Practical Issues on the Use of the CASPT2/CASSCF Method in Modeling Photochemistry: the Selection and Protection of an Active Space

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Outline

A Tutorial

- The CASSCF/CASPT2 Paradigm
- General rules for selecting an active space
- Orbital representations: atomic orbitals
- Orbital representations: localized molecular orbitals
- Same-but-different: purpose designed active space
- Dirty tricks: Active space stabilization

The CASPT2/CASSCF Paradigm

Is a single determinant wave function enough?

No!

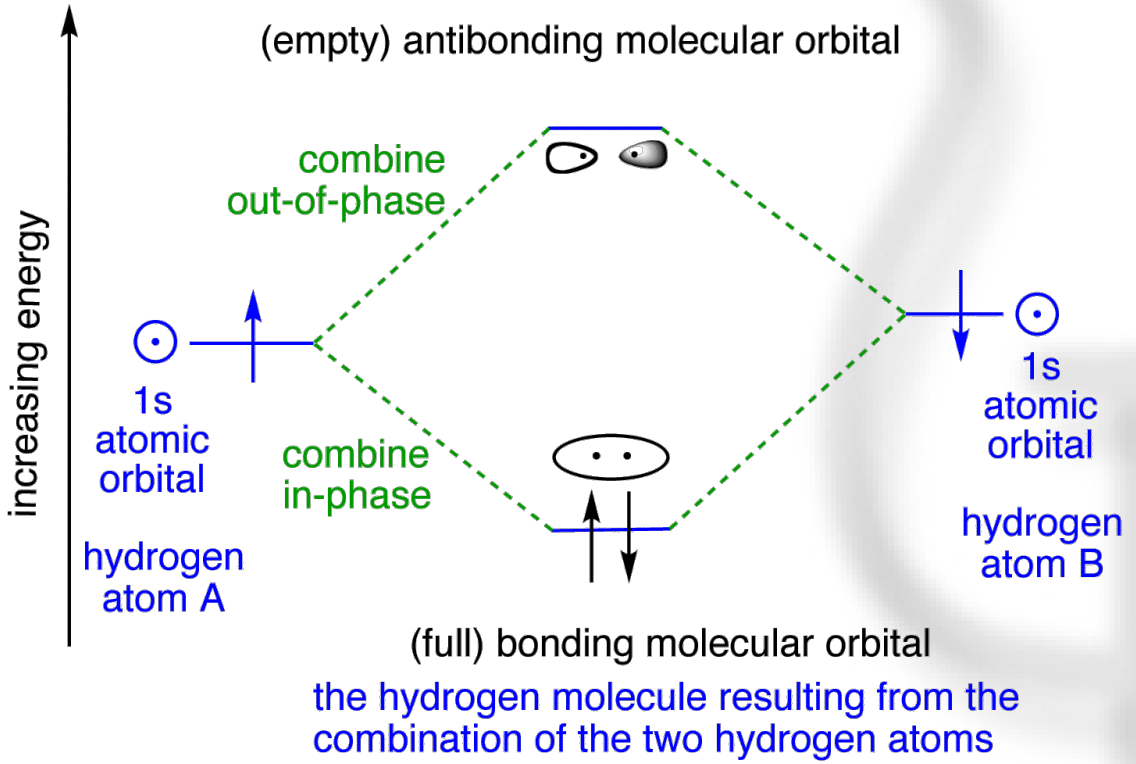
Because it can not:

- in general describe a Bond Formation/Breaking
- describe a Transition State Structure
- describe a Conical Intersection
- describe a singlet biradical structure
- on equal footing describe several states at the same time.

(Photo)Chemistry include many situations in which two or several electronic configurations are near or exactly degenerate. We need a method which can simulate this.

Breaking the H_2 bond

$$\sigma_u(r) = N_u(1s_A(r) - 1s_B(r))$$



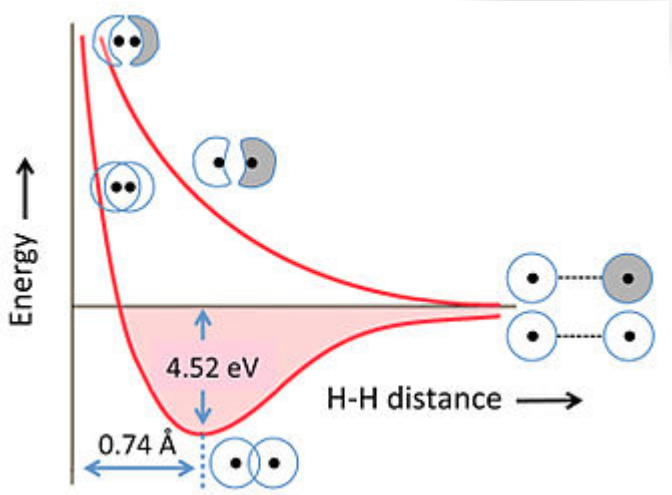
$$\sigma_g(r) = N_g(1s_A(r) + 1s_B(r))$$

H_2 wave functions

The molecular orbitals:

$$\sigma_g(r) = N_g(1s_A(r) + 1s_B(r))$$

$$\sigma_u(r) = N_u(1s_A(r) - 1s_B(r))$$



The **SCF** wave function:

$$\psi = \sigma_g(r_1)\sigma_g(r_2)\upsilon_{2,0}$$

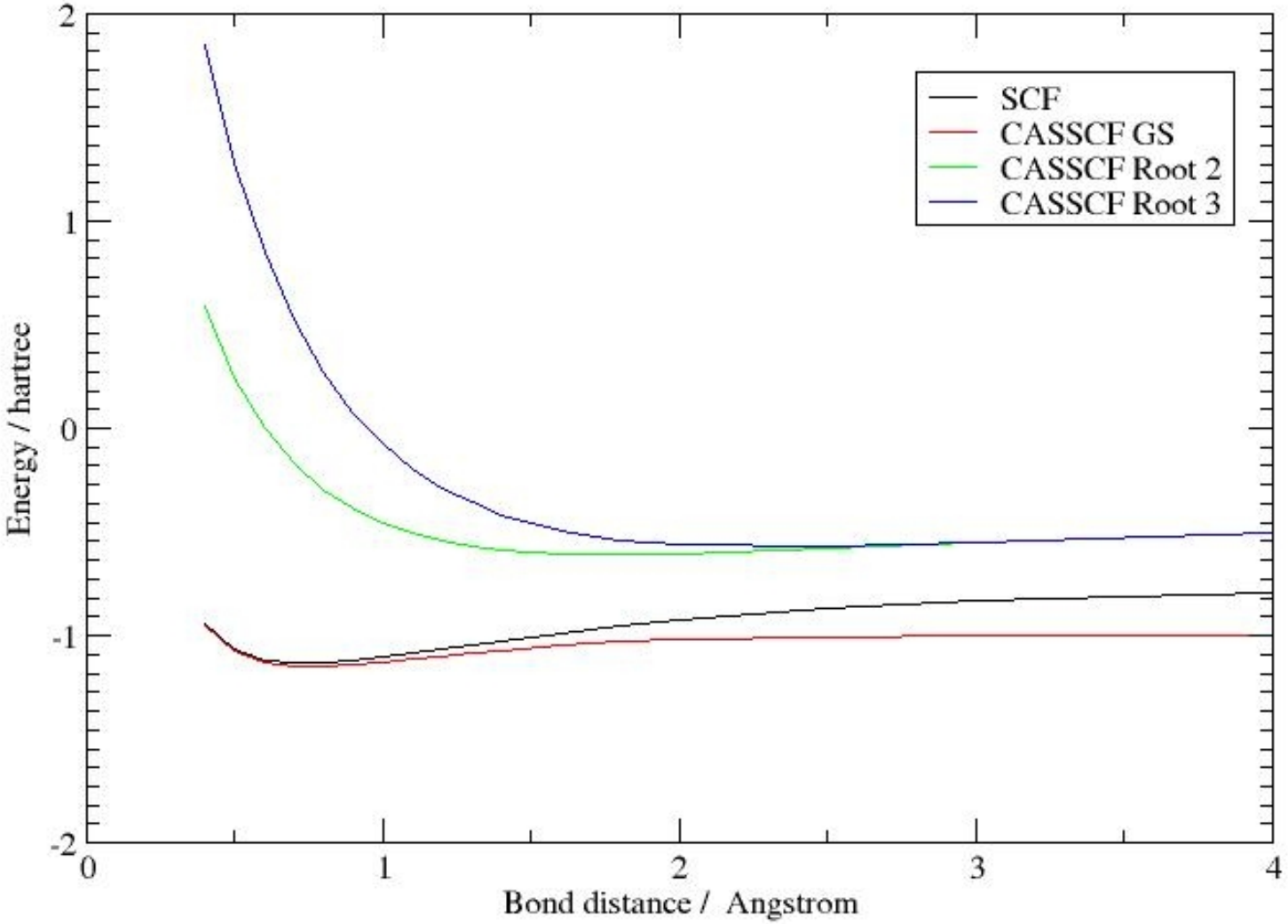
$$\psi = N_g^2(1s_A(r_1)1s_A(r_2) + 1s_A(r_1)1s_B(r_2) + 1s_B(r_1)1s_A(r_2) + 1s_B(r_1)1s_B(r_2))\theta_{2,0}$$

The single configuration wave function contains both terms as "H + H", "H^- + H^+" and "H^+ + H^-" in a fixed ratio! *We need some flexibility.*

The **CAS** wave function:

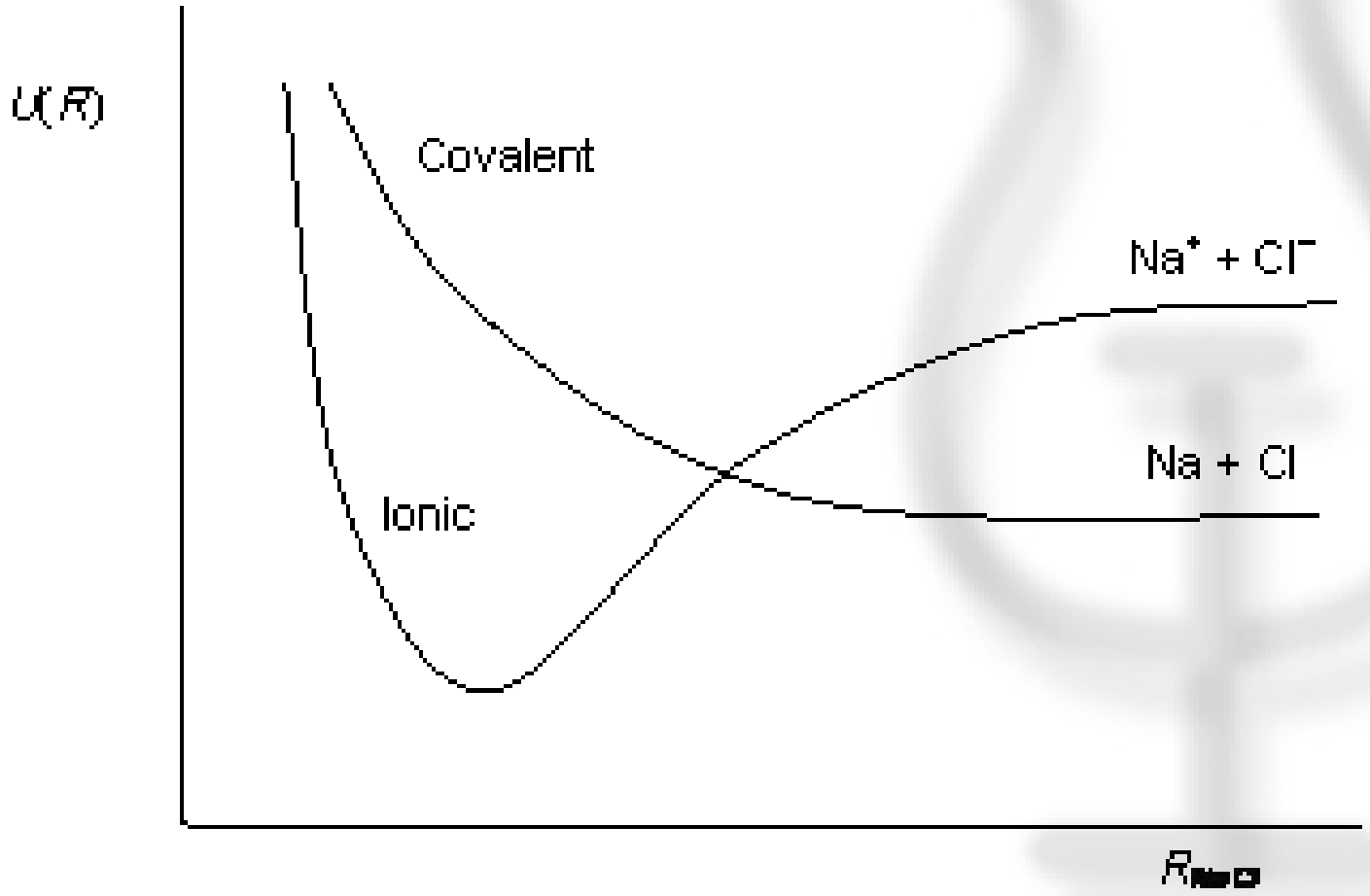
$$\psi = (C_1 1s_A(r_1)1s_A(r_2) + C_2 1s_A(r_1)1s_B(r_2)$$
$$+ C_3 1s_B(r_1)1s_A(r_2) + C_4 1s_B(r_1)1s_B(r_2))\theta_{2,0}$$

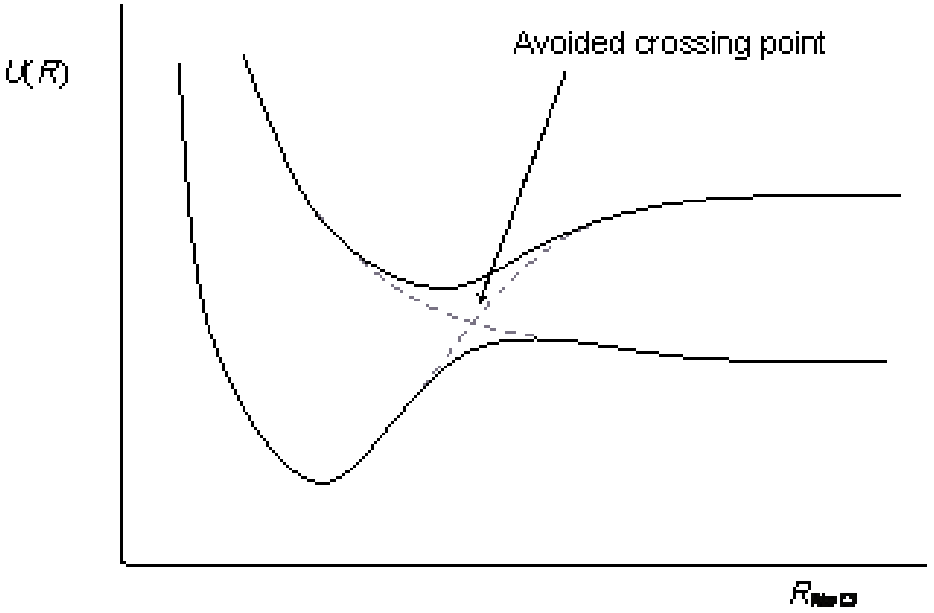
H_2 the CASSCF way: 2-in-2

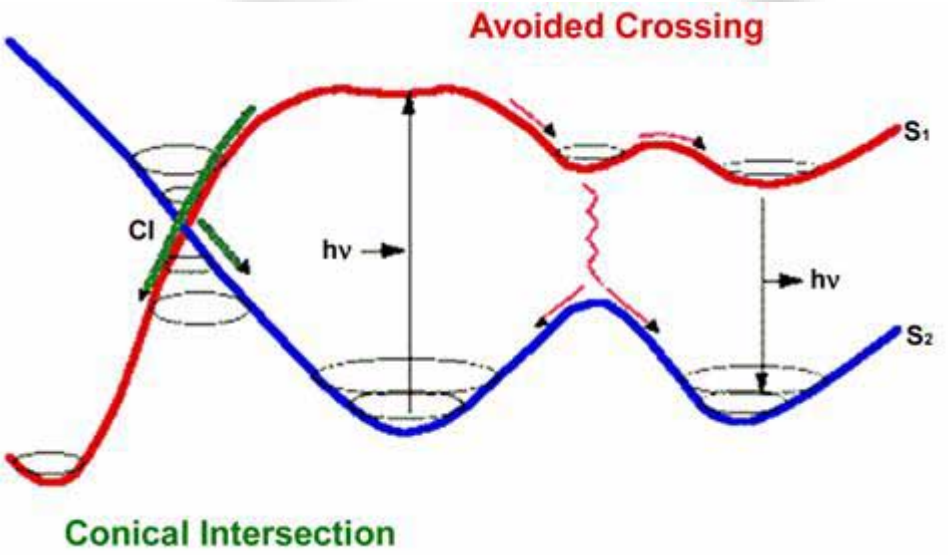


The CASSCF wave function has the correct asymptotic behavior!

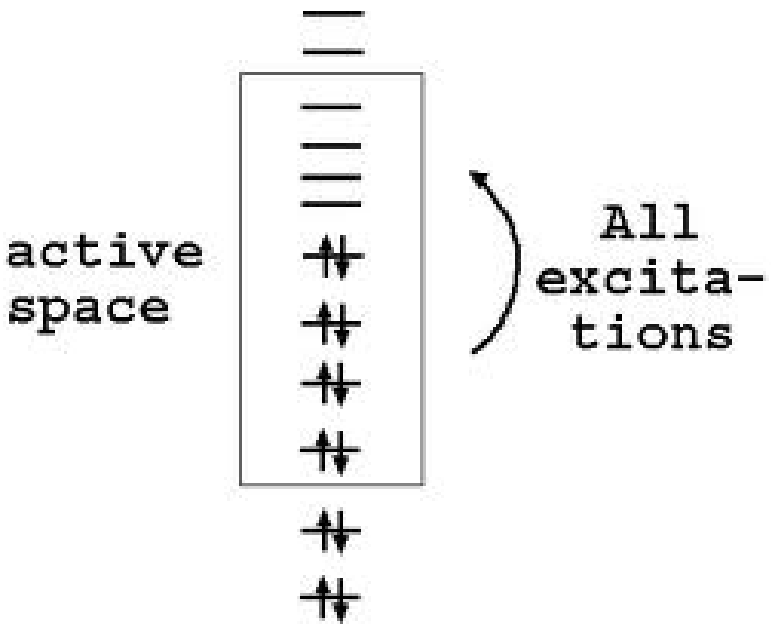
Avoided crossings: a two state phenomena - the mother of transition states




Avoided crossing point
U(R)
R


Avoided Crossing
CI
hν
hν
S1
S2
Conical Intersection

The Complete Active Space SCF



The (SA-)CASSCF model treats the static correlation.
For qualitative accuracy add e-e correlation with perturbation - ((X)MS)-CASPT2.

The CASSCF model :

- Inactive orbitals
- Active space orbitals
- Virtual orbitals

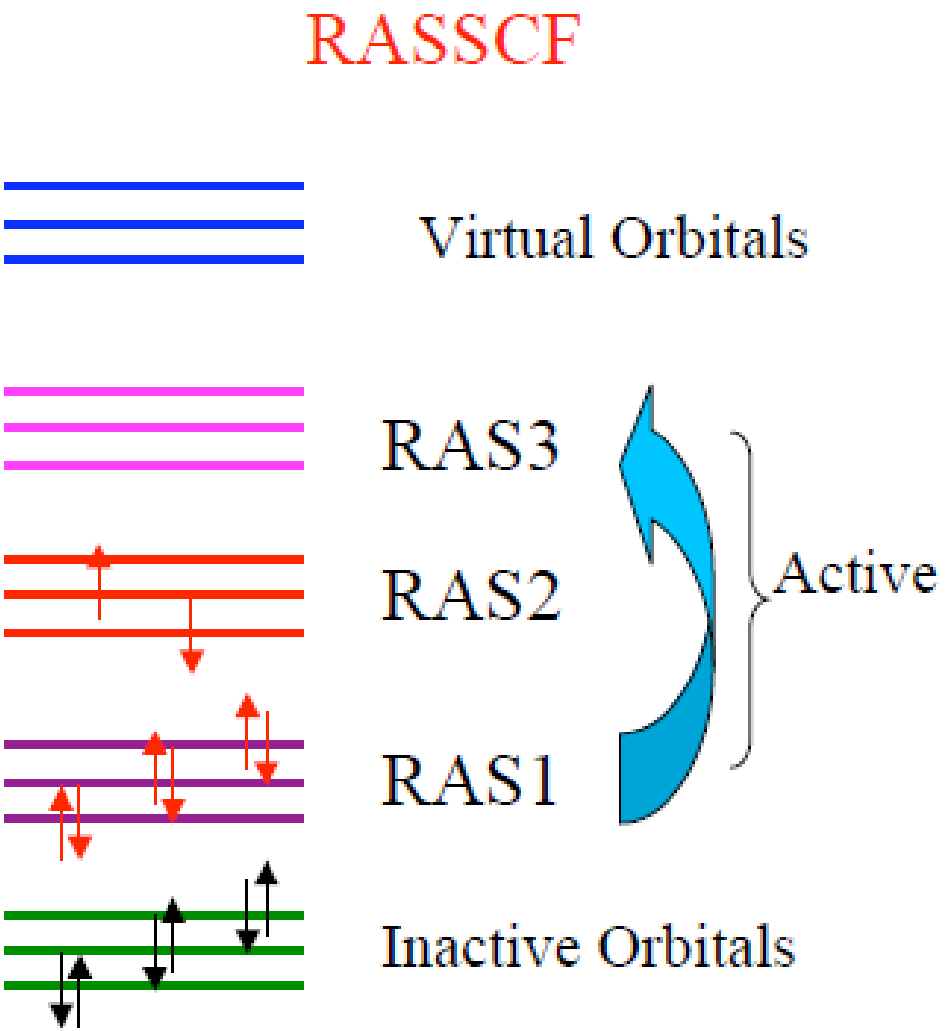
The CASSCF is a Full-CI in a subspace of the orbital space.

It is a spin eigenfunction.

Natural orbital analysis gives partial occupation numbers (0-2).

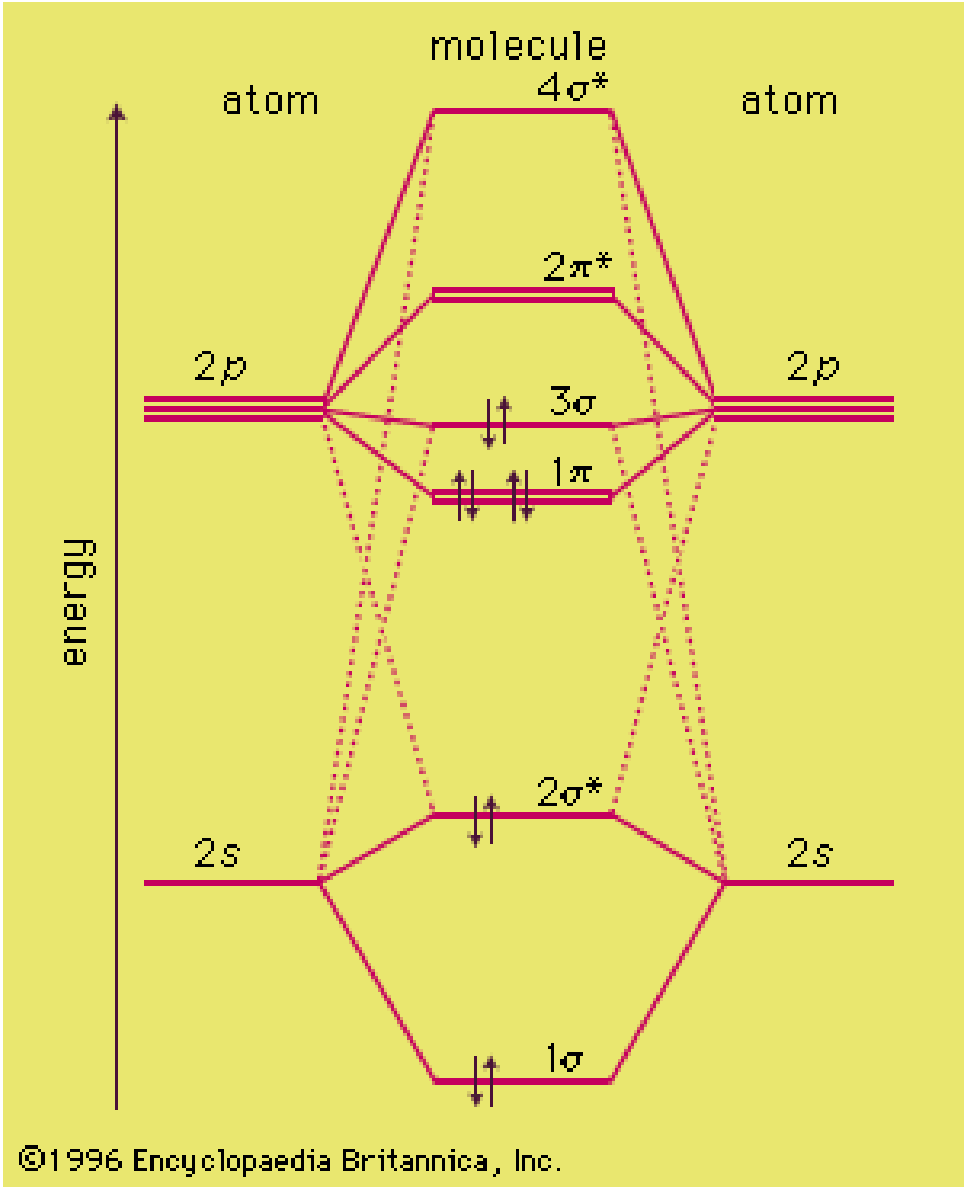
State Average CASSCF treats several states at the same time.

The Restricted Active Space SCF



Generalized active space SCF - GASSCF

The active space



Select active orbitals to:

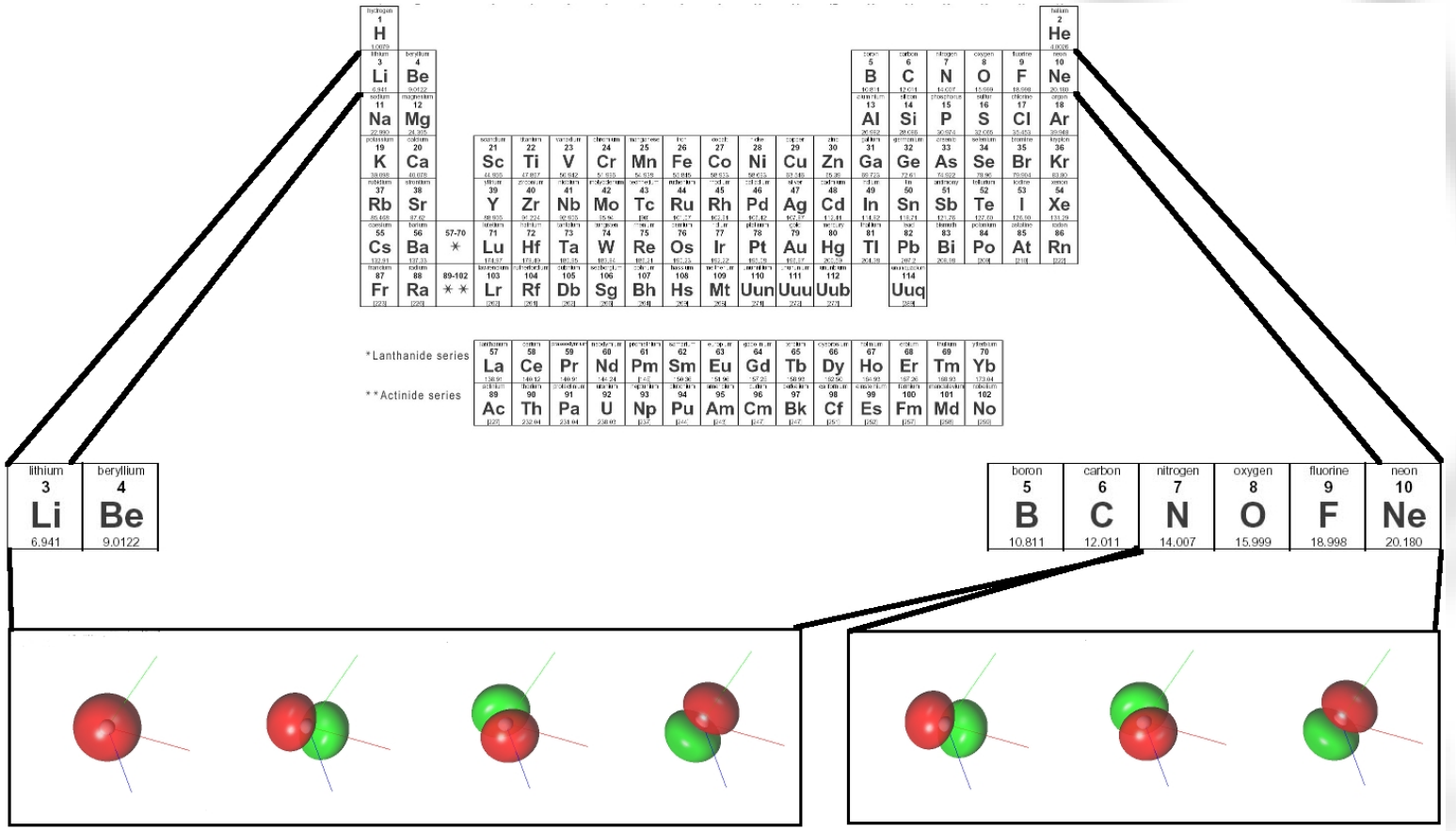
- Give correct dissociation
- Correct degeneracies (incomplete shells)
- Correct excited states
- Treat near-degeneracies

The orbitals around the Fermi gap are the candidates (be careful!!!).

Perfect pairs: σ-σ*, π-π*, δ-δ*
Lone pairs (n): maybe.

General rules for selecting active orbitals: atoms and atomic ions

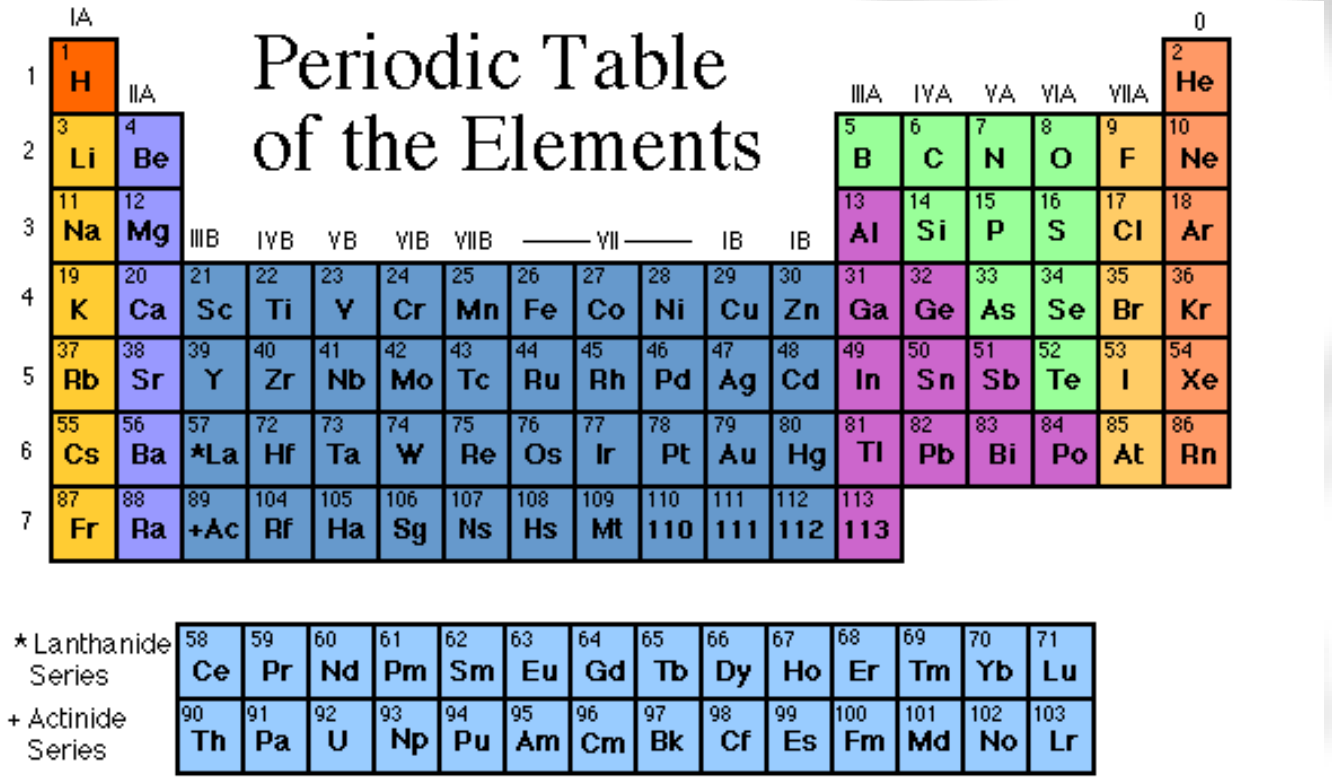
2^{nd} row elements: 2*s* and 2*p* (more than 4 valence electrons skip the 2*s*).



General rules for selecting active orbitals: atoms and atomic ions

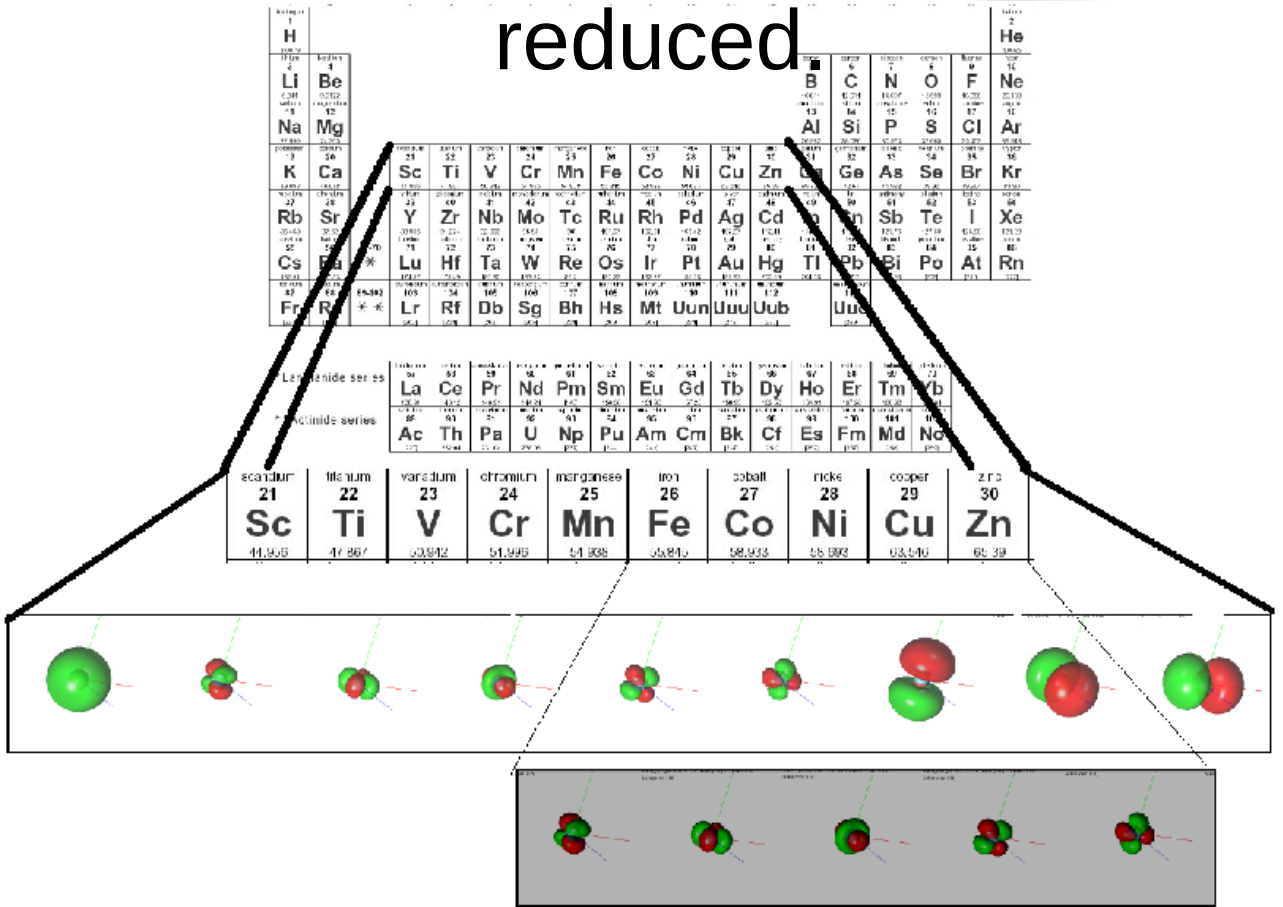
3rd row elements: 3*s* and 3*p* (more than 3 valence electrons skip the 3*s*).

As the sp^x hybridization is reduced down the periodic table do not include the *s*-shell.



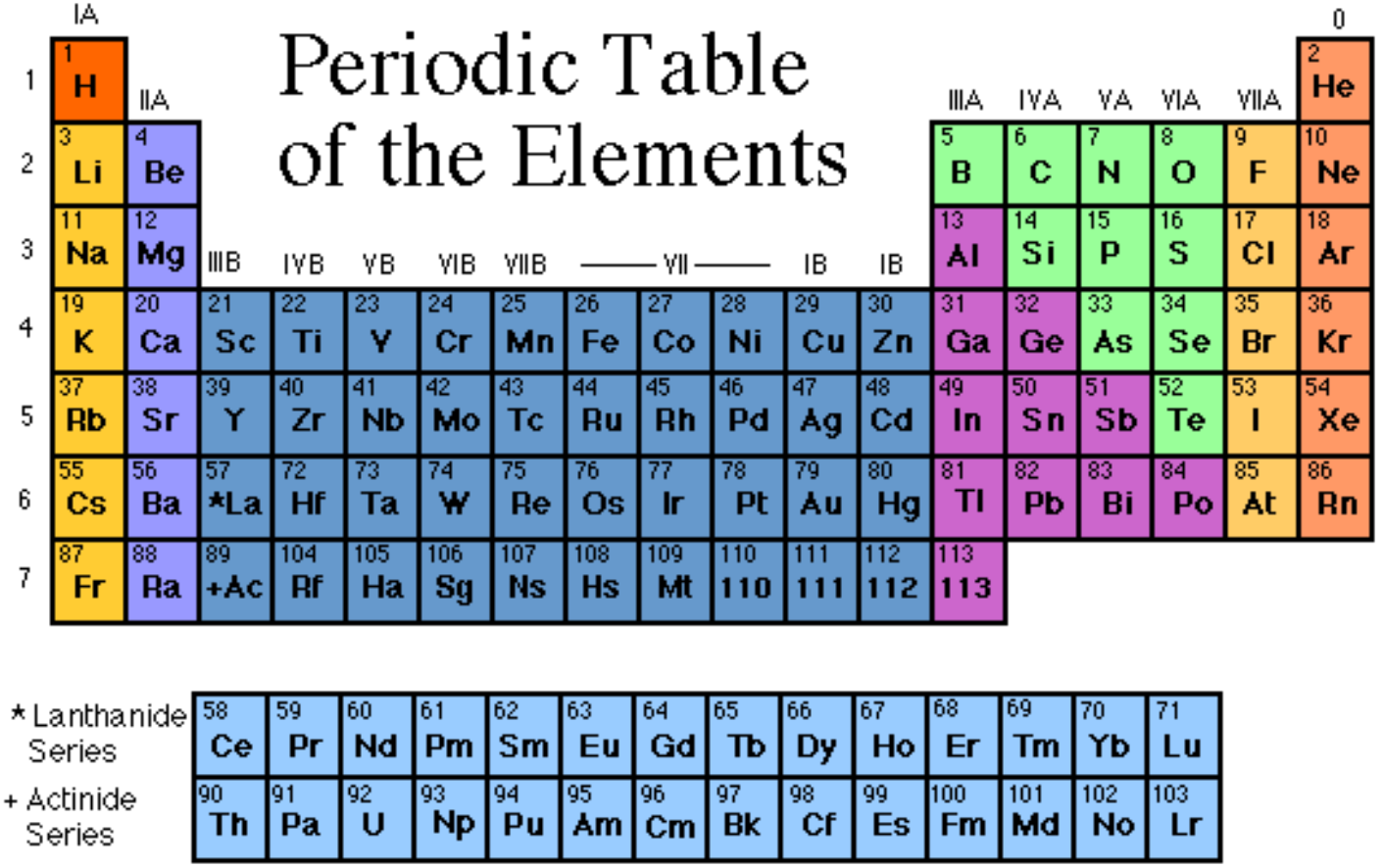
General rules for selecting active orbitals: atoms and atomic ions

1st Transition Metals: 4*s*, 3*d* and 4*p* (more than 5 d-electrons might need 4*d* – *double-shell effect*). For higher row TMs the double-shell effect is reduced



General rules for selecting active orbitals: atoms and atomic ions

Lanthanides: 4*f*, 6*s*, 6*p* and 5*d*
Actinides: 5*f*, 7*s*, 7*p* and 6*d*
Be careful wrt double-shell effects for the *f*-orbitals



General rules for selecting active orbitals: atoms and atomic ions

For Rydberg states: include these in the active space.

Note: use Rydberg specific basis sets!

General rules for selecting active orbitals: Molecules

Look for:

- “correlating pairs”: σ-σ*, π-π*, etc.
- orbitals of the excited state: n and Rydberg
- “equivalent” partners

What is the process we are studying?

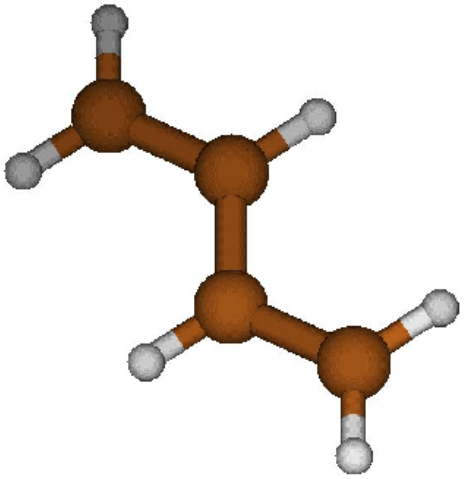
Some sloppy rules:

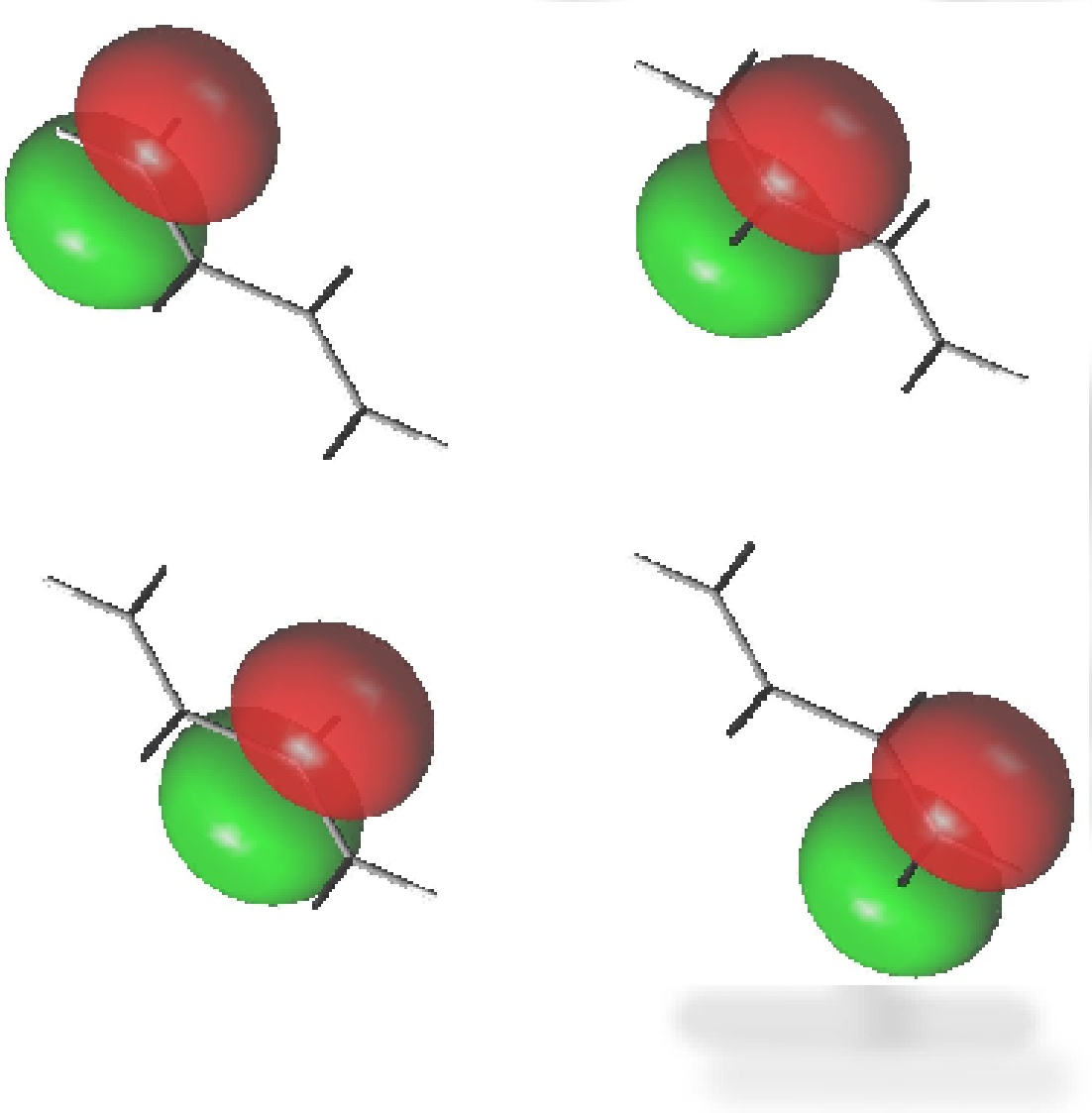
- CH bonds can be inactive
- All p orbitals in unsaturated molecule
- Rydberg orbitals for excited states above 5 eV

Orbital Representation

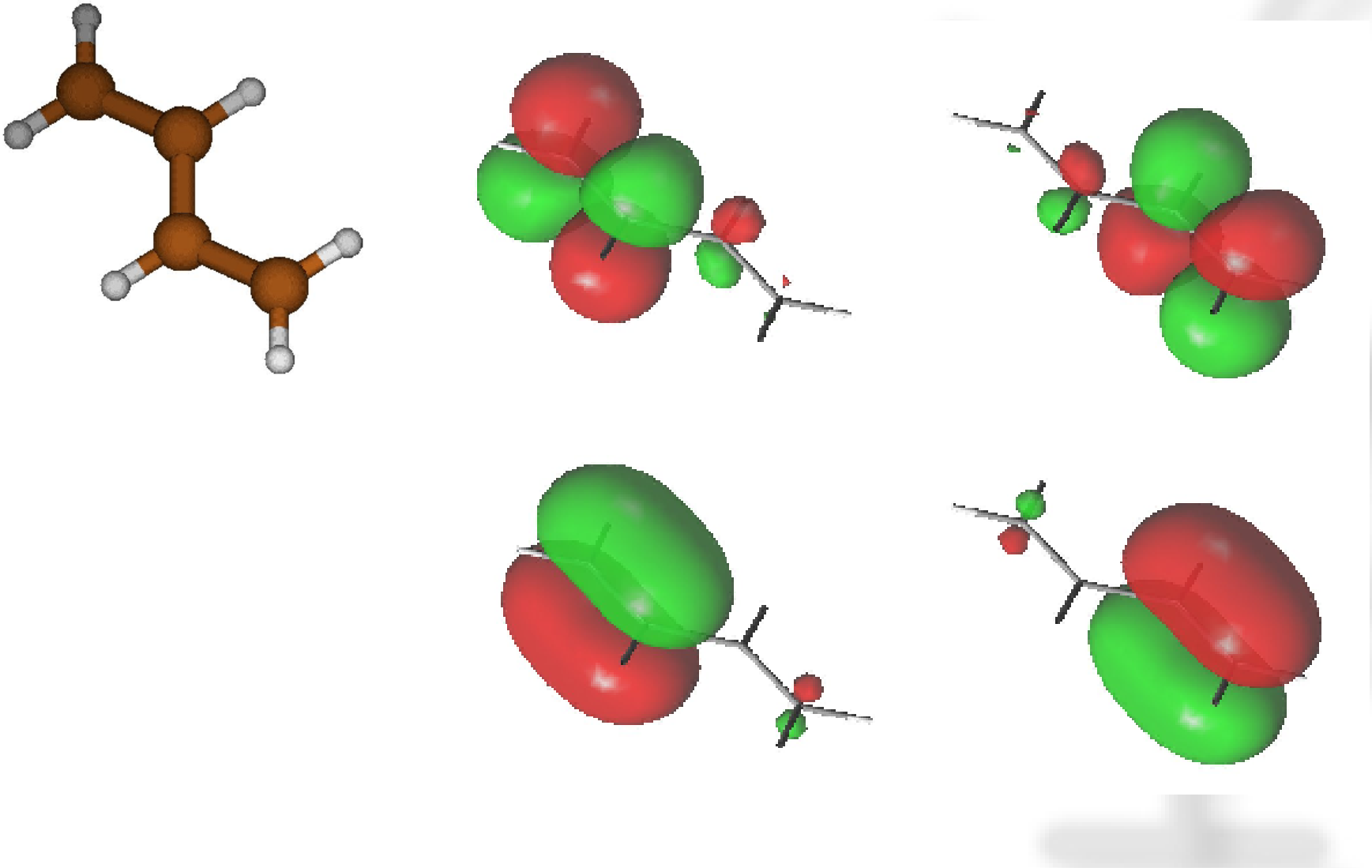
After we have selected the active space (x-in-y), which is an intellectual challenge,we have to generate it, this is more of a technical challenge!

Orbital Representations: atomic orbitals



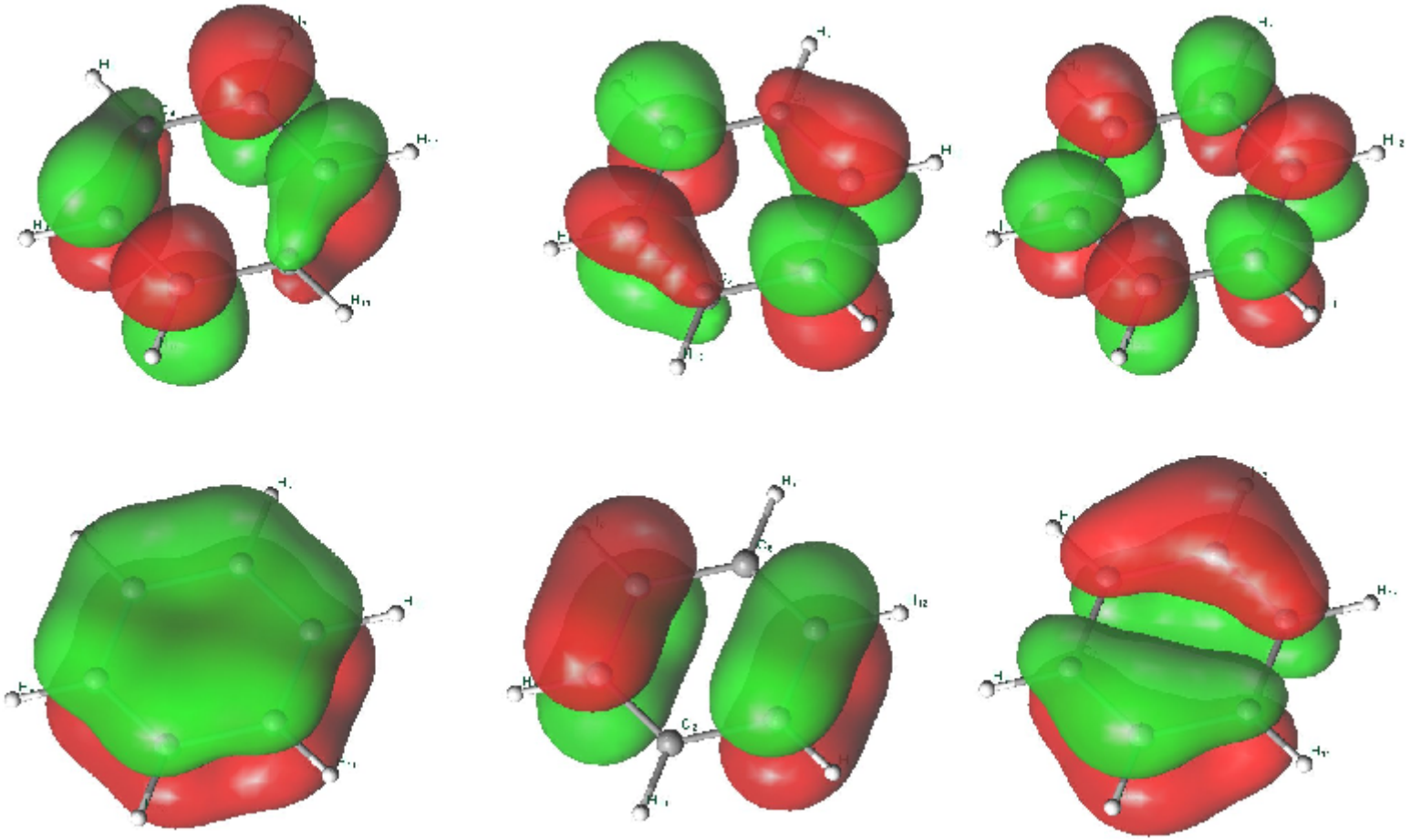


Orbital Representations: localized molecular orbitals



Localized occupied and virtual SCF orbitals, respectively.

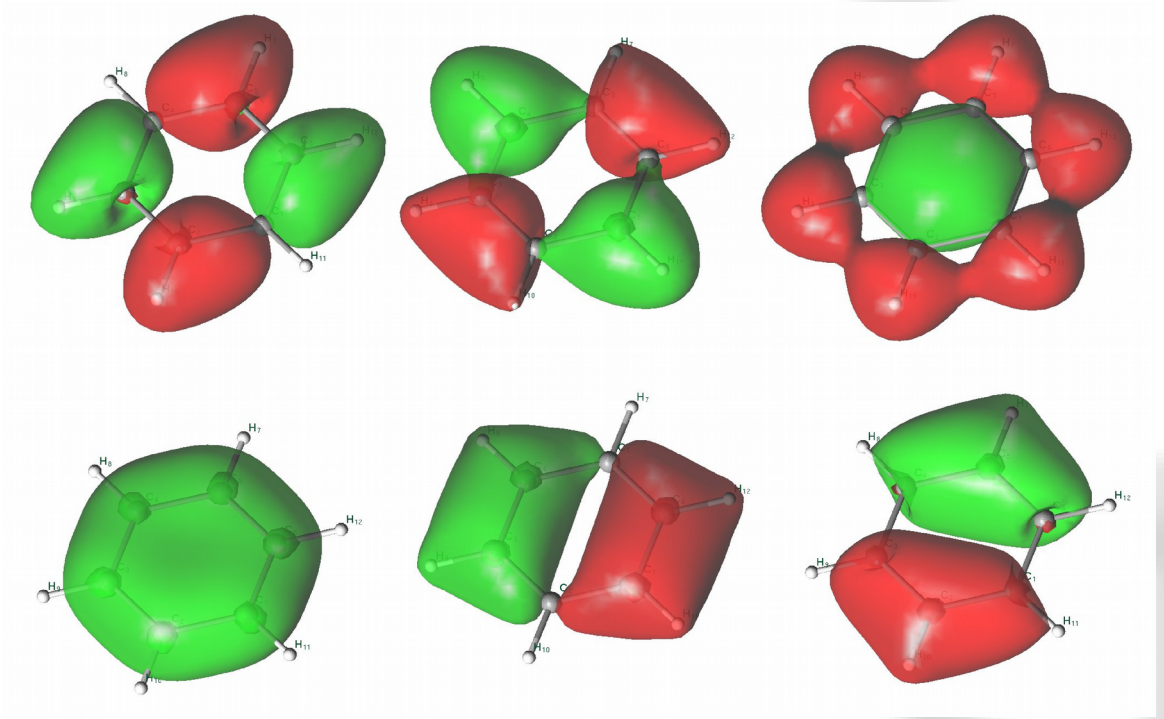
Orbital Representations: the SCF orbitals



The SCF orbitals are ***delocalized***!
Virtual orbitals are not well defined!

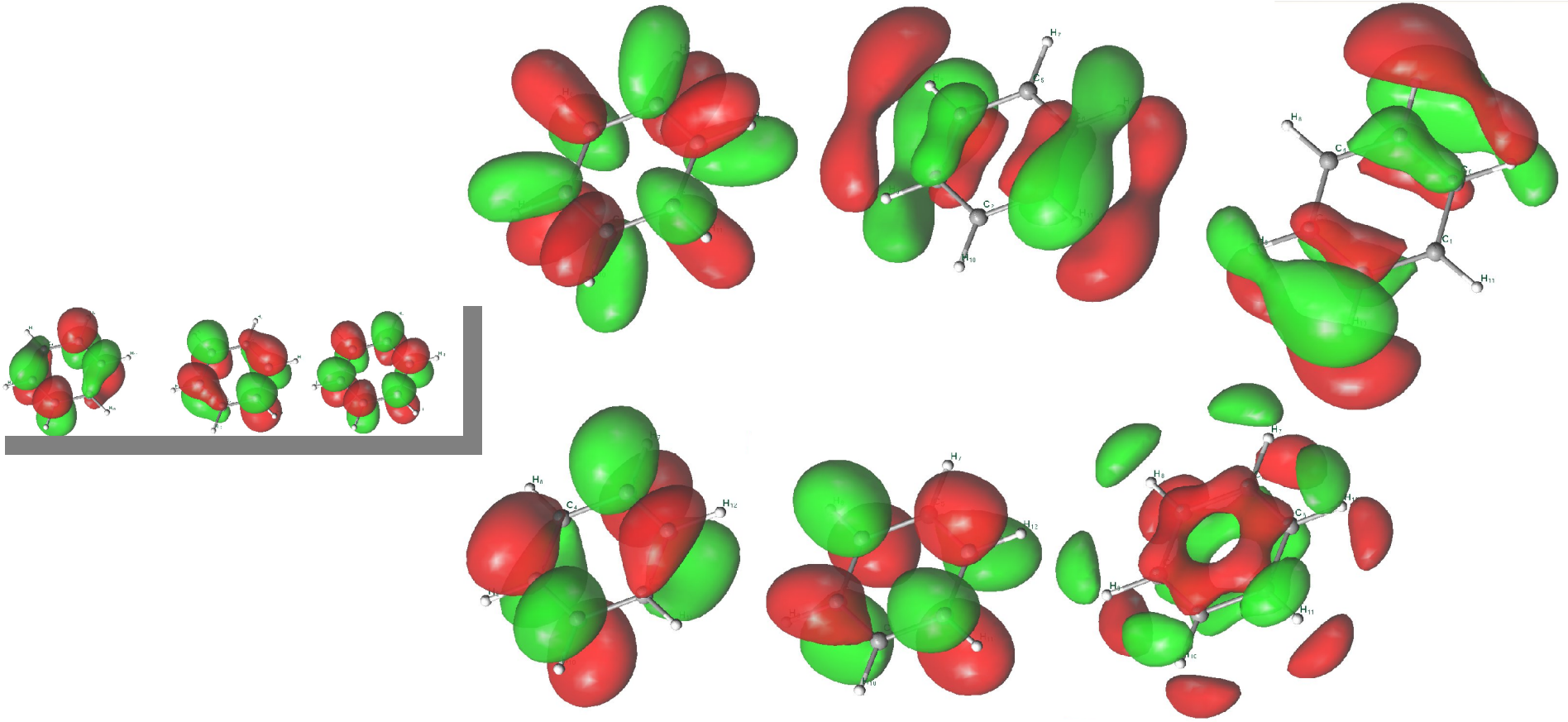
Note that these orbitals are from a minimal basis calculation.

Orbital Representations: the SCF orbitals



The SCF orbitals are ***delocalized***!
Useless for localized processes (e.g. H abstraction)

Orbital Representations: the virtual SCF orbitals



Virtual Orbitals are not well define!

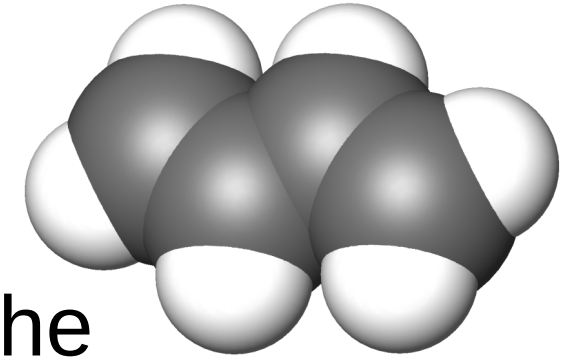
The six lowest virtual SCF π orbitals in a triple-ς basis.

Orbital representations: Strategy

- Use localized orbitals, AOs or MOs
- Do “never” use SCF orbitals
- Start with a MB basis and expand
- Double check all the time!
- Protect your orbitals once you have found them
- Be paranoid

Same-but-Different

The MCSCF solution to a specific active space is **not** unique!



Demonstration:

For butadiene we would like to study the fragmentation process of:

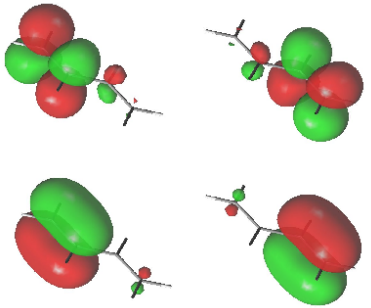
a) $C_4H_6 \rightarrow 2\ C_2H_3$

b) $C_4H_6 \rightarrow C_3H_4 + CH_2$

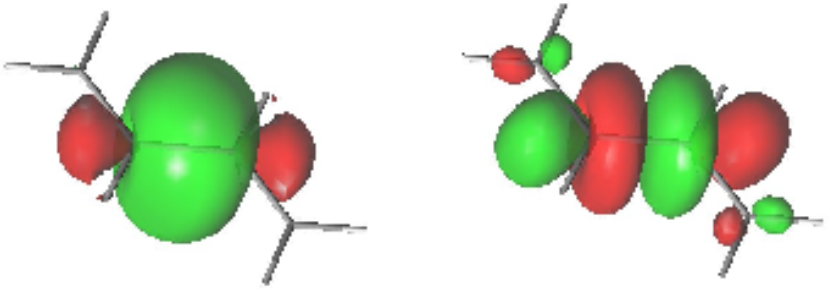
In both cases we will have the 4 π orbitals active together with the correlating pair of the bond which we are breaking (σ-σ*), that is a 6-in-6 CAS in both cases.

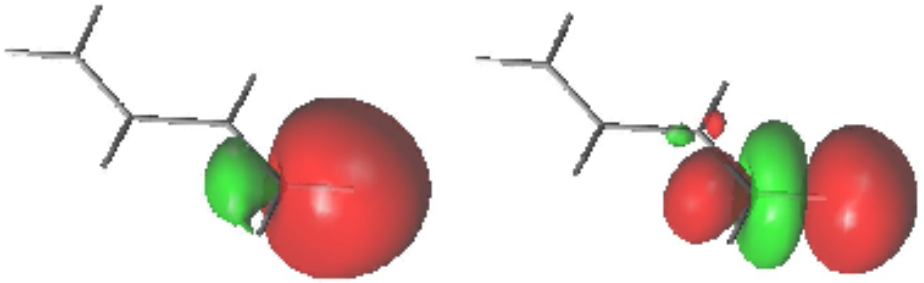
Same-but-Different: The Starting Orbitals

The π-space:



The correlating pairs in the σ-space:



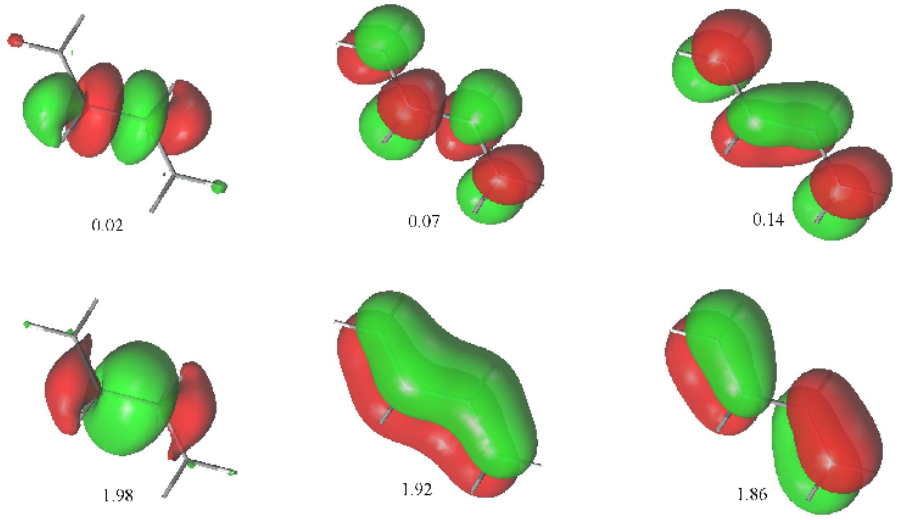


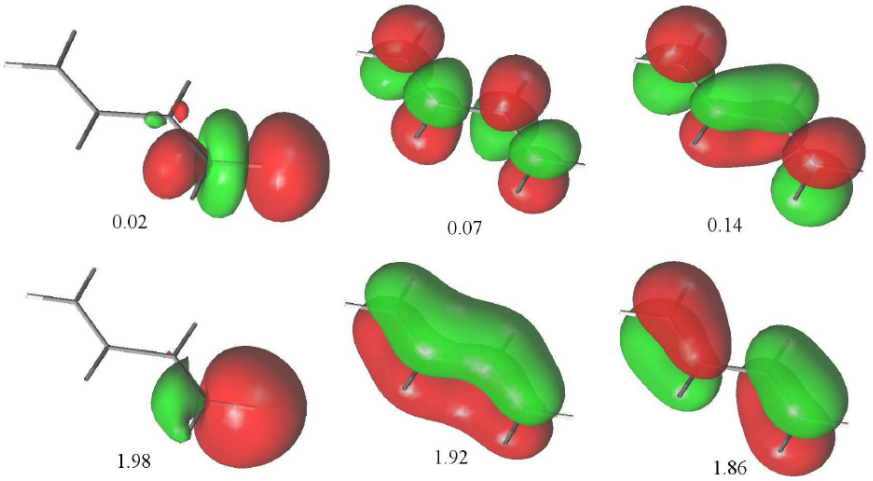
$C_4H_6 \rightarrow 2\ C_2H_3$

$C_4H_6 \rightarrow C_3H_4 + CH_2$

By carefully selecting the starting orbitals I select the “most likely” CASSCF solution.

Same-but-Different: The CASSCF Orbitals





$C_4H_6 \rightarrow 2\ C_2H_3$

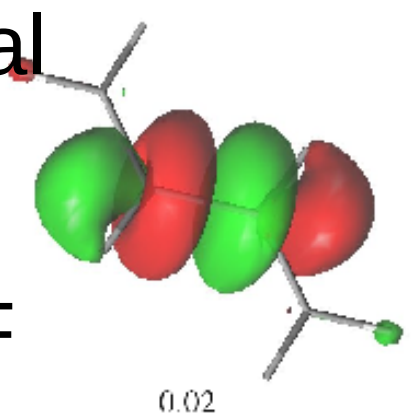
$C_4H_6 \rightarrow C_3H_4 + CH_2$

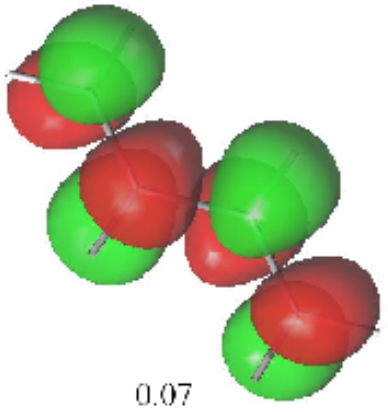
Bingo!

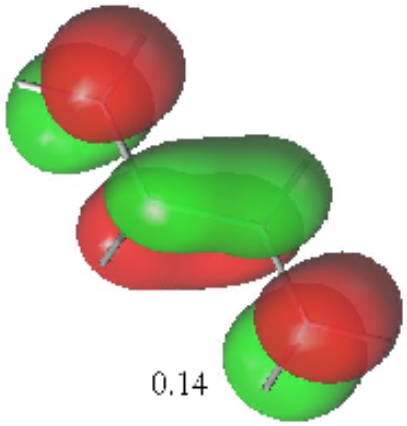
Note the active space on the right does not preserve equivalent methyl bonds.

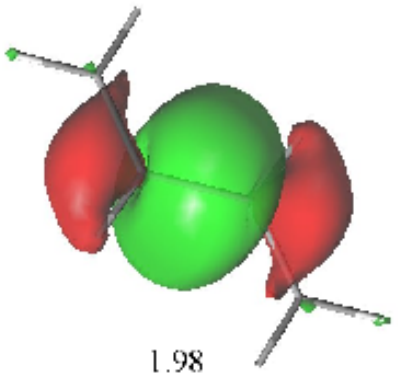
Dirty Tricks:
Active Space Stabilization

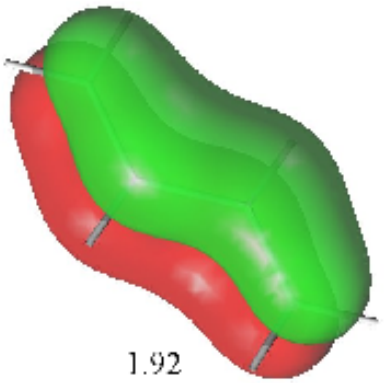
The mathematical (local) solution to the MCSCF equations are those that have strong correlating pairs.

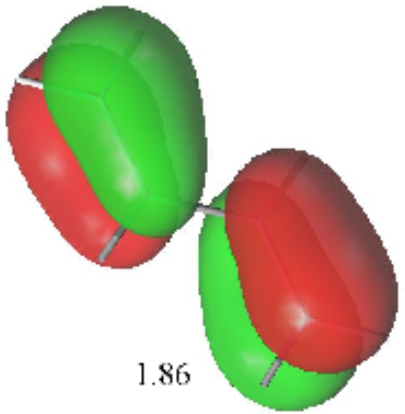












The σ bonds and lone pairs are the general problems.

Dirty Tricks:

Two near-degeneracies destabilize the (local) mathematical solution:

- Active orbitals with an occupation close to 2
- Active orbitals with an occupation close to 0

The orbitals can slip into the inactive or the virtual space, respectively.

We need to have a mathematical model for which the occupation number are not close to 2 or 0!

Dirty Tricks:

The solution to the problem is SA-CASSCF!

The SA-CASSCF occupation numbers depend on the average occupation numbers of all the states that are included in the calculation.

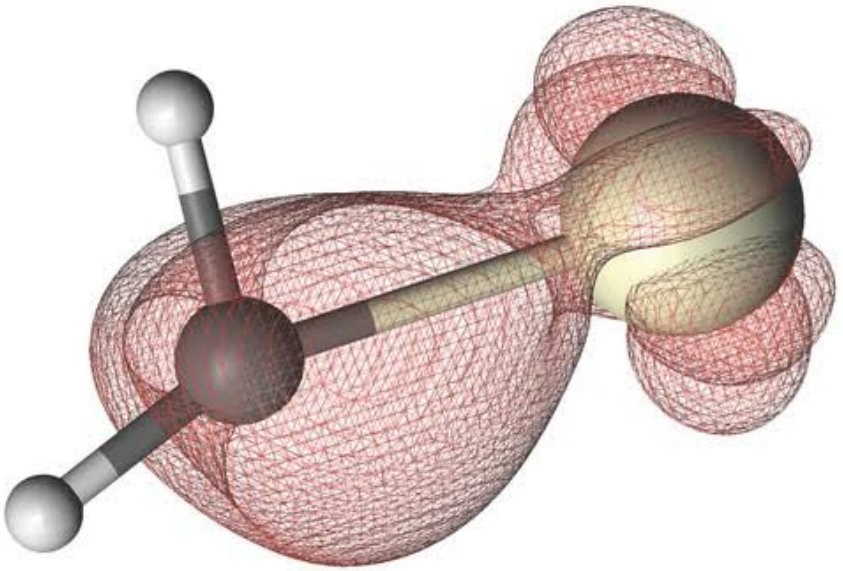
-Stabilize σ orbitals by including a state in which you have some excitation out of the σ orbital.
-Stabilize n orbitals by including a state in which you have some (n-σ* or) n-π* excitation.

This trick is only possible if you start with the correct active orbital manifold!!!

Summary

- Why Multi-configurational Methods
- The CASSCF model
- The active space
- Different orbital representations
- Be careful with SCF orbitals
- Standard AO active orbitals
- MO active orbitals
- Localized starting MO orbitals
- The solution to the MSCF eq. is not unique!!!
- Tricks
- Dynamical Electron correlation and Dispersion with (MS-)CASPT2

Multiconfigurational Quantum Chemistry



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