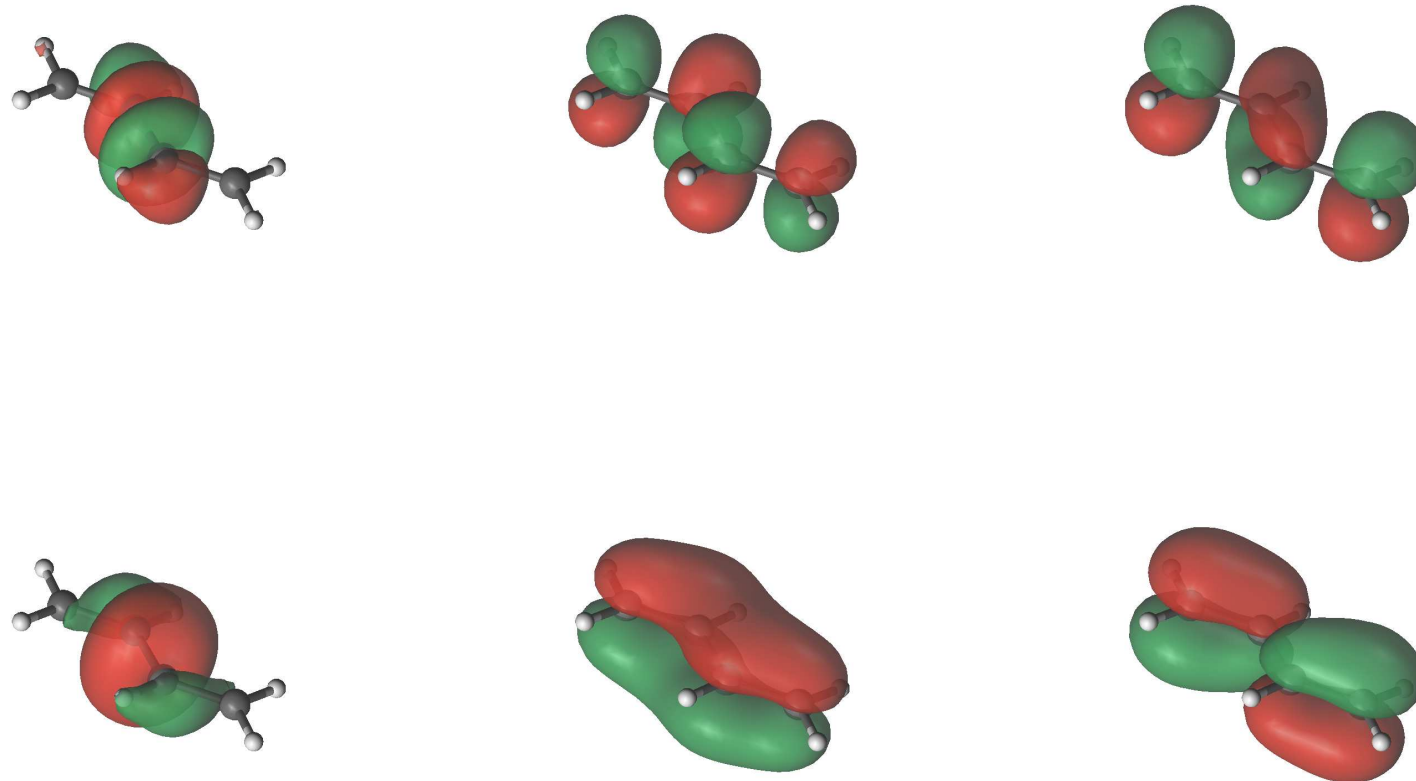
Ways to find active space..

- Active space depends on your problem!
- **Always** do you calculations in two steps:
 - ◆ construct initial guess
 - ◆ run the actual calculation
- tools for active space selection
 - ◆ visual selection (GV, ‡)
 - ◆ localization (to make orbital recognizable)
 - ◆ use small basis set as a start ‡
 - ◆ RAS-probing : make small RAS1/RAS3 calculation ‡
- **Always** check that you active space did not change

‡ - examples included into CASPT2 lab

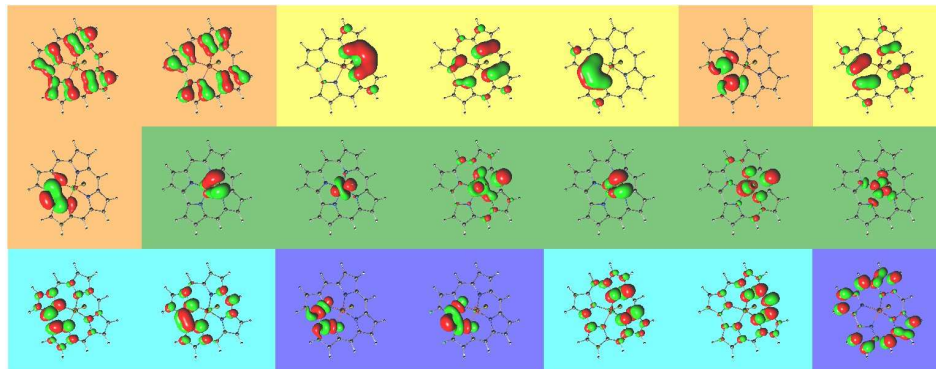
Visual inspection of orbitals

Selection of active orbitals for reaction of dissociation of trans-butadiene molecule into two vinyl radicals



More complicated case

- run preliminary calculation
- visualize orbitals, using GV code

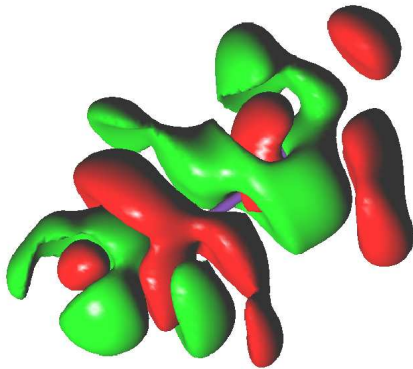


different background corresponds to different orbital types

- identify the active space
- use orbital file with selected active space, as an input for CASSCF/RASSCF calculation
- verify that your active space has been preserved
- reduce active space removing orbitals with 0/2 occupation

Basis set expansion

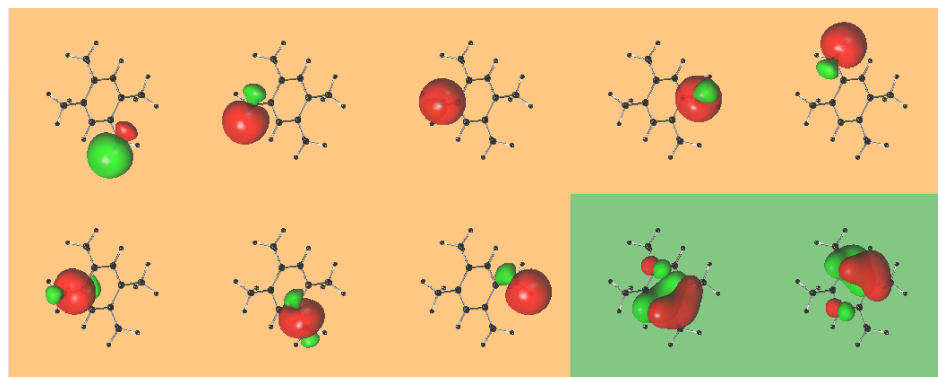
The basis set must be large in 'real calculations'. However, it is very difficult to recognize an orbital, computed with extended basis set.



- make a calculation with minimal basis set
- identify orbitals
- use EXPBAS tool to transform them to larger basis set
- (bonus) faster convergence due to a better starting point

Localization of orbitals

Localization is mostly used to get charges, bond orders.
But it can also be used to recognize the orbitals.
Especially, it is important for virtual orbitals.



RAS probing

The idea:

give a freedom, and see how it was used...

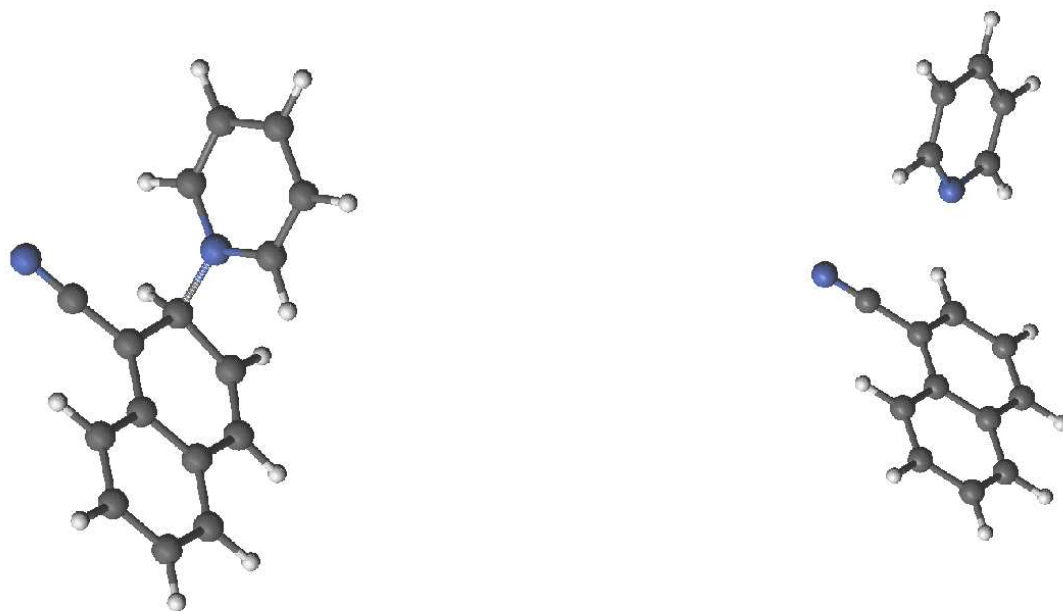
RAS1/RAS3 (or MRCI) calculation is relatively cheap,
it can be used to expose easy-to-excite orbitals

- add orbitals to the active space for RASSCF calculation
- check the occupation numbers
- keep those in between 0 and 2
- make another active space

Exciplex formation

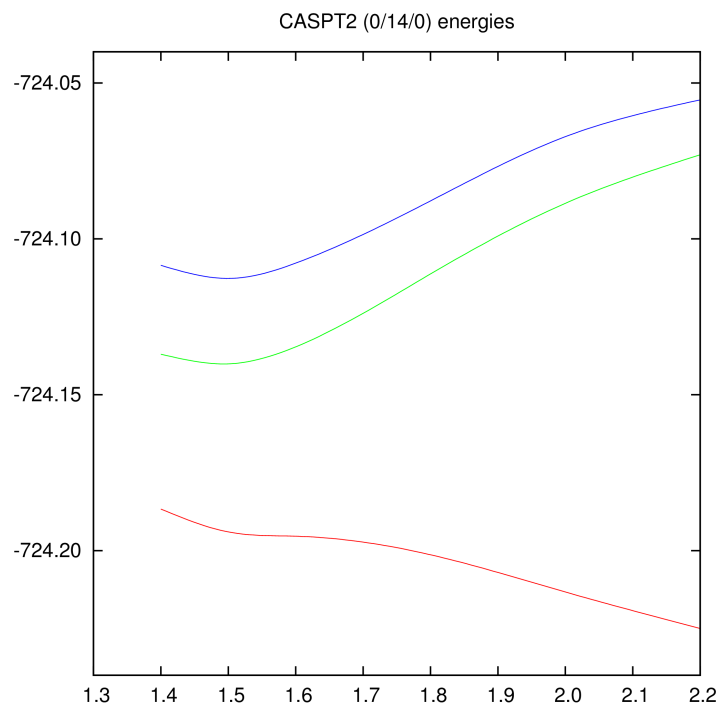
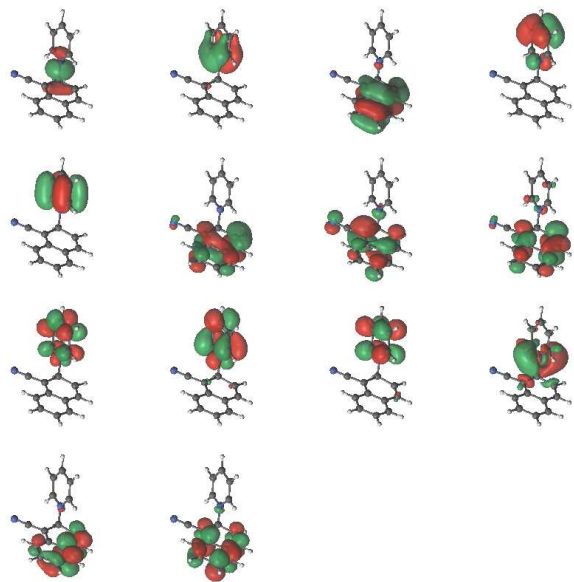
Pyridine and cyanonaphthalene can form an exciplex with distance 1.45 Å between the molecules.

experiment shows repulsive interaction for the ground state and a weak minimum for excited states



23 potentially interesting orbitals. Too many for CASSCF/CASPT2...

Playing games with active space



Two variants of active spaces:

pyridine-like (for non interacting molecules) /9/4/8/

and complex (for short distances) /11/3/9/ vs. CAS /0/14/0/.

to read

Theory:

1. K.Andersson, B.O.Roos, Multiconfigurational second-order perturbation theory, in Modern Electronic Structure Theory, ed. D.R.Yarkony. World Scientific, 1995.
2. B.O.Roos Multiconfigurational self-consistent theory, in ESQC book ed. B.O.Roos, P-O.Widmark.

MS-CASPT2:

J.Finley, P-Å.Malmqvist, B.O.Roos, L.Serrano-Andrés CPL, 288 (1998) 299

Selection of active space:

V.Veryazov, P-Å.Malmqvist, B.O.Roos, IJQC 111 (2011) 3329

Molcas tutorials:

<http://www.molcas.org/>

CASPT2 Benchmarks:

M. Schreiber, M. Silva-Junior, S. Sauer, W. Thiel, JCP 128 (2008) 134110

Message to take home...

Remember, CASPT2 is a *correction* to CAS wavefunction. It can catch some missing correlation, but it can't, for example, cure the active space!

What we need is a full CI.

We found a good recipe how to obtain the similar result but by much cheaper means...