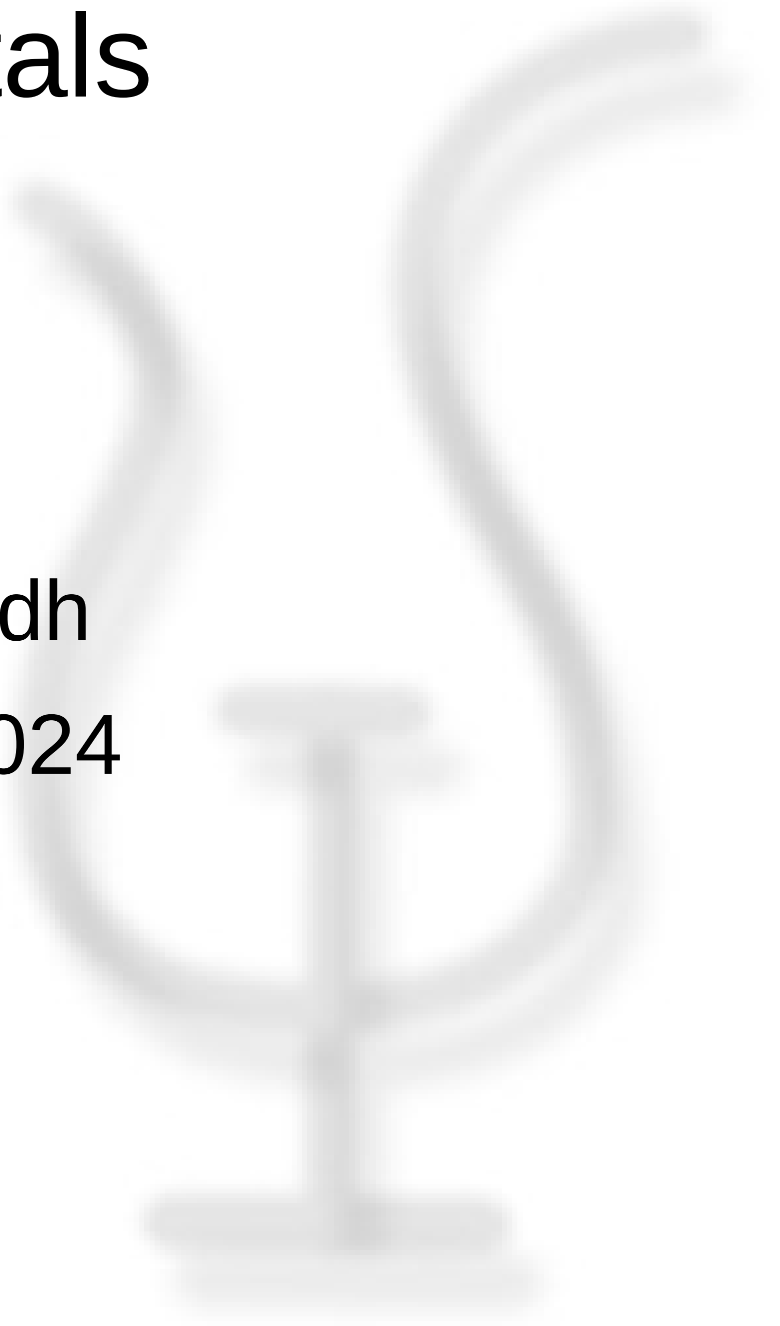
Some rules and tricks for selecting active orbitals

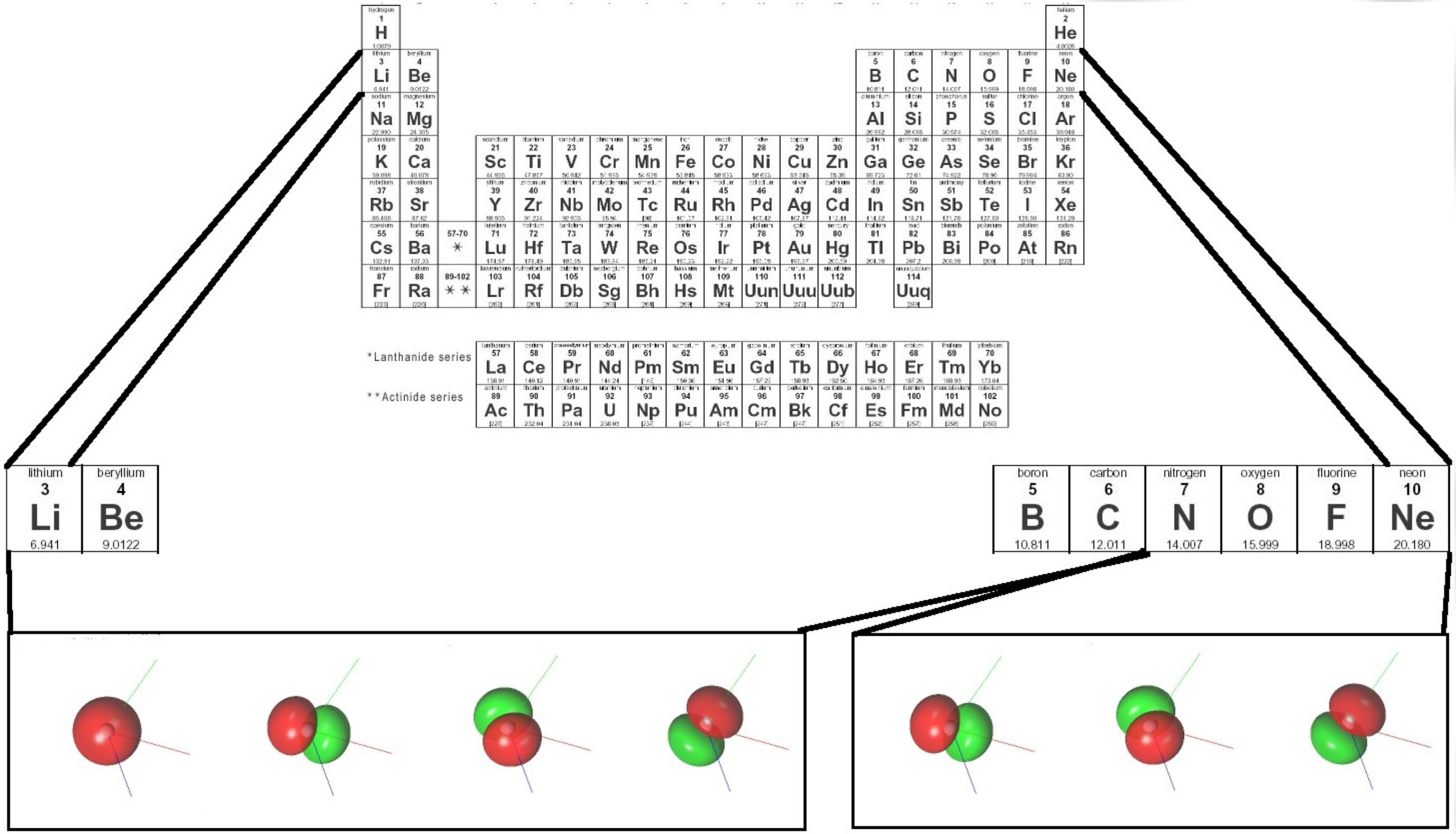


Roland Lindh

@ ESQC 2024

General rules for selecting active orbitals: atoms and atomic ions

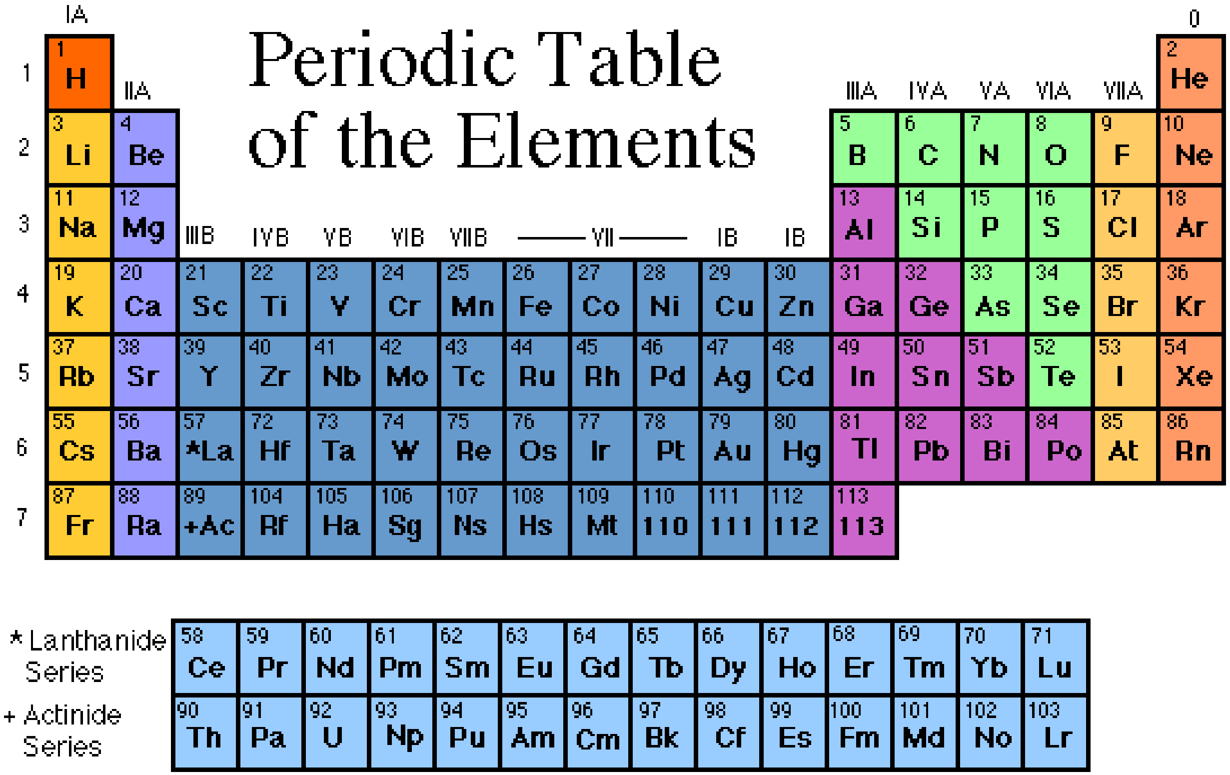
2^{nd} row elements: 2*s* and 2*p* (more than 4 valence electrons skip the 2*s*).



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.



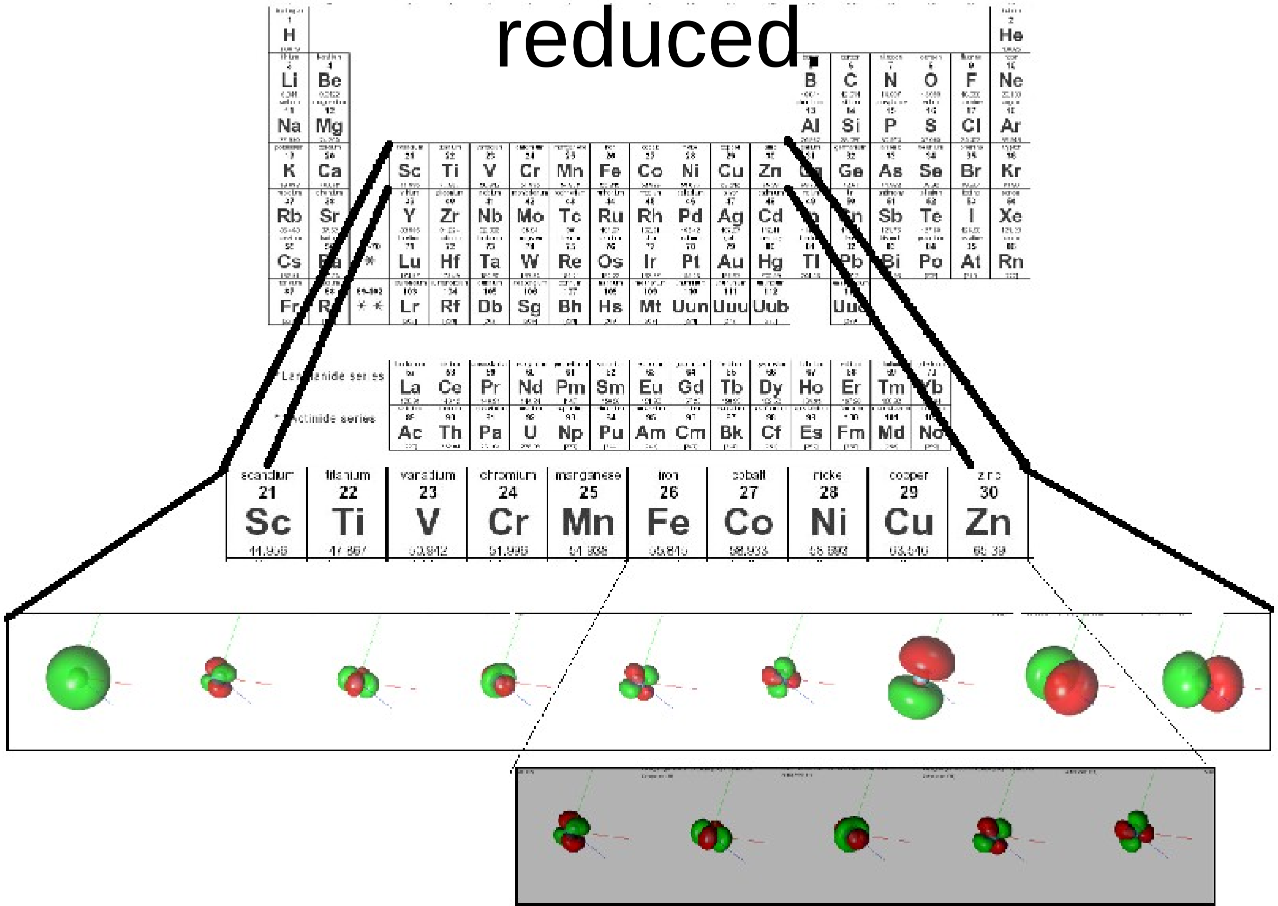
Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	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	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

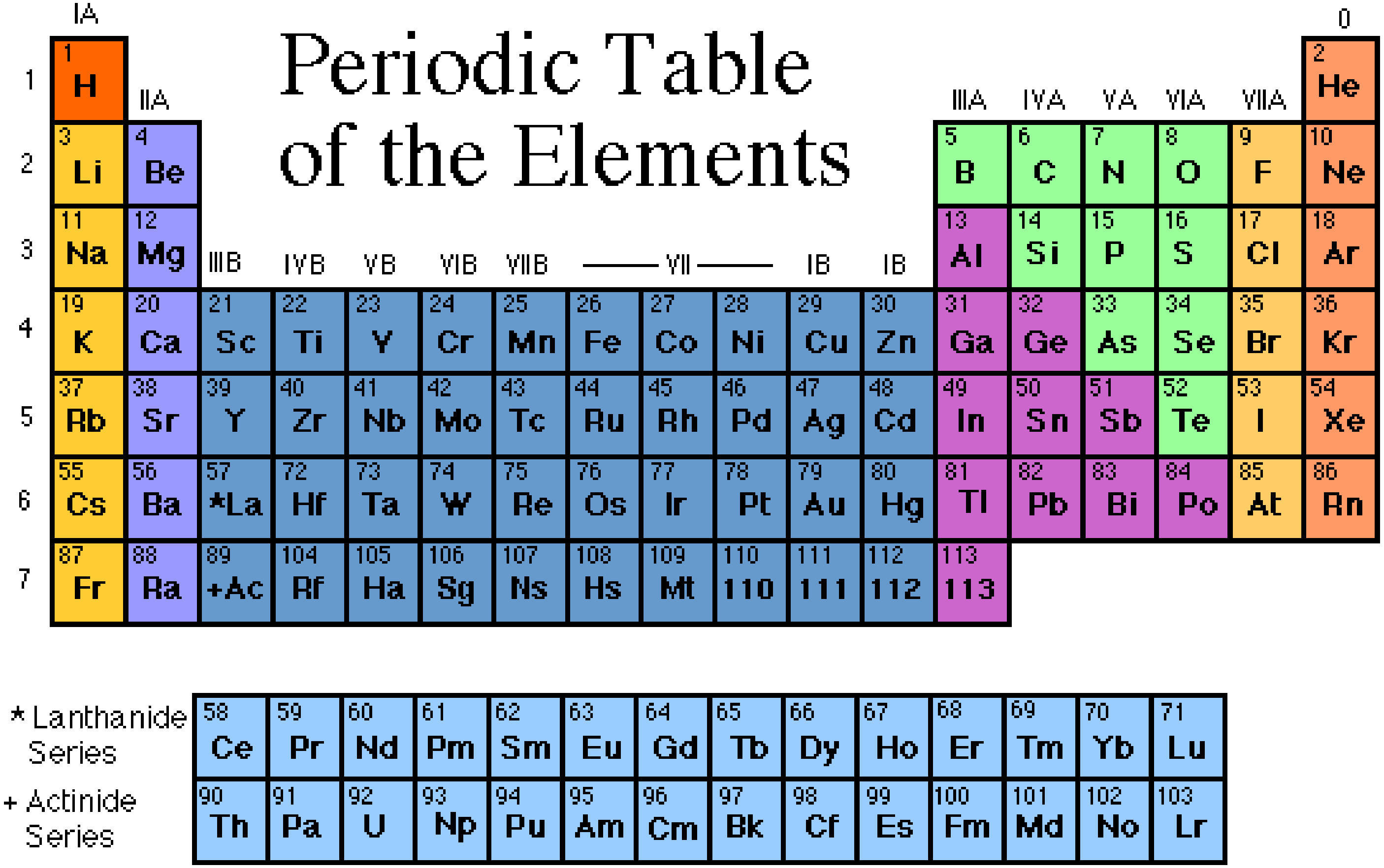
General rules for selecting active orbitals: atoms and atomic ions

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



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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?

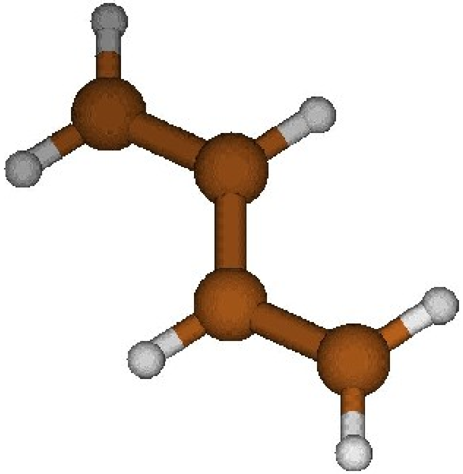
Some sloppy rules:

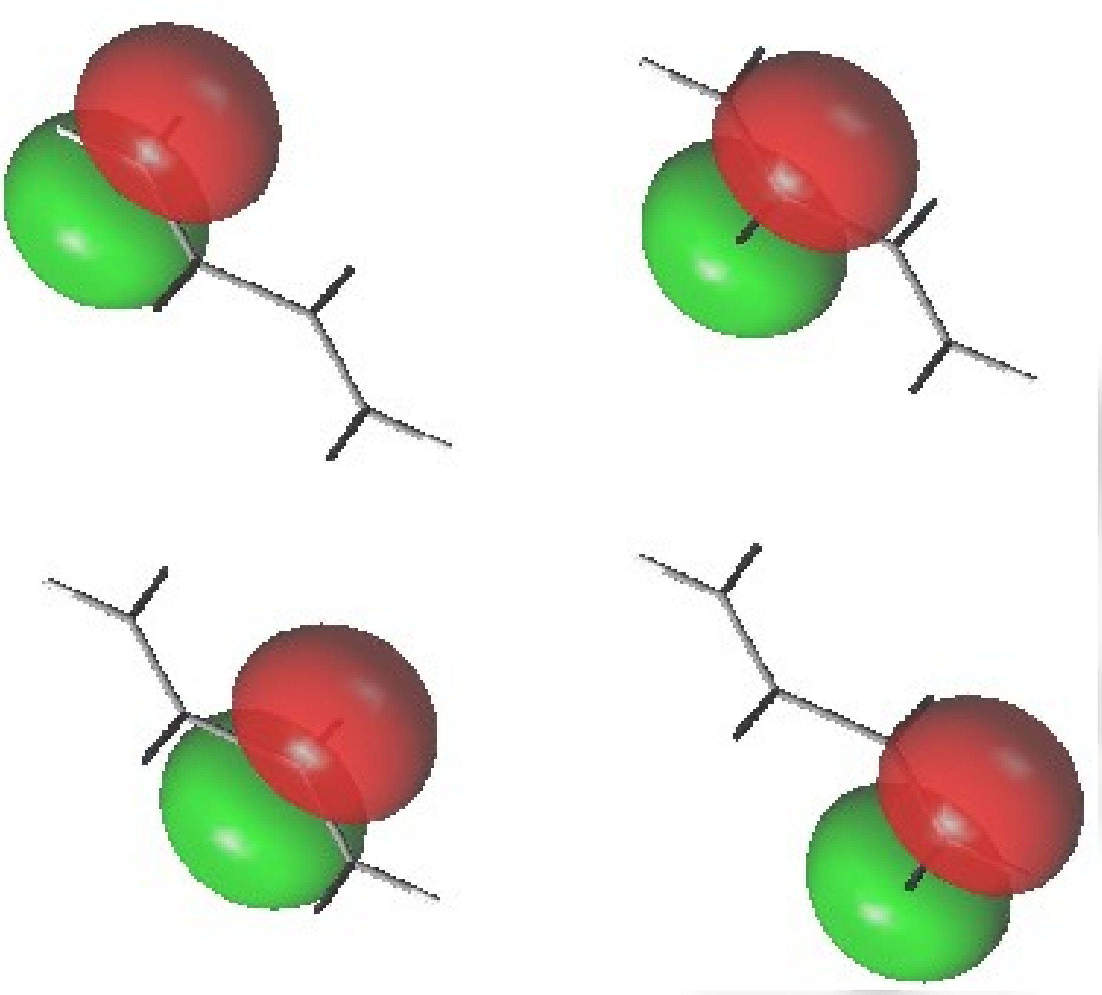
- CH bonds can be inactive
- All p orbitals in unsaturated molecule
- Rydberg orbitals for excited states above 5 eV

Orbital Representation

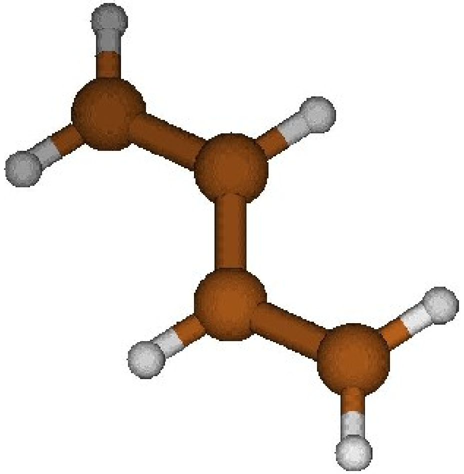
After we have selected the active space (x-in-y), which is an intellectual challenge, we have to generate it, this is more of a technical challenge!

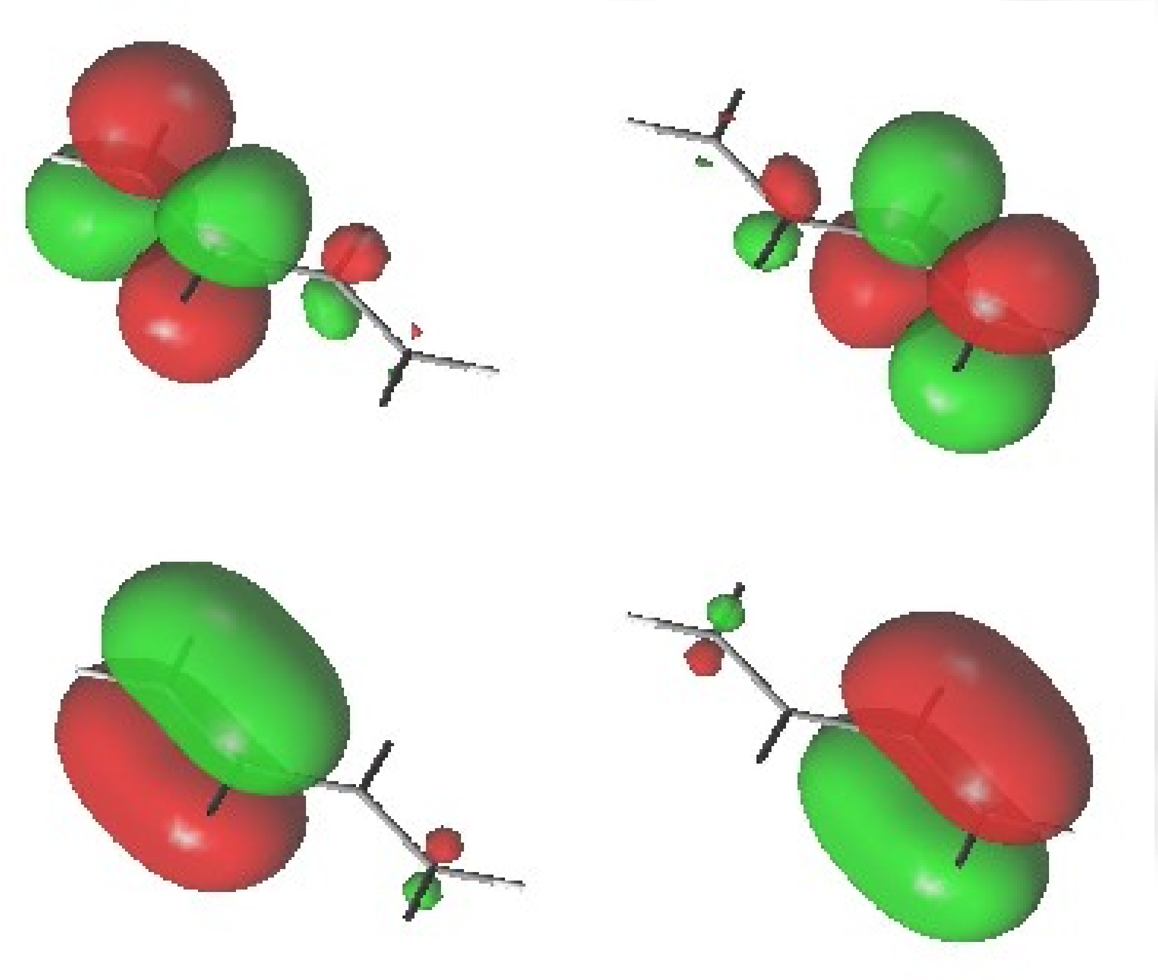
Orbital Representations: atomic orbitals





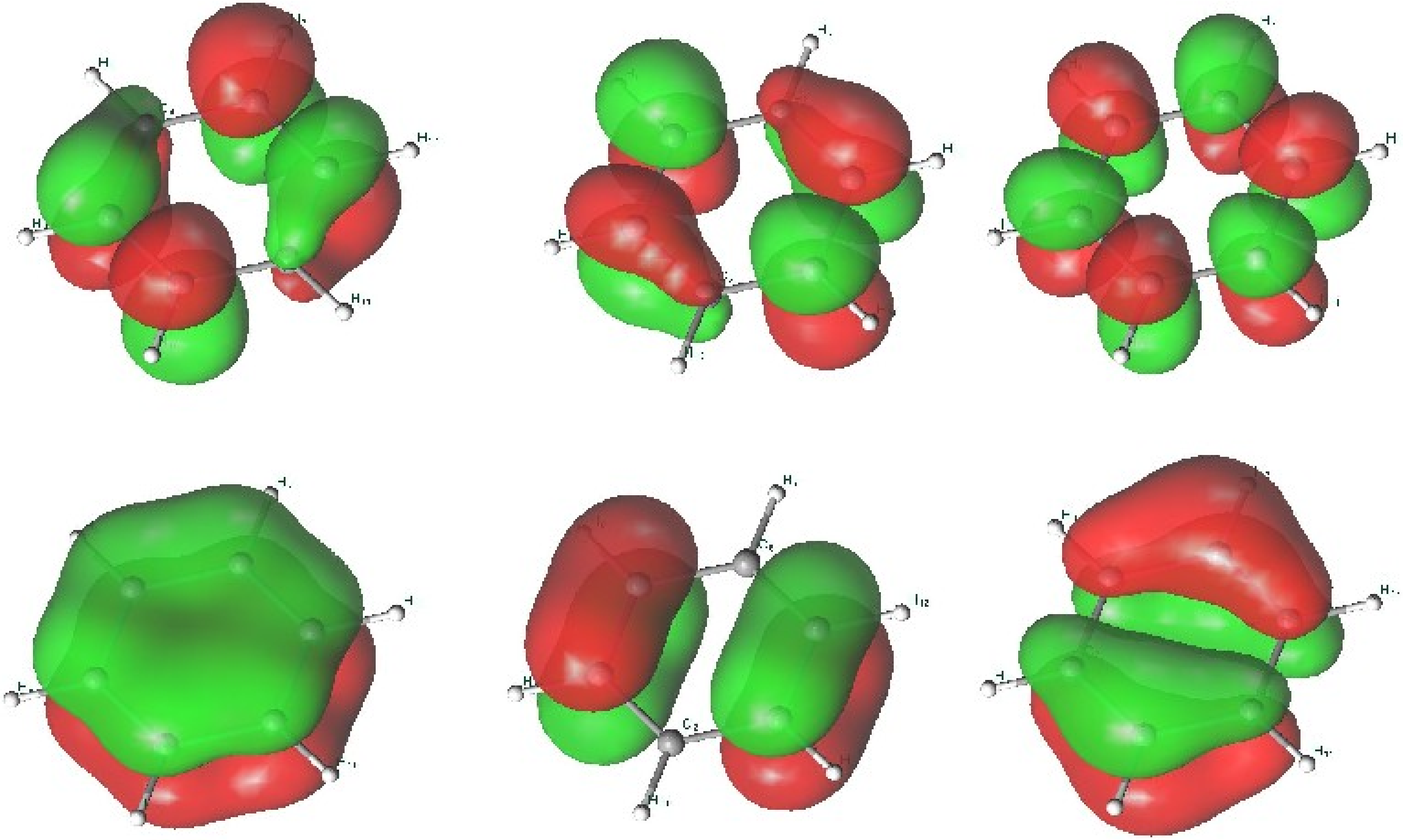
Orbital Representations: localized molecular orbitals





Localized occupied and virtual SCF orbitals, respectively.

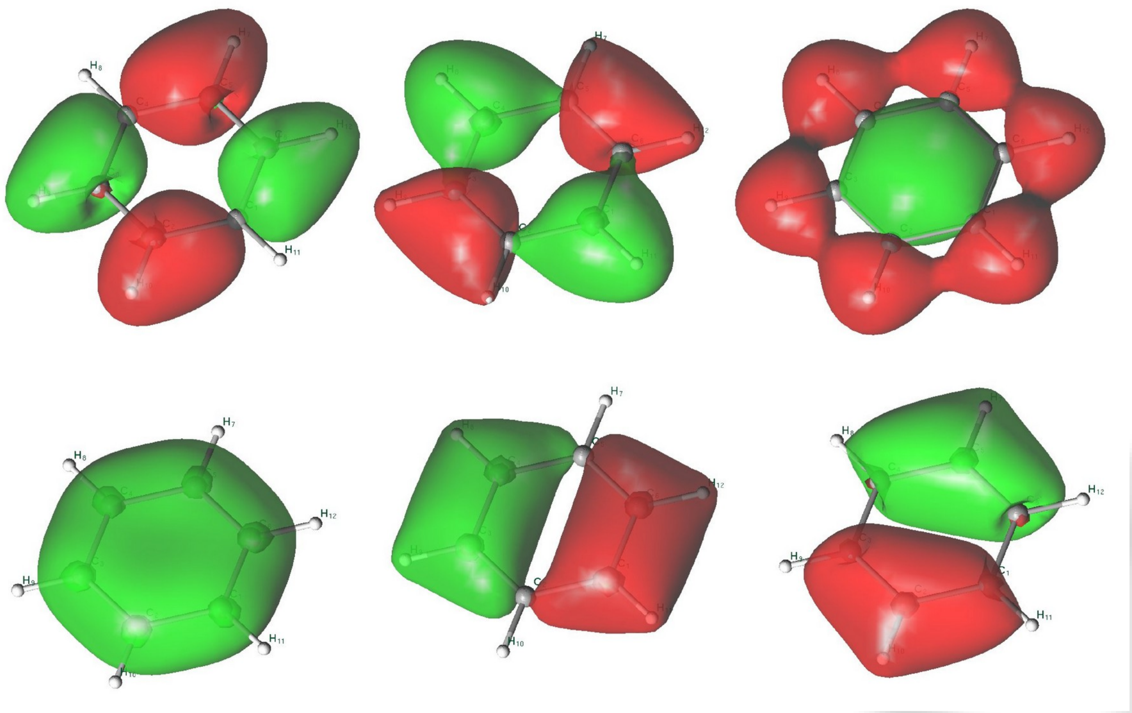
Orbital Representations: the SCF orbitals



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

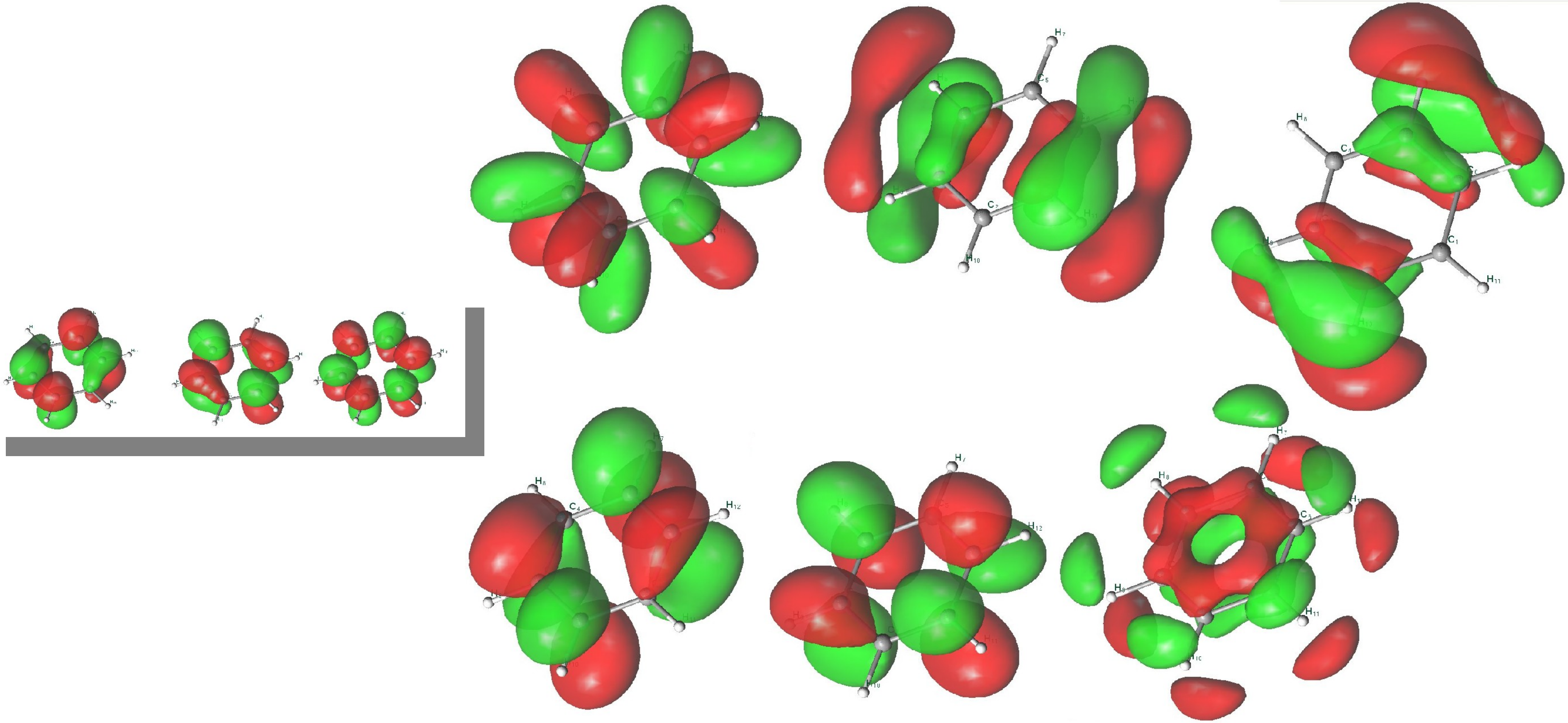
Note that these orbitals are from a minimal basis calculation.

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:

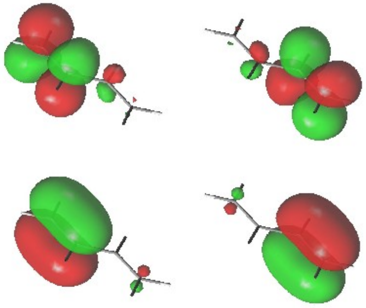
a) $C_4H_6 \rightarrow 2\ C_2H_3$

b) $C_4H_6 \rightarrow C_3H_4 + CH_2$

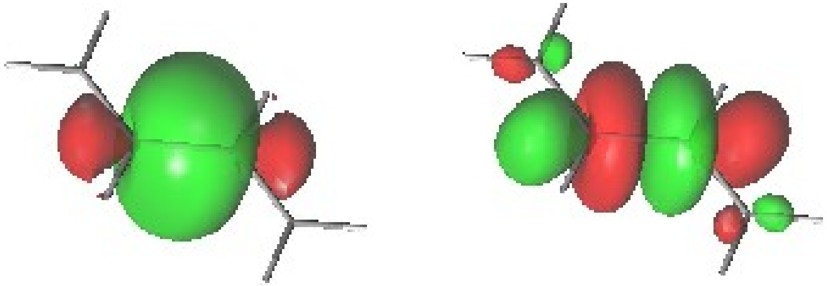
In both cases we will have the 4 π orbitals active together with the correlating pair of the bond which we are breaking (σ-σ^*), that is a 6-in-6 CAS in both cases.

Same-but-Different: The Starting Orbitals

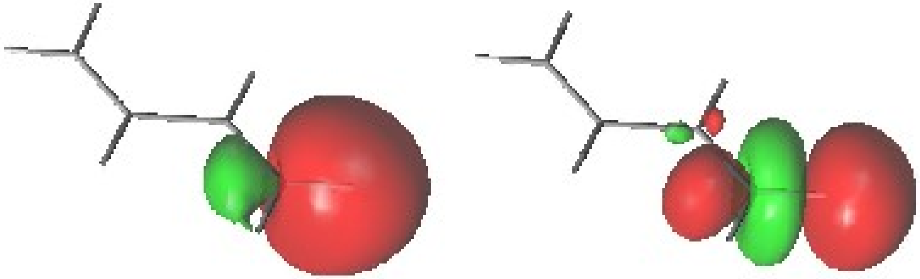
The π-space:



The correlating pairs in the σ-space:



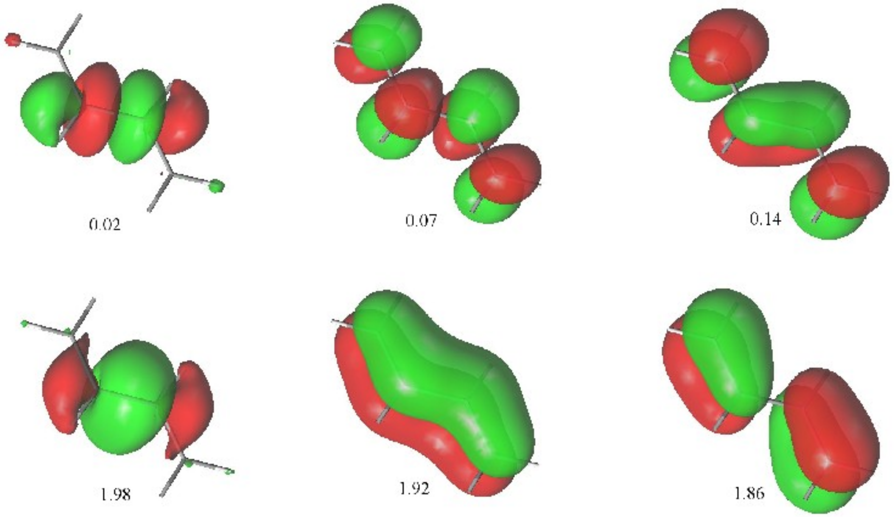
$C_4H_6 \rightarrow 2\ C_2H_3$

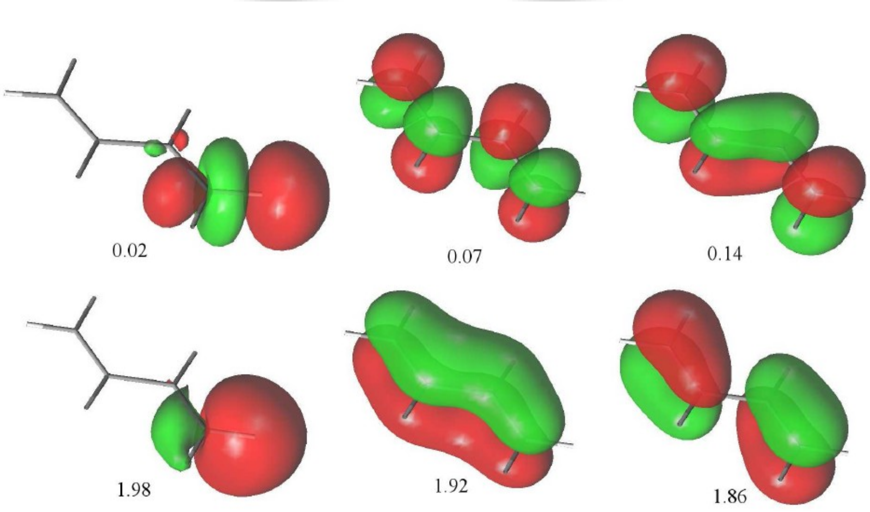


$C_4H_6 \rightarrow C_3H_4 + CH_2$

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

Same-but-Different:
The CASSCF Orbitals





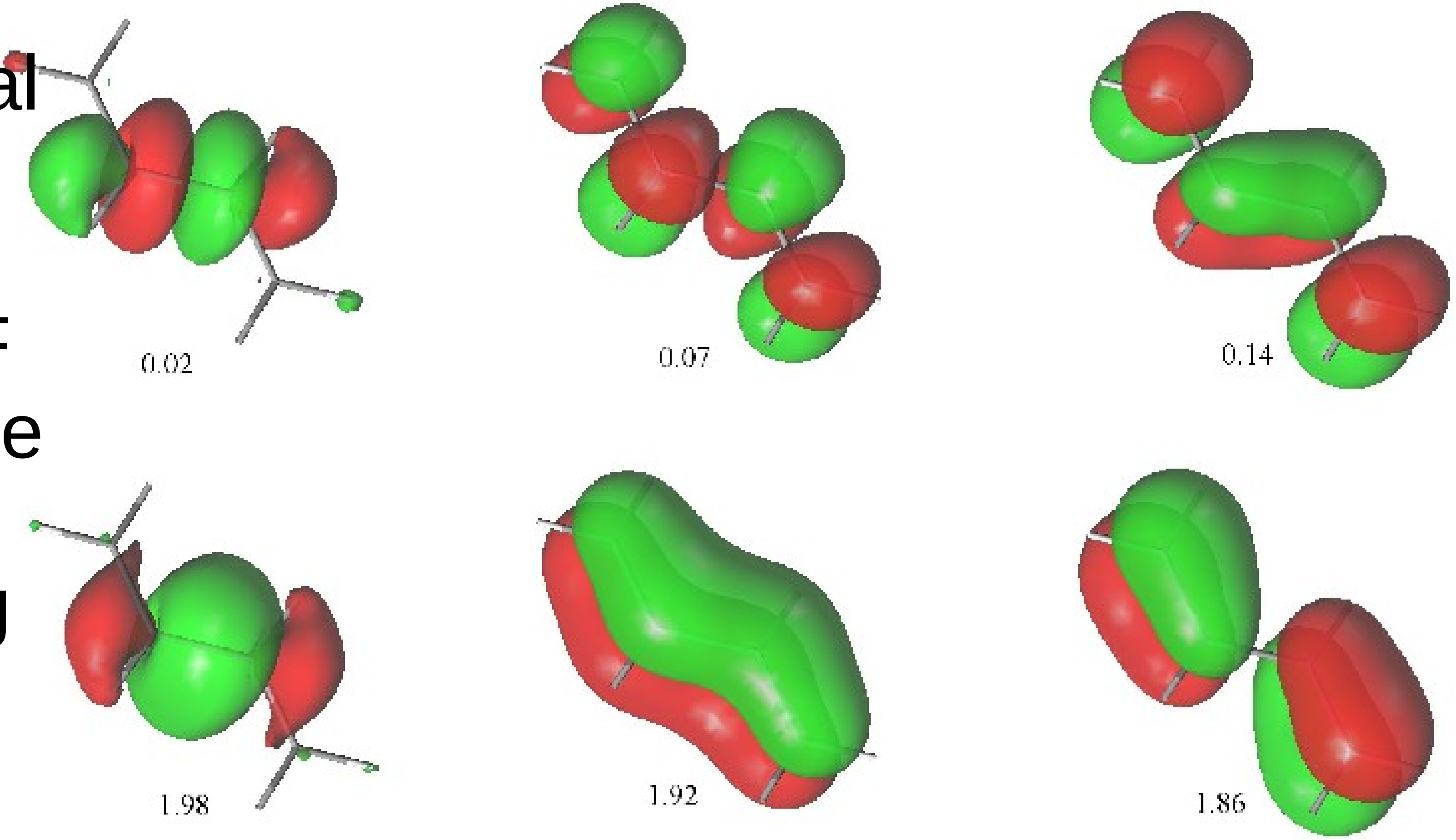
$C_4H_6 \rightarrow 2\ C_2H_3$

$C_4H_6 \rightarrow C_3H_4 + CH_2$

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

- Different orbital representations
- Be careful with SCF orbitals - expand
- Standard AO active orbitals
- MO active orbitals
- Localized starting MO orbitals
- The solution to the MSCF eq. is not unique!!!
- Tricks