Open-Shell Calculations

Unpaired Electrons and
Electron Spin Resonance Spectroscopy

Video IV.vi

Winter School in Physical Organic Chemistry (WISPOC)
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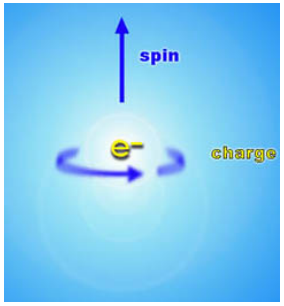
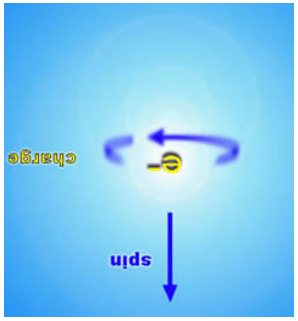
Lecture 2: • open-shell species



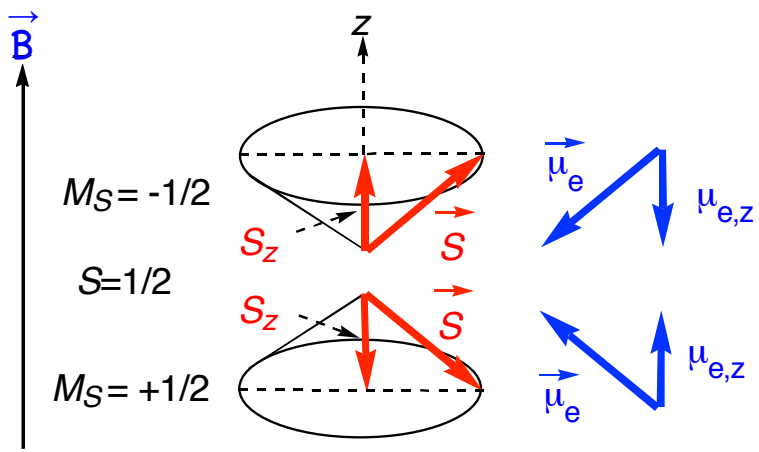
open-shell species:
atoms or molecules that contain one or more
unpaired electrons

⇩

one must deal with the issue of
the electron's spin



- electrons have a *magnetic moment*, called spin $\vec{S}$, associated with a *spin quantum number* S
- for the electron S is equal to 1/2
- in the presence of a magnetic field $\vec{B}$, the spin precesses rapidly around the axis of the field (which defines the z-direction)

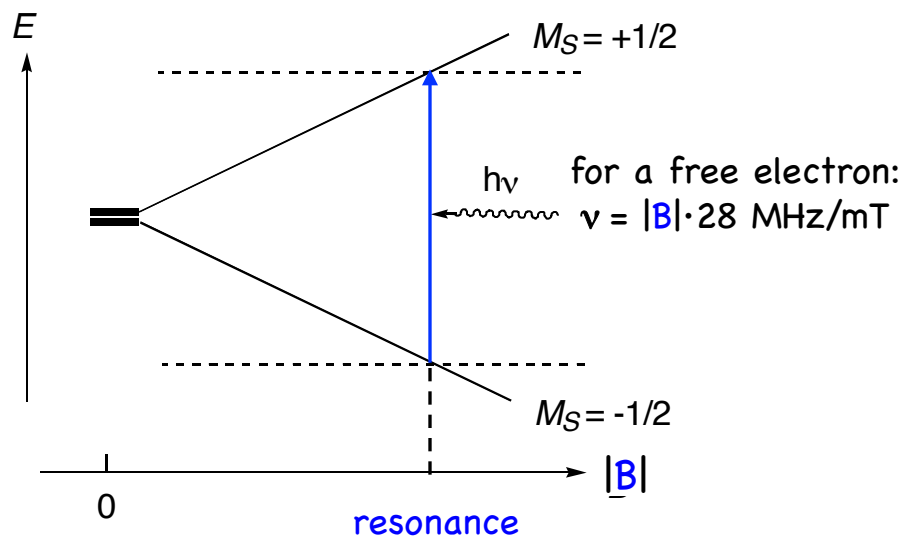


depending on its *magnetic quantum number* M_S (±1/2, corresponding to α and β-electrons, respectively), the z-component of the spin, S_z, is oriented parallel or antiparallel to $\vec{B}$

the magnetic moment $\vec{\mu}_e$ is proportional but antiparallel to $\vec{S}$

the energy of interaction of the spin with the magnetic field is $E = |\mu_{e,z}|\cdot|B| = g_e\cdot\mu_B\cdot M_S\cdot|B|$

Due to the interaction with the magnetic field, the energy levels of α and β electrons are different (Zeeman-splitting). Transitions between these levels can be induced by electromagnetic radiation (→ ESR spectrosocpy)



If this would be all there is to ESR spectroscopy, it would not be a very interesting experiment. What makes it interesting are the *nuclear magnetic moments* and their interaction with the magnetic moments of the electrons

Like electrons, some important nuclei (^1H, ^{13}C) have a spin I of 1/2 which can be *parallel or antiparallel* to a magnetic field ($M_I = \pm 1/2$). As for electrons, the energy levels of opposite nuclear spins undergo Zeeman-splitting in a magnetic field, and transitions between the levels can be incuded by electromagnetic radiation (NMR-spectroscopy)

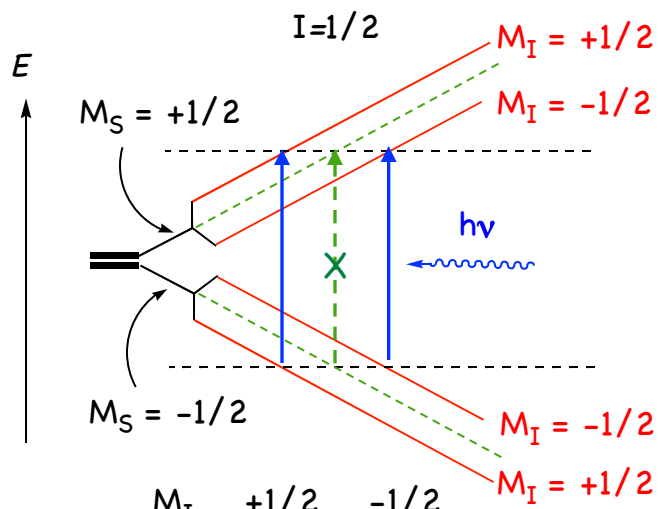
Interaction of electron and nuclear magnetic moments (spins)

dominant anisotropic contribution: the *Fermi contact term*

$$E_{Fc} = C \cdot \rho_s(0) \cdot M_S \cdot M_I \qquad \rho_s = \rho_\alpha - \rho_\beta$$

spin density at the nucleus

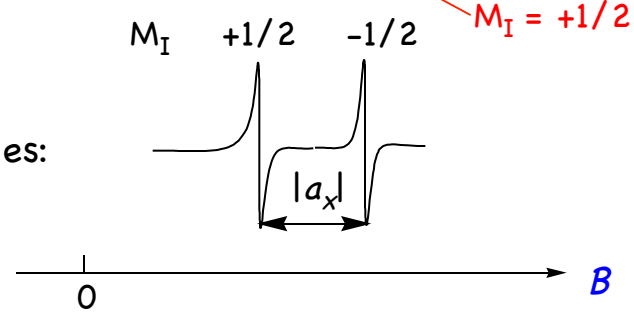
the contribution of this interaction to the energy is much smaller than that of the interaction with the external field → *hyperfine splitting*



ESR selection rules:

$\Delta M_S = \pm 1$; $\Delta M_I = 0$

ESR-lines:

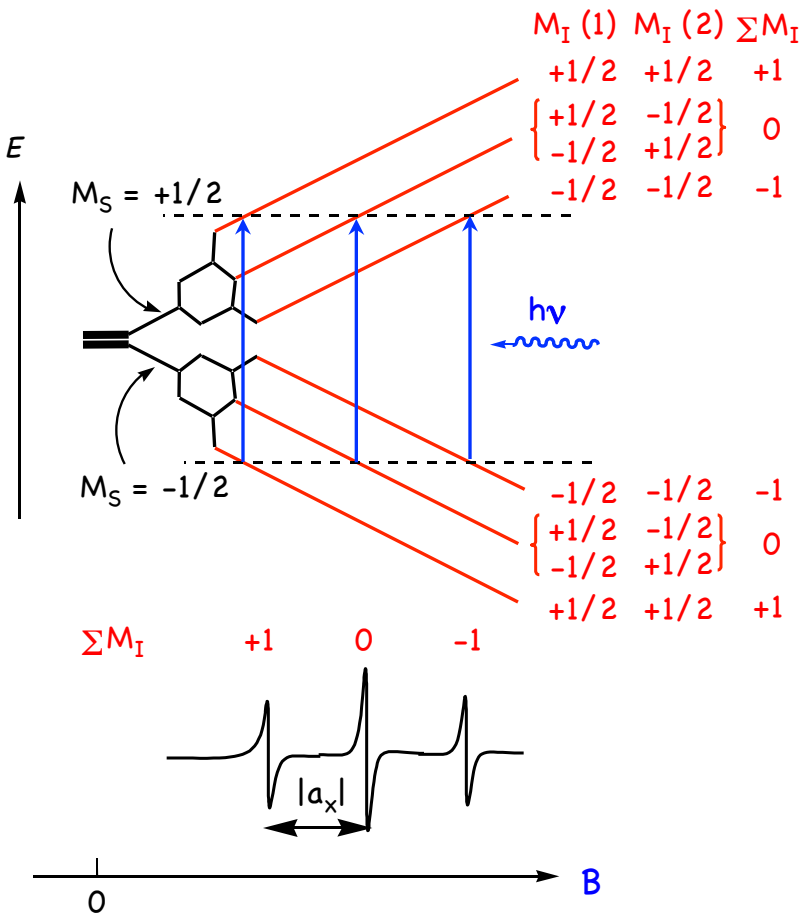


hyperfine splitting a_X:

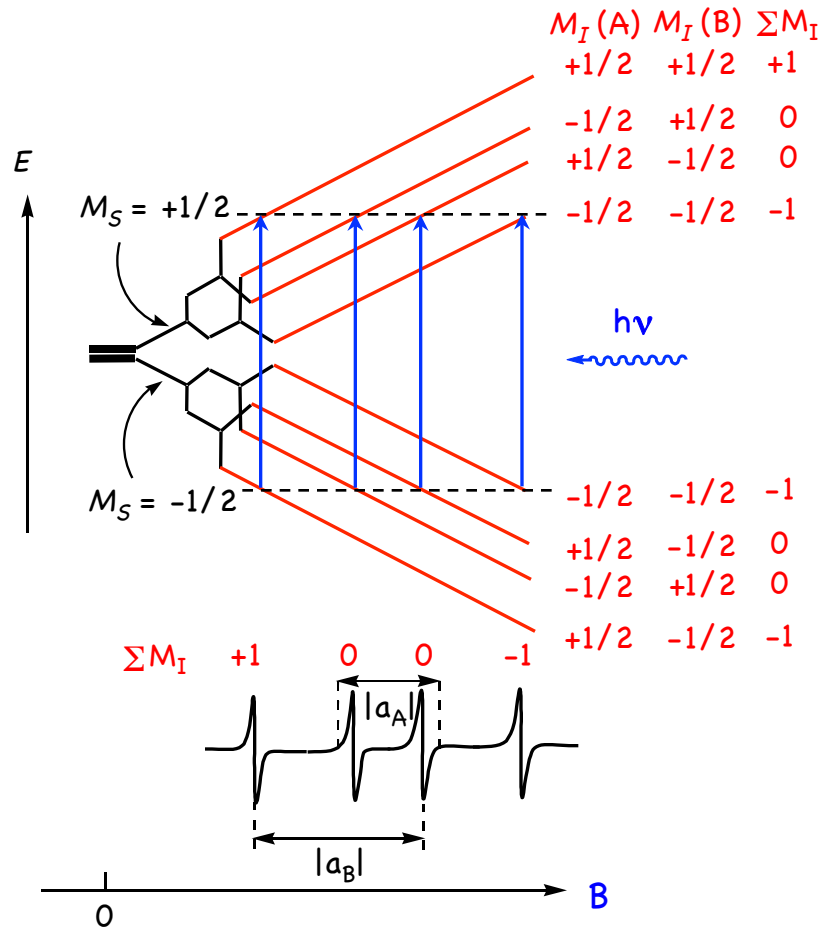
$$|a_X| = K_X \cdot \rho_s(0) \quad [T]$$

Interaction of electron and nuclear magnetic moments (spins)

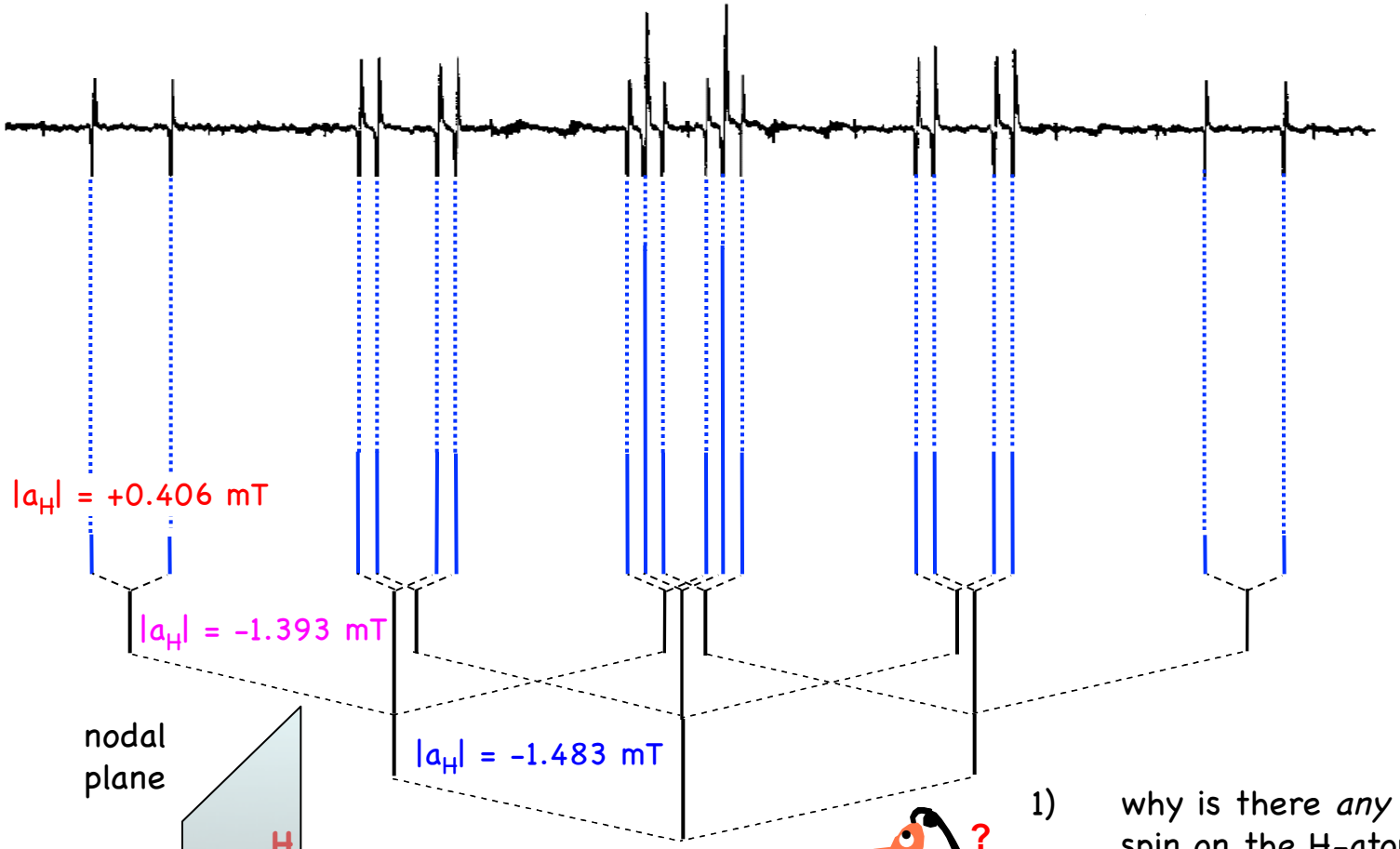
two equivalent nuclei

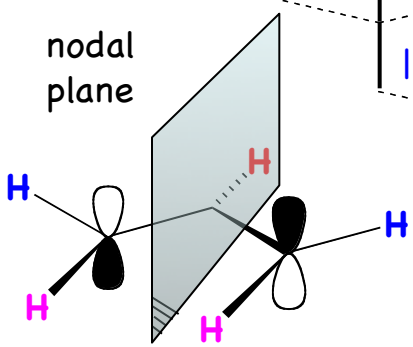


two non-equivalent nuclei



^{1}H ESR-spectrum of the allyl radical (Fessenden & Schuler 1963)



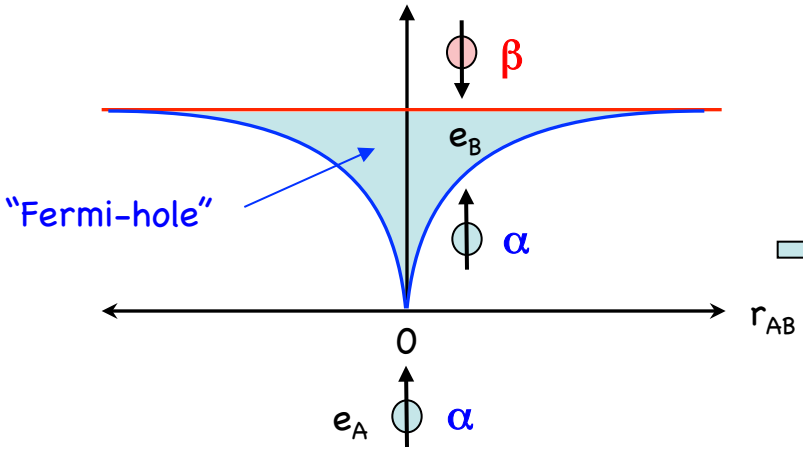


singly occupied MO (SOMO) of the allyl radical

1) why is there *any* electron spin on the H-atoms?
2) why is there any electron spin on the *central* H-atom?
3) why is there *negative* spin density on the outer Hs?

spin polarization

(purely statistical) probability of finding e_B at distance r_{AB} of e_A



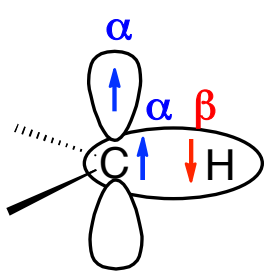
Pauli principle:

"two electrons of the same spin can never be at the same place at the same time"

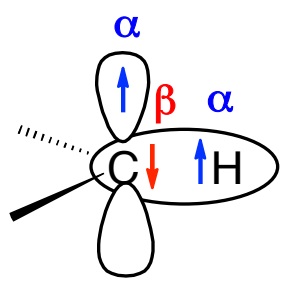
for *the same distribution of a pair of electrons*, two electrons of the same spin suffer less repulsion than two electrons of opposite spin ("exchange interaction")

electrons of opposite spin have a higher propensity to avoid being in similar regions of space than two electrons of the same spin do.

planar π-systems



more favorable situation

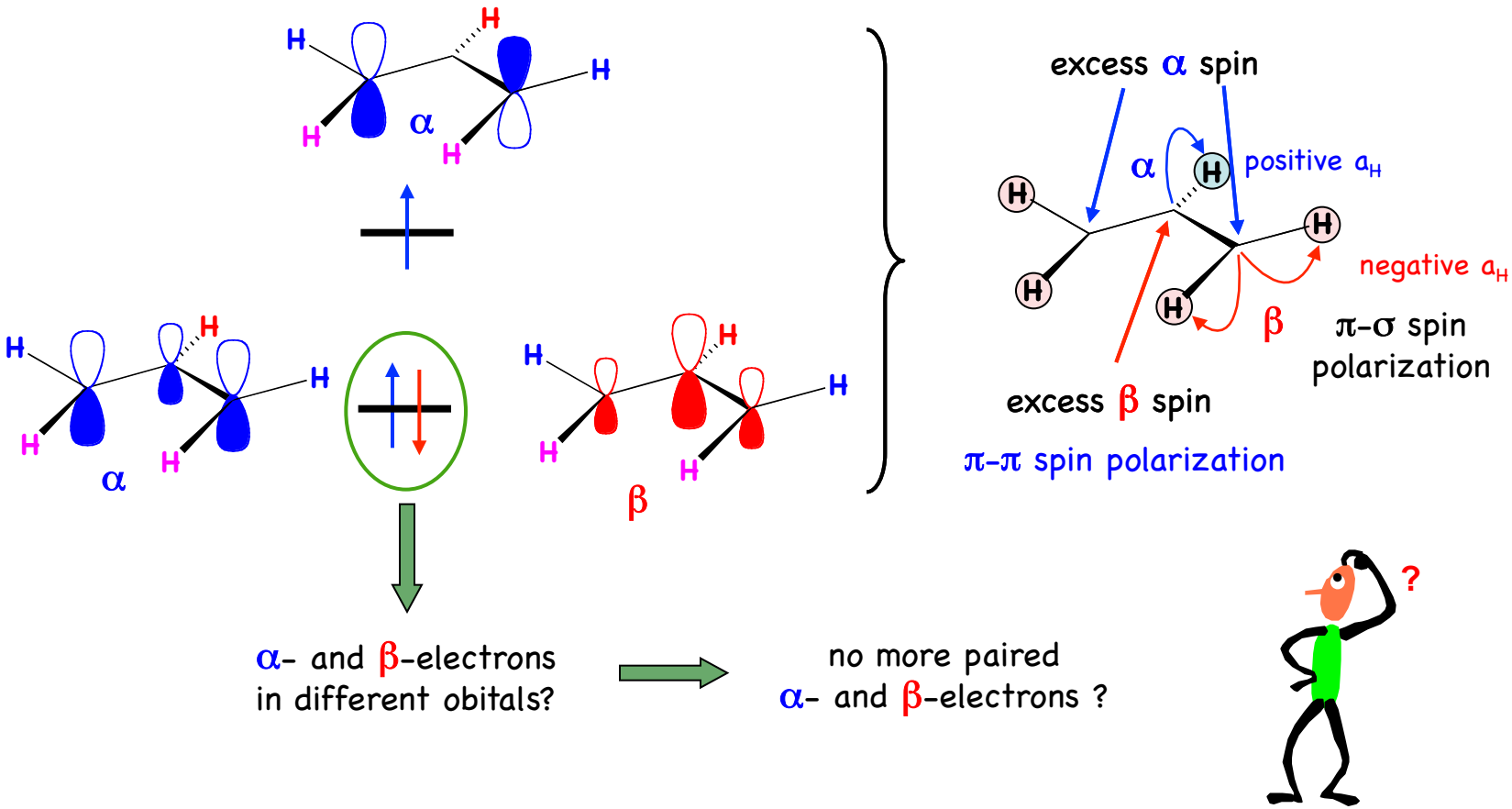


less favorable situation

excess negative (β) spin density on H

π-σ spin polarization

π-spin polarization

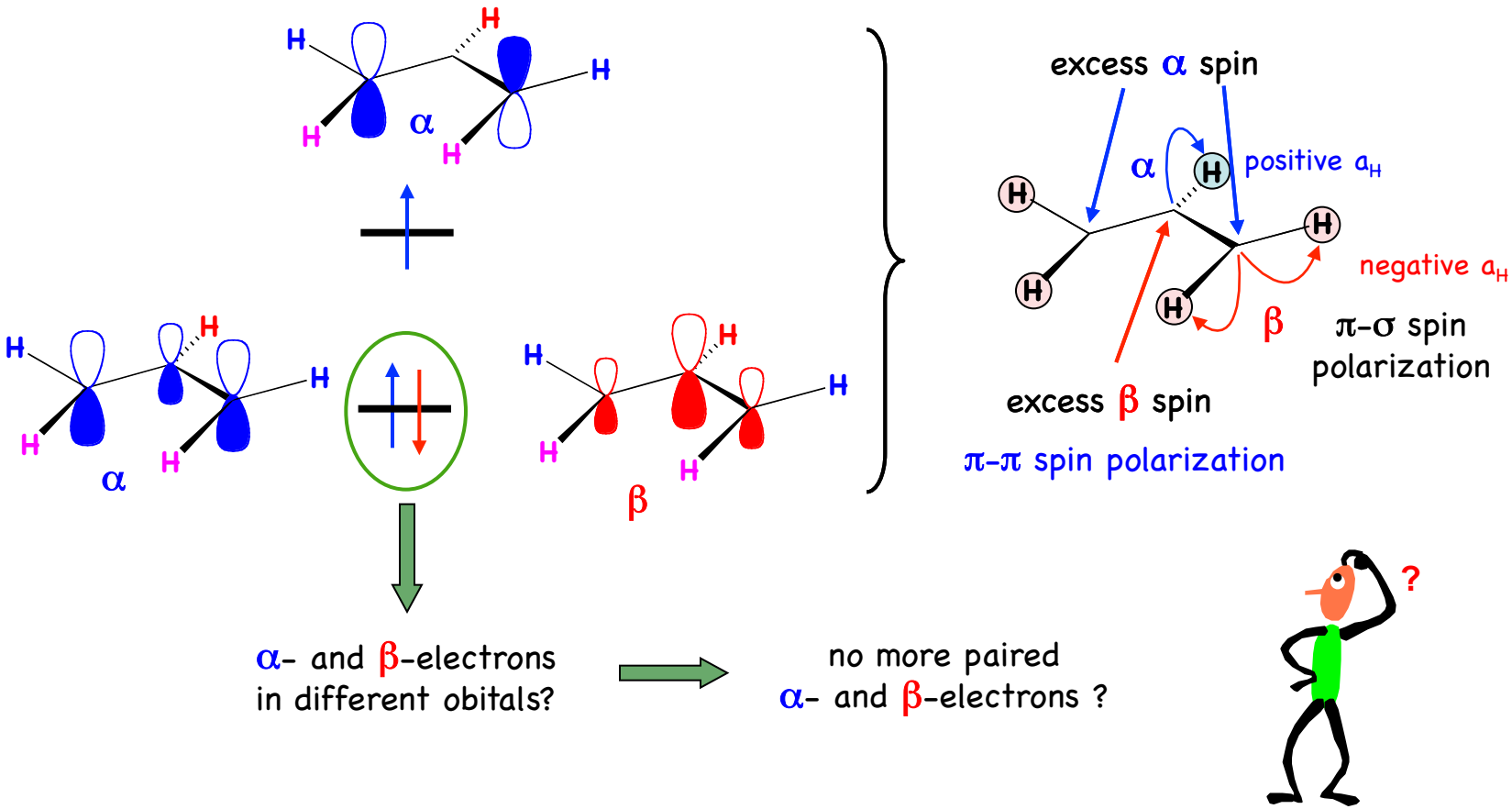


Open-Shell Calculations

Handling Unpaired Electrons
Restricted Open-shell vs Unrestricted

Video IV.vii

π-spin polarization



how to model open-shell systems ?

paired orbitals:
restricted open-shell
(ROHF or RODFT)

- physically incorrect (prevents spin polarization)
- technically cumbersome (multiple operators, MP2)
- leads often to artefactual symmetry breaking

⇒ different orbitals for different spins (DODS, unrestricted HF or DFT)

- allows (in principle) to model spin polarizazion
- technically easy to implement, including MP2
- gives lower electronic energy than ROHF/RODFT

However: unrestricted wavefunctions show "spin contamination"!

$|S|$ (or S^2) and $|S_z|$ are *molecular properties* that can be computed as *expectation values* from wavefunctions using corresponding *operators* $\hat{S}^2$ and $\hat{S}_z$

$$\langle\Psi|\hat{S}^2|\Psi\rangle = \langle S^2\rangle \qquad \langle\Psi|\hat{S}_z|\Psi\rangle = \langle S_z\rangle$$

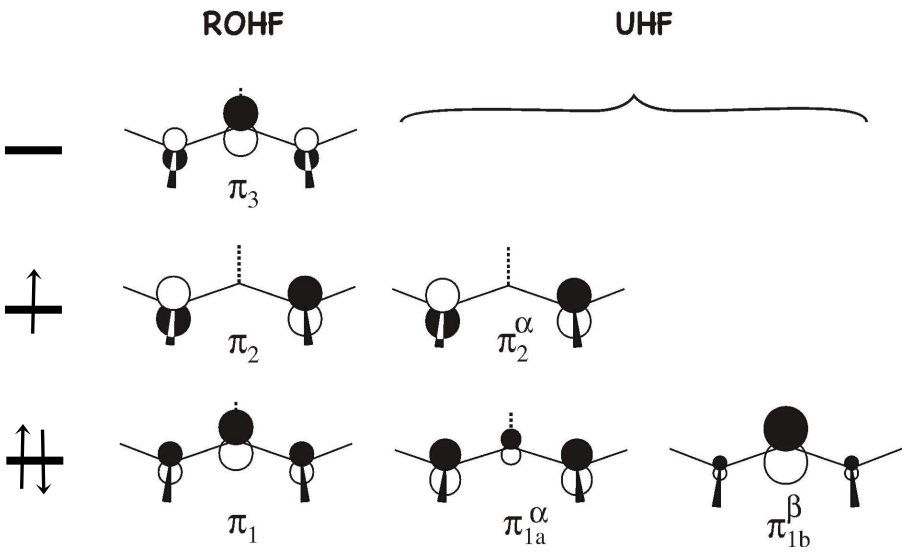
the correct values for S^2 is $S(S+1)$, i.e. 0.75 for radicals ($S=1/2$), 2 for triplets ($S=1$)

$\langle S^2\rangle$ for *restricted* open-shell wavefunctions correspond to these (correct) values

$\langle S^2\rangle$ for *unestricted* open-shell wavefunctions are invariably *higher* than these values

unrstricted wavefunctions are not eigenfunctions of the S^2 $\hat{o}$perator, because they contain admixtures from (they are "contaminated" by) higher spin states

this is demonstrated below for the allyl radical:



$$\Psi_{ROHF} = \left|\pi_1^\alpha \pi_1^\beta \pi_2^\alpha\right\rangle \qquad \pi_{1a} = \pi_1 - \lambda\cdot\pi_3 \qquad \pi_{1b} = \pi_1 + \lambda\cdot\pi_3$$

$$\Psi_{UHF} = \left|\pi_{1a}^\alpha \pi_{1b}^\beta \pi_2^\alpha\right\rangle = \left|\left(\pi_1 + \lambda\cdot\pi_3\right)^\beta \left(\pi_1 - \lambda\cdot\pi_3\right)^\alpha \pi_2^\alpha\right\rangle$$

$$= \underbrace{\left|\pi_1^\alpha \pi_1^\beta \pi_2^\alpha\right\rangle}_{\Psi_{ROHF}} - \lambda^2\cdot\underbrace{\left|\pi_3^\alpha \pi_3^\beta \pi_2^\alpha\right\rangle}_{\Psi_{ROHF}^{**}} + \lambda\cdot\boxed{\left(\left|\pi_1^\beta \pi_2^\alpha \pi_3^\alpha\right\rangle - \left|\pi_1^\alpha \pi_2^\alpha \pi_3^\beta\right\rangle\right)}$$

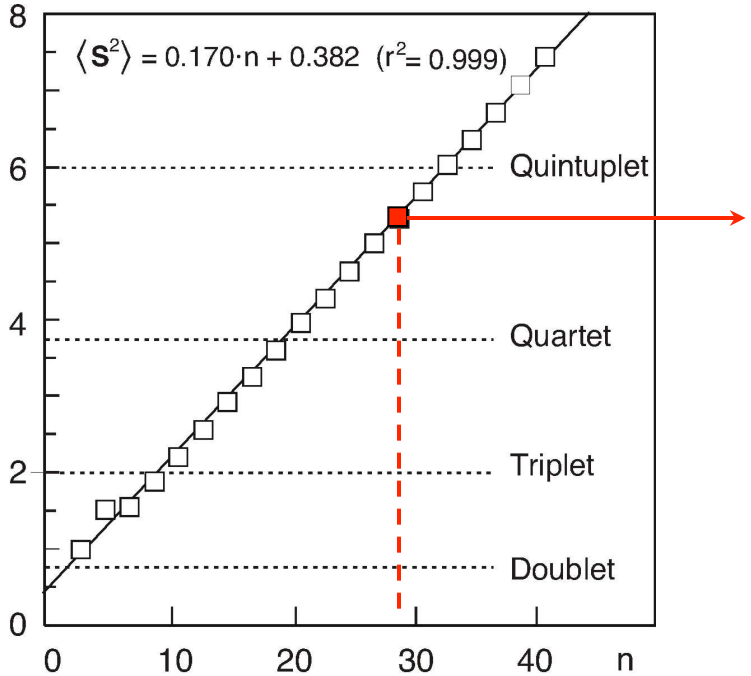
$\Psi_{ROHF}^{**} \longrightarrow$ provides for some dynamic correlation

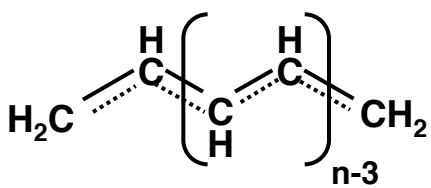
the bigger λ, the higher is spin contamination

linear combination of a doublet configuration and the $\langle S_z \rangle$=0.5 component of a quartet state !

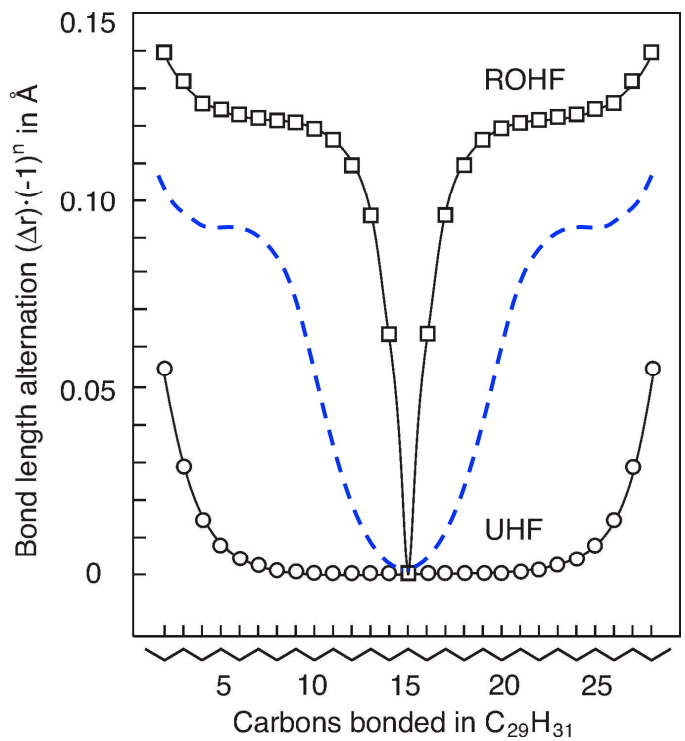
This spin contamination can become quite a nuisance, especially in *highly delocalized systems* where the α and β-electrons in subjacent MOs are *easily polarized*

polyenyl radicals





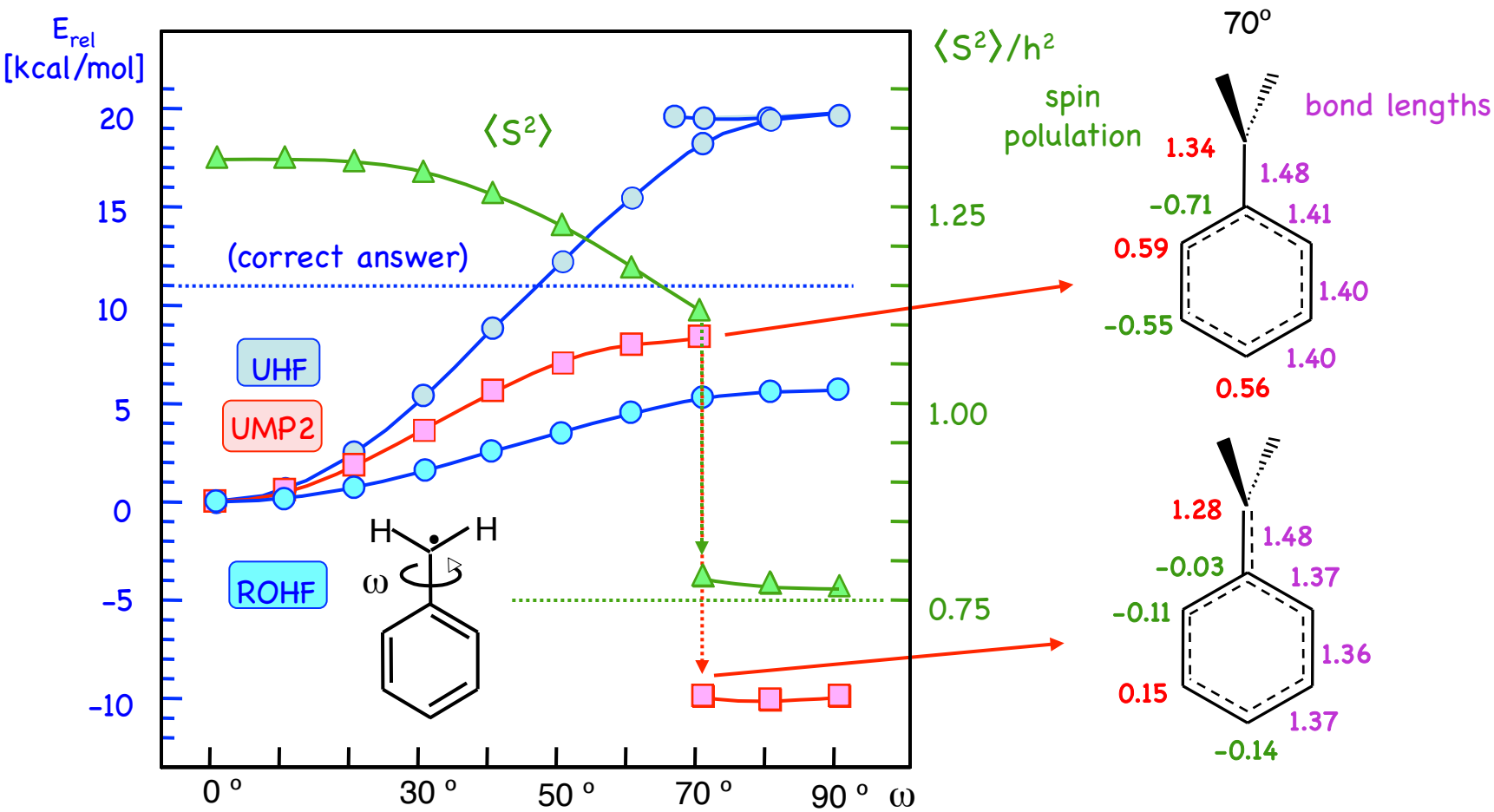
soliton in polyacetylene



As a consequence of spin contamination, UHF overestimates spin polarization

Spin contamination causes also problems in post-HF methods to recover dynamic correlation that are based on many-body perturbation theory (MP2, CCSD), because the perturbation through high-spin states is too big to be handled by these methods

This can lead to quite absurd results, as shown below for the benzyl radical



Note that for well localized radicals (alkyl, oxo- aminyl- or nitroxy radicals) these problems are usually less severe.

But: be watchful of $\langle S^2 \rangle$ in UHF-based calculations !

How about DFT?

within the KS model, DFT can be formulated in an unrestricted way, just like HF, by optimizing *individual spin densities* $\rho_\alpha(r)$ and $\rho_\beta(r)$ instead of the total densityy $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$.

Of course unrestricted KS wavefunctions (for a fictional system of noninteracting electrons) will also contain terms due to higher spin states, but it is not quite clear whether spin contamination of a KS wavefunction means that the *true wavefunction* is bad (which is what it means in UHF!)

Nevertheless it is comforting to note that spin contamination in KS wavefunctions is usually much less severe than in HF wavefunctions (the more HF exchange density is admixed in hybrid functionals, the worse spin contamination becomes).

In spite of this UDFT is quite good at modelling spin polarization (better than UHF which overestimates it), and the energetics and properties of open-shell systems seem to be predicted just as well as those of closed-shell systems.

modelling ESR spectra: does this work ?

remember: the dominant anisotropic contribution to hyperfine coupling is the *Fermi contact term*

$$E_{Fc} = C \cdot \rho_s(0) \cdot M_S \cdot M_I \qquad \rho_s = \rho_\alpha - \rho_\beta$$

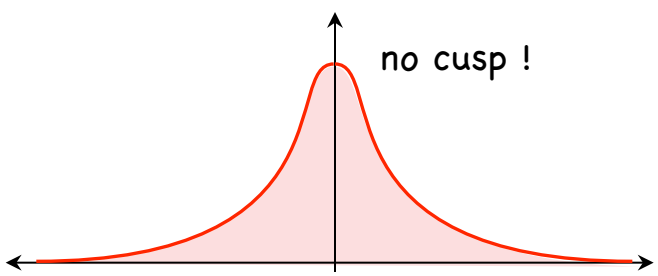
spin density at the nucleus $\propto \Psi^2(r=0)$

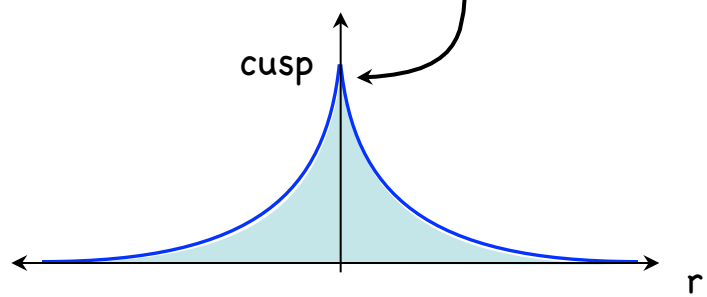
but in calculations AOs are usually composed of Gaussian functions

$$\Psi^2 = A \times \exp(-2\xi\,(r/r_0)^2)$$

1s-AO of H: $\Psi^2 = 1/(\pi \cdot r_0^3) \times \exp(-2r/r_0)$, $r_0 = 0.53 \cdot 10^{-10}$m

$$\Psi^2(r=0) = 2.148 \cdot 10^{30}\ m^{-3}$$





How can this ever work?

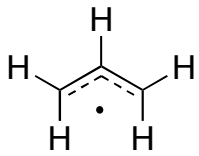
⇒ use very compact Gaussians (large ξ) to compose your AOs, and thus "mimick" a cusp (ESR specific basis sets).

suprisingly, with DFT, one can make pretty good predictions with "normal" basis sets such as 6-31G*, probably due to a fortuitious cancellation of errors.

some ESR hyperfine coupling constants

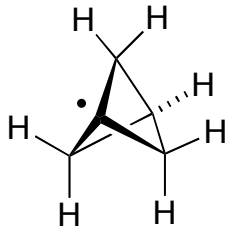
(Batra et. al. *J. Phys. Chem.* 100, 18371 (1996)
BLYP or B3LYP/6-31G*

BLYP	0.32	0.11	12.49 1.54
B3LYP	0.50	0.11	12.56 1.82
exp	0.41	0.41	12.62 1.93

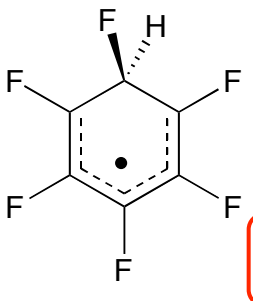


1.65
1.48
1.47

1.39
1.58
1.41



6.96
6.36
6.61



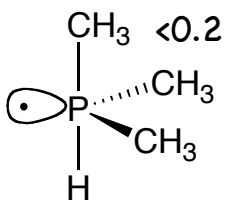
1.54
2.17
2.41

-0.36
-0.79
0.58

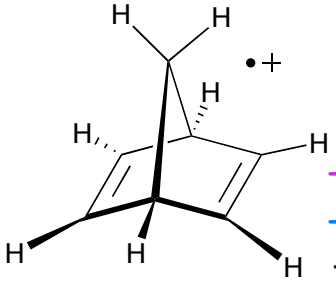
2.16
3.09
3.76

0.1
0.1
<0.2

42.3
44.0
48.4

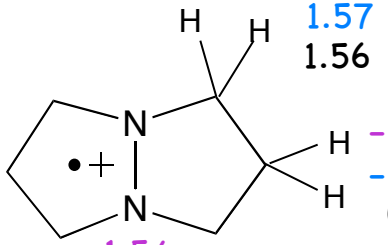


16.5
17.5
18.2



-0.75
-0.79
-0.78

-0.04
-0.05
-0.05

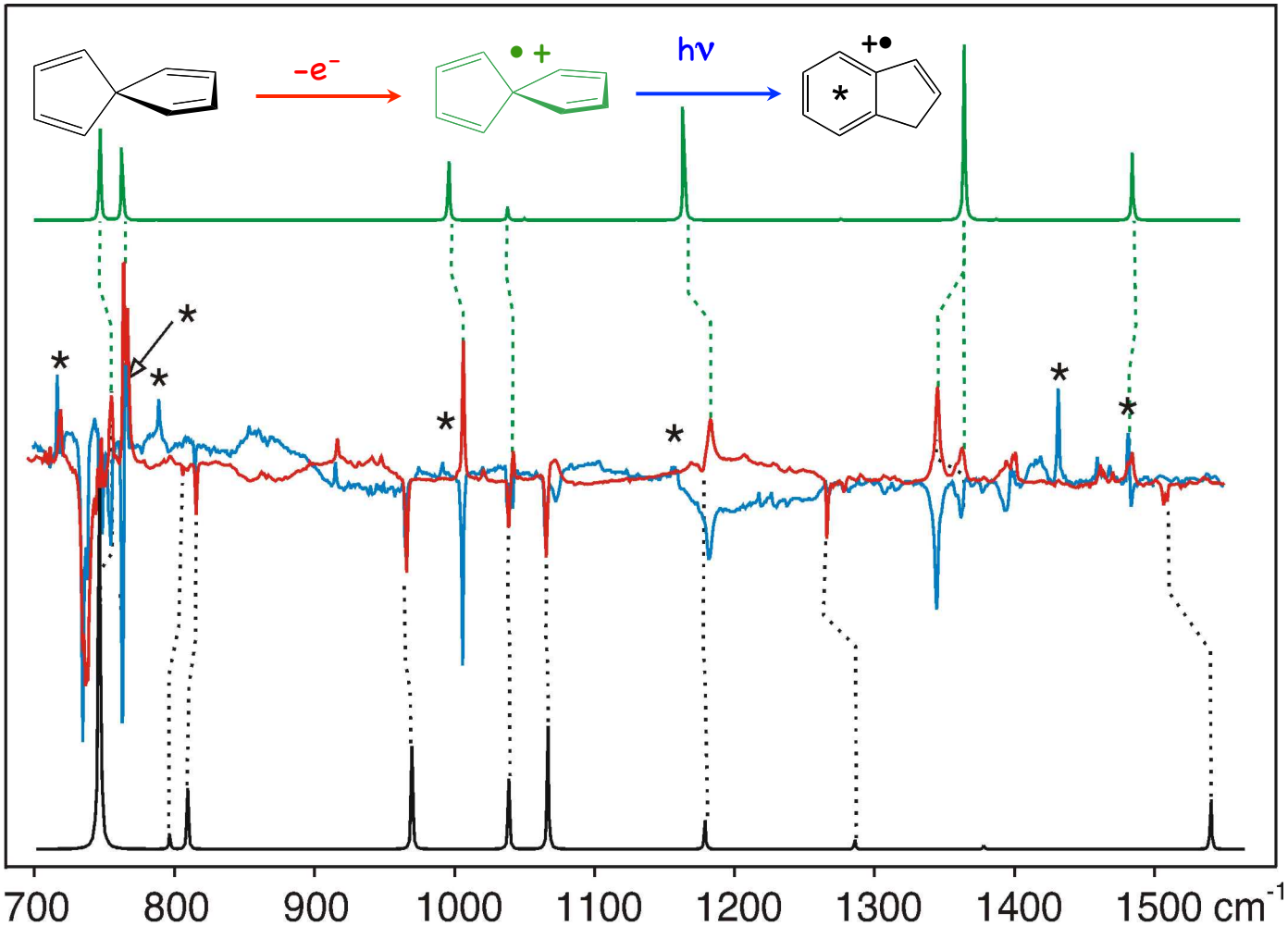


1.54
1.57
1.56

-0.05
-0.06
0.08

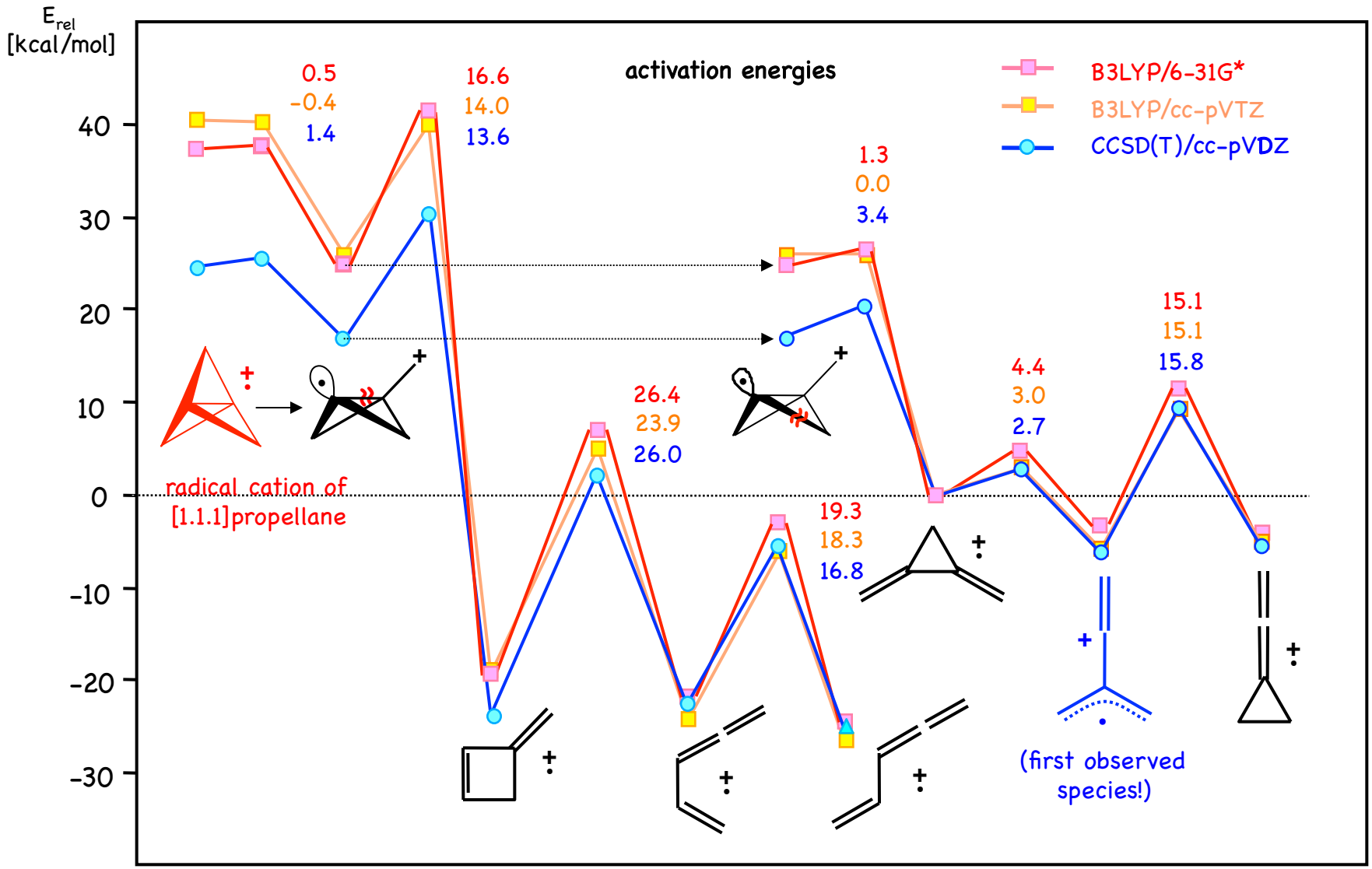
1.54
1.65
1.76

an IR-spectrum of a radical cation

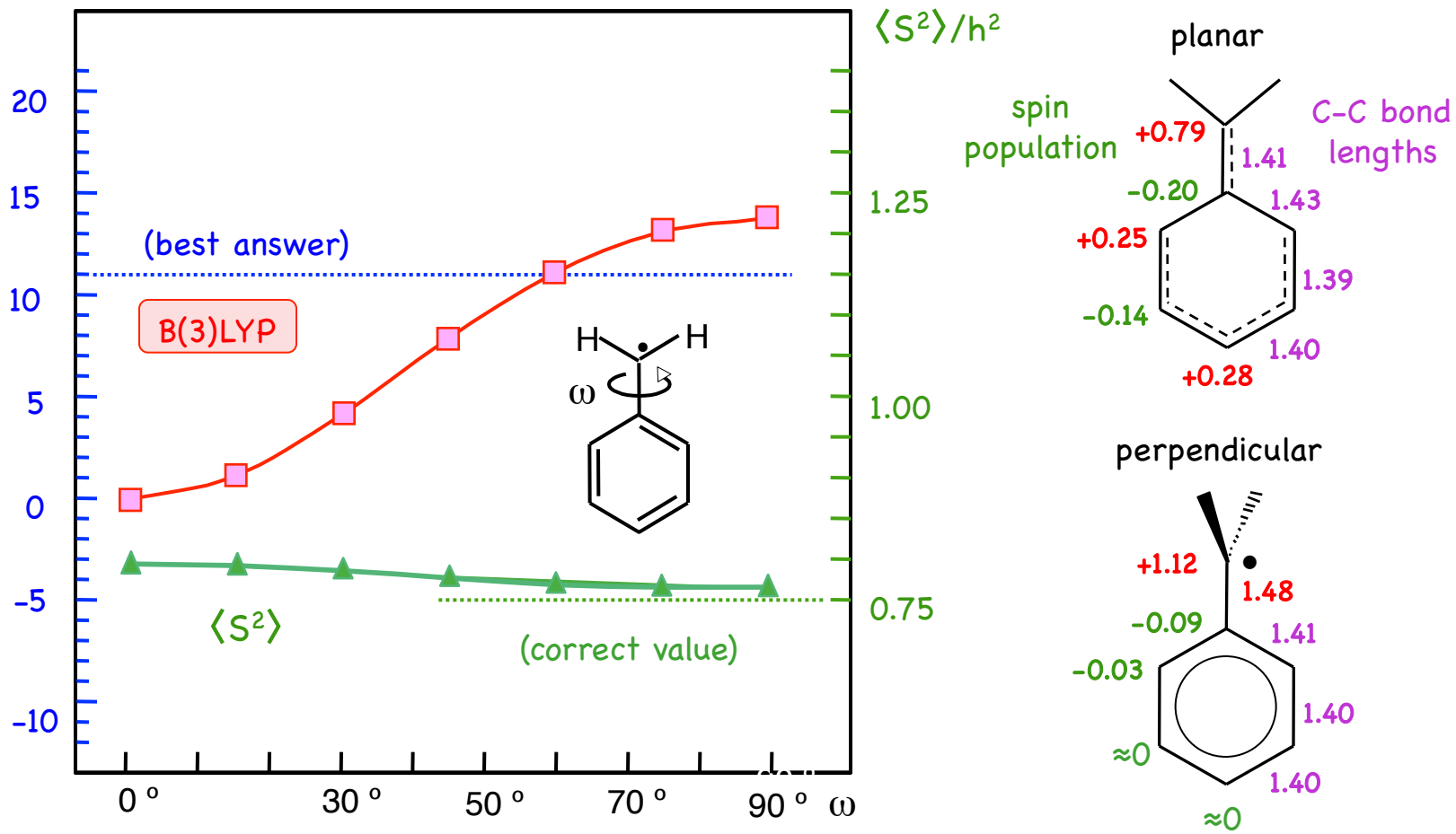


Haselbach et al. *Helv. Chim. Acta.* **84**, 1670 (2001)

some energetics of radical cations

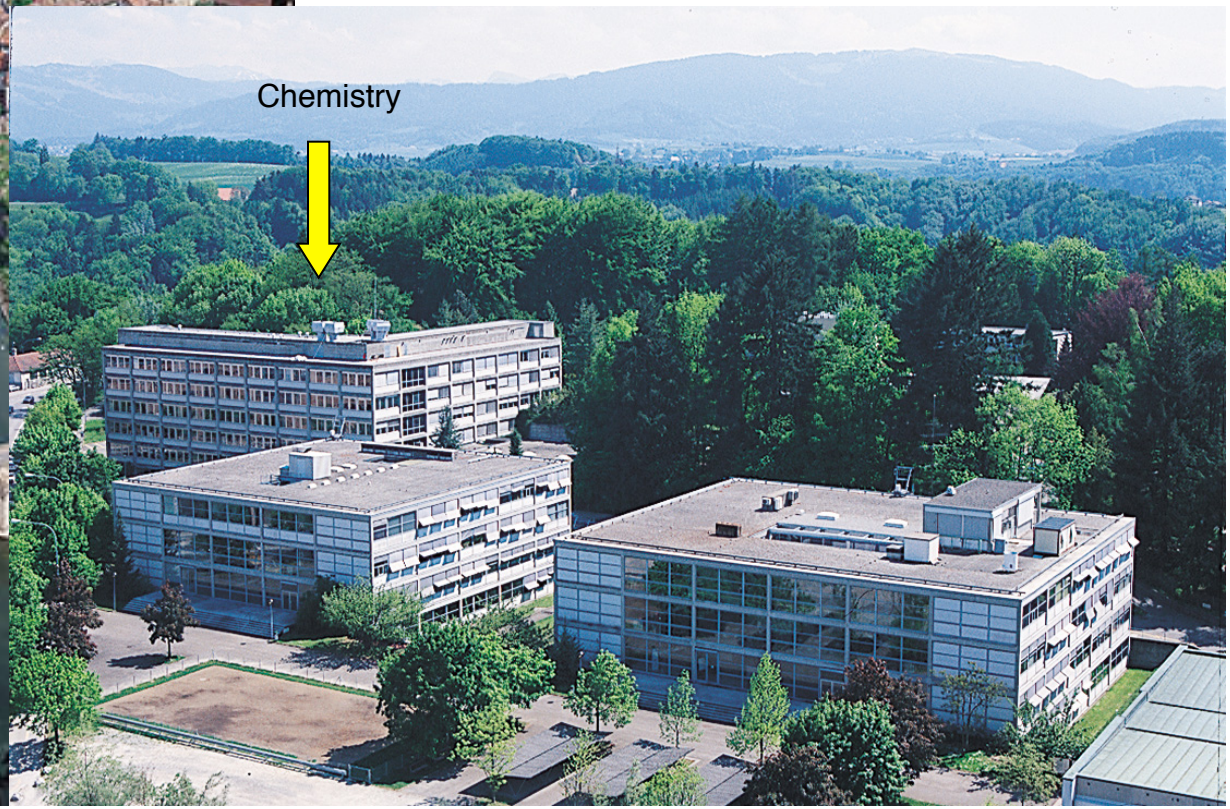


How about the pathological benzyl radical ?



DFT ist quite well-behaved

THANK YOU FROM CHRIS TO THOMAS !

Fribourg

… a friendly little city
in the heart of Switzerland