CHM 673
Lecture 11: Non-dynamical correlation. Multiconfigurational self-consistent field
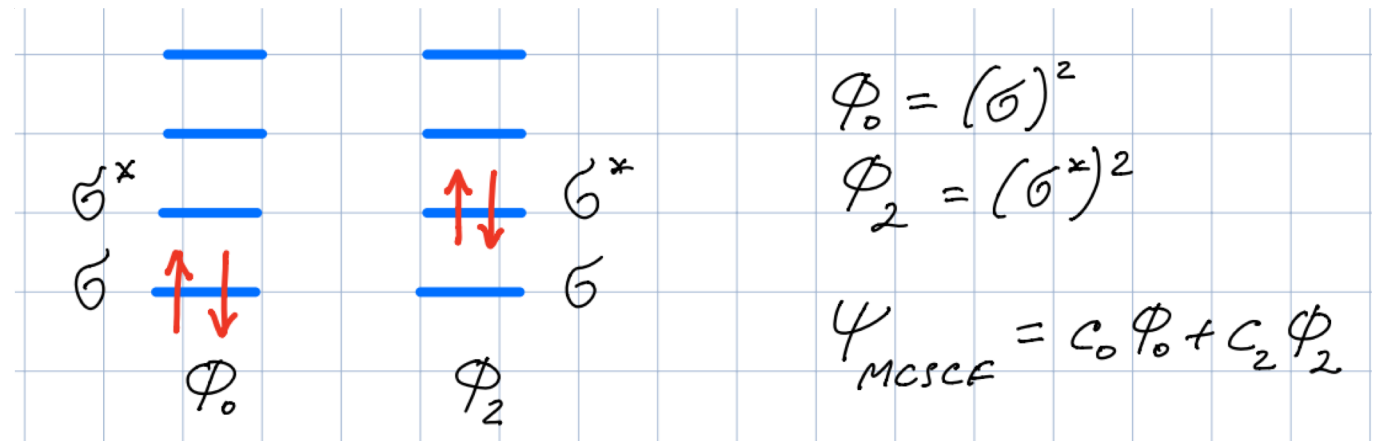
Multi-configurational self-consistent field (MCSCF)

MCSCF

Idea: prune Full CI Hamiltonian based on chemical bonding, rather than on formal excitation level

Pros: can prune harder → smaller Hamiltonian

Cons: molecule-at-a-time method, not general; expertise is required

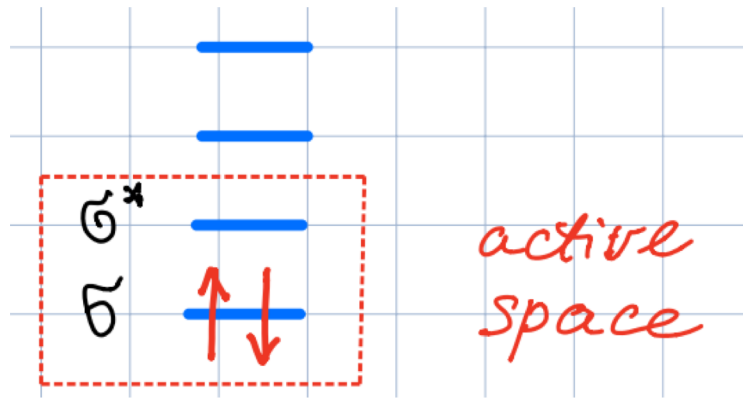Example: dissociation in H_2
To properly describe single bond breaking, MCSCF wave function should contain only 2 determinants!

$$\begin{pmatrix} \Phi_{HF} & \Phi_S & \Phi_D & \Phi_T & \Phi_Q & \cdots \end{pmatrix}$$

$$\begin{matrix} \Phi_{HF} \\ \Phi_S \\ \Phi_D \\ \Phi_T \\ \Phi_Q \\ \vdots \end{matrix} \begin{pmatrix} E_{HF} & 0 & x & 0 & 0 & 0 \\ 0 & E_S & x & x & 0 & 0 \\ x & x & E_D & x & x & 0 \\ 0 & x & x & E_T & x & x \\ 0 & 0 & x & x & E_Q & x \\ 0 & 0 & 0 & x & x & \ddots \end{pmatrix}$$

$$\Phi_0 = (\sigma)^2$$
$$\Phi_2 = (\sigma^*)^2$$
$$\Psi_{MCSCF} = c_0 \Phi_0 + c_2 \Phi_2$$

Multi-configurational self-consistent field (MCSCF)

H$_2$ case: two-configurational SCF = TCSCF

General case
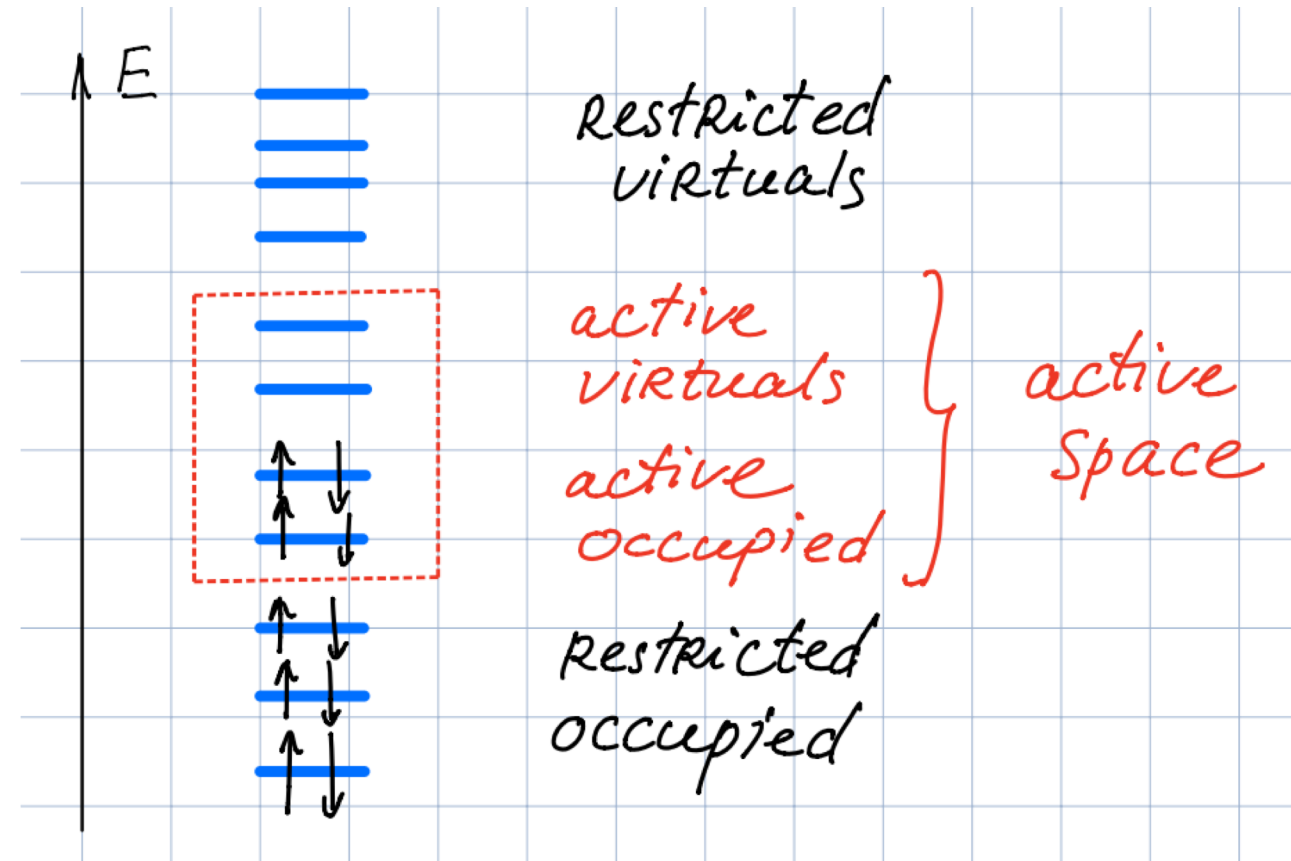

When is MSCSF used?
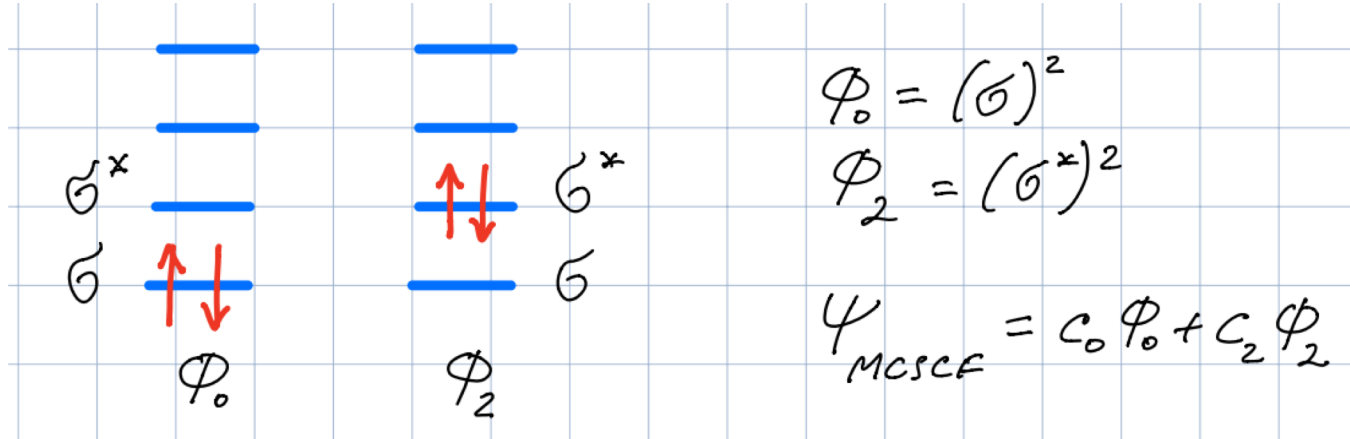
To describe non-dynamical correlation!

(Recall: wavefunction contains a few determinants with large weights)

Multi-configurational self-consistent field (MCSCF)

$$\Phi_0 = (\sigma)^2$$
$$\Phi_2 = (\sigma^*)^2$$
$$\Psi_{MCSCF} = c_0 \Phi_0 + c_2 \Phi_2$$

Standard CI procedure: solve HF, obtain Φ_0, construct and pick excited determinants (Φ_2), diagonalize Hamiltonian in the basis of these determinants

Not good for MCSCF: at bond-breaking, Φ_0 and Φ_2 are equivalent; however, orbitals were optimized for Φ_0, i.e. Φ_2 will have higher energy → unbalanced description

Solution: both orbitals and CI coefficients are optimized variationally at the same time to produce the lowest energy for the wave function $\Psi = \sum_i c_i \Phi_i$

Cons: variational space is two-dimensional → convergence becomes much more problematic HF: almost always converges by itself; MCSCF: almost never converges by itself!

Complete active space SCF (CASSCF)
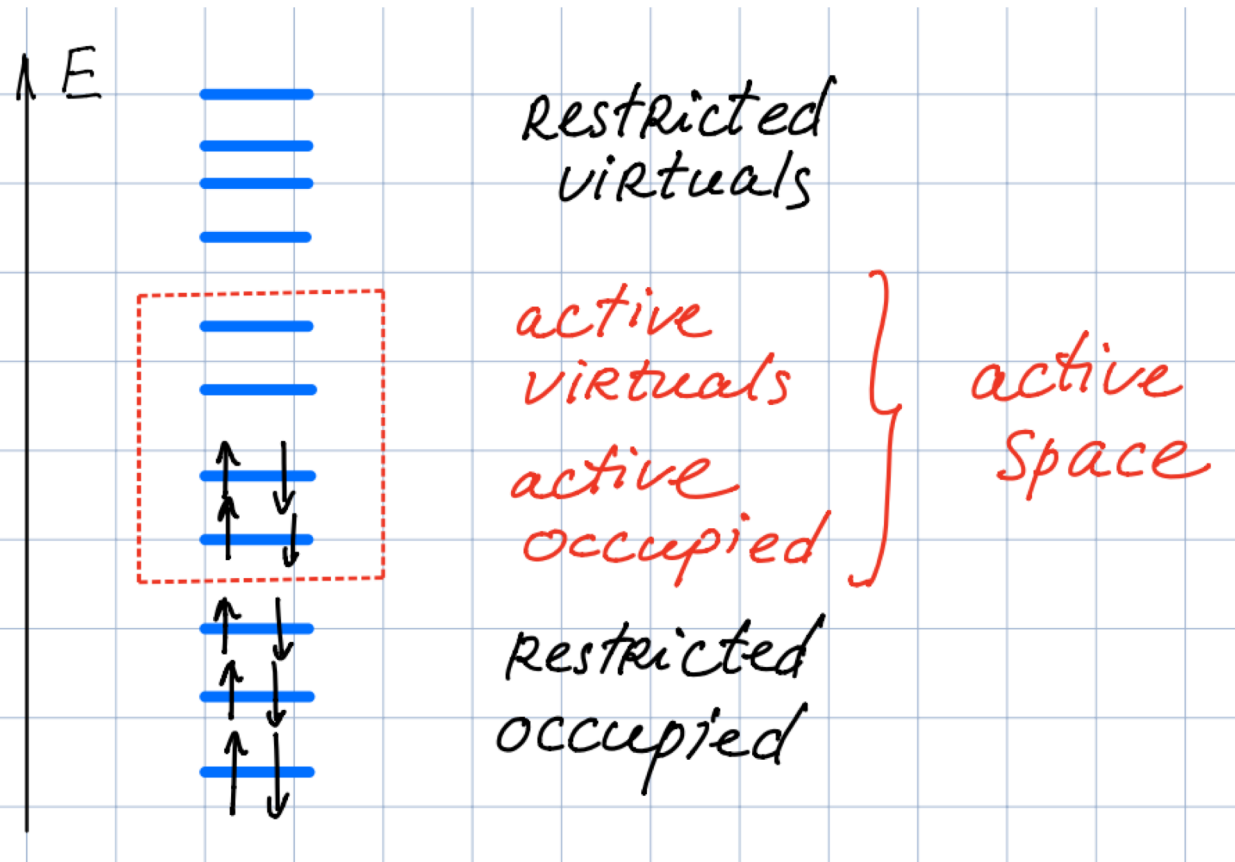
If all possible determinants formed in the active space are included in the wave function (i.e. FCI in the active space) → CASSCF

CASSCF:
- null active space → Hartree-Fock
- All-orbital active space → FCI

Full valence space

Consider bond-breaking in the following molecules:

- H_2: one bond → active space $\sigma, \sigma*$ → full valence space
- F_2: one bond → active space $\sigma, \sigma*$ → not full valence space!

  $\sigma, \sigma*$ dominating space,
  but other configurations from valence space might be important

- H_2O: two bonds → active space $\sigma, \sigma*, \sigma', \sigma'*$ → for dissociating several bonds, active
  space should include more than two orbitals
- O_2: two bonds → active space should include at least 4 configurations
- N_2: three bonds → active space should include at least 6 configurations

Full valence CASSCF wave function, i.e. wave function that includes all electronic configurations that can be formed by distributing the valence electrons among the valence orbitals (bonding, antibonding, lone-pairs) is capable of breaking any number of bonds simultaneously and any type of bonds

Non-dynamical correlation

Non-dynamical (static) correlation can be defined as the difference between Full CI within the space of all valence orbitals (full valence CASSCF) and Hartree-Fock:

$$E_{static} = E_{valence\ FCI} - E_{HF}$$

Dynamical correlation is the correlation in correlation within the higher lying orbitals:

$$E_{dynamic} = E_{FCI} - E_{valence\ FCI}$$

The cost of computing non-dynamical correlation grows exponentially with molecular size; limit – 2-3 heavy atoms
Typical limit on the active space size: 16 /16 (i.e. 16 electrons on 16 active orbitals)

Approximation to non-dynamical correlation in larger systems:
perform CASSCF in smaller active space →
not complete description of non-dynamical correlation in the 0-order wave function →
arbitrariness: active space is not uniquely defined anymore, becomes problem-dependent
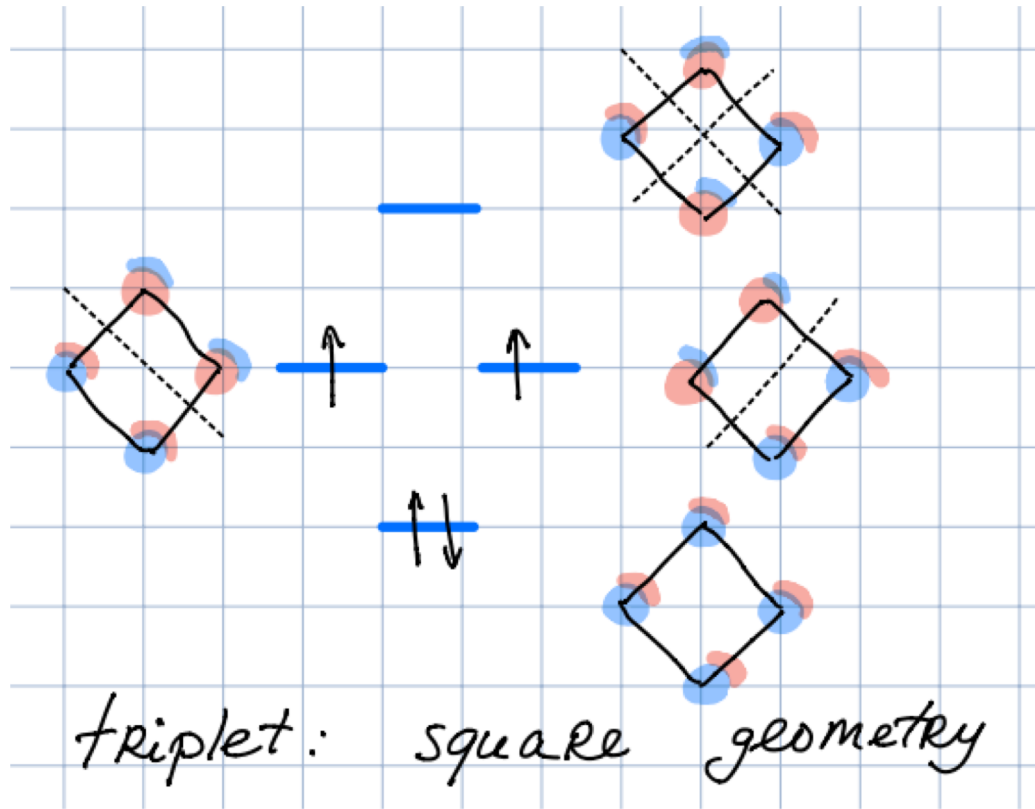
Example: cyclobutadiene
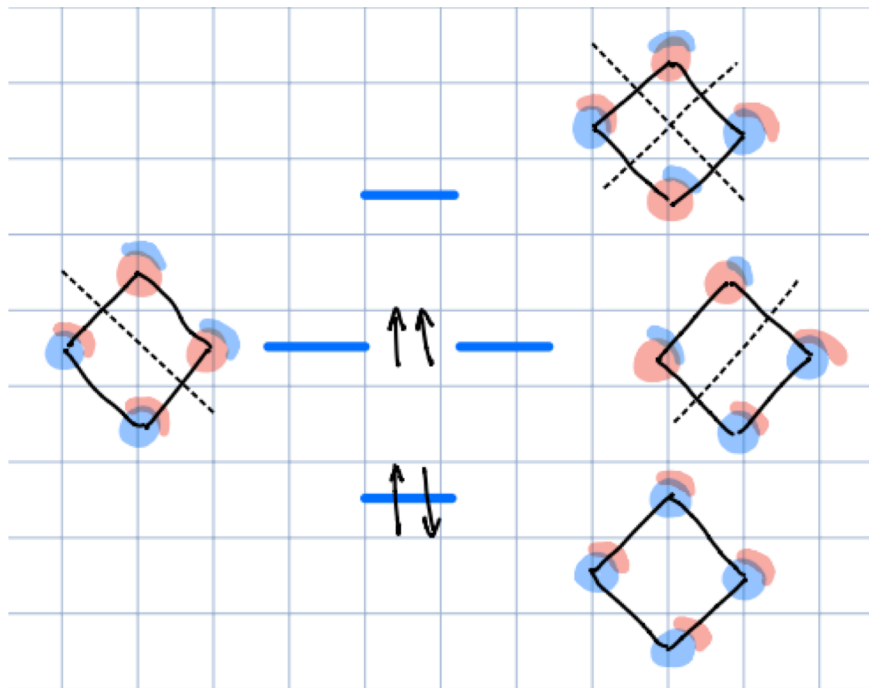
Cyclobutadiene: 4 electrons on 4 π orbitals
at symmetric square geometry:
One bonding, one antibonding, two degenerate non-bonding orbitals
Singlet or triplet?

Recall: Pauli exclusion stabilizes high-spin states (e.g. in atomic C and O, in molecular O_2)
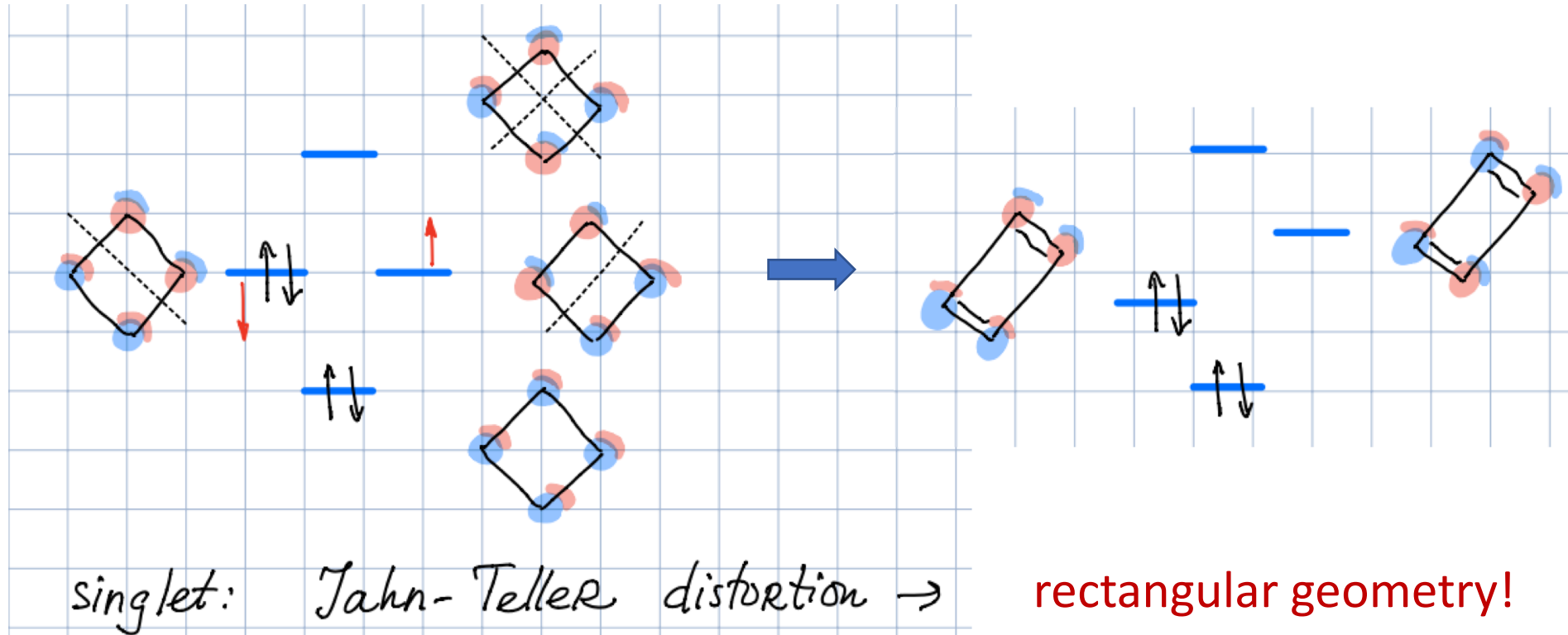
triplet: square geometry

Triplet state:
Both degenerate orbitals are singly occupied →
will preserve square geometry

Example: cyclobutadiene

singlet: Jahn-Teller distortion → rectangular geometry!
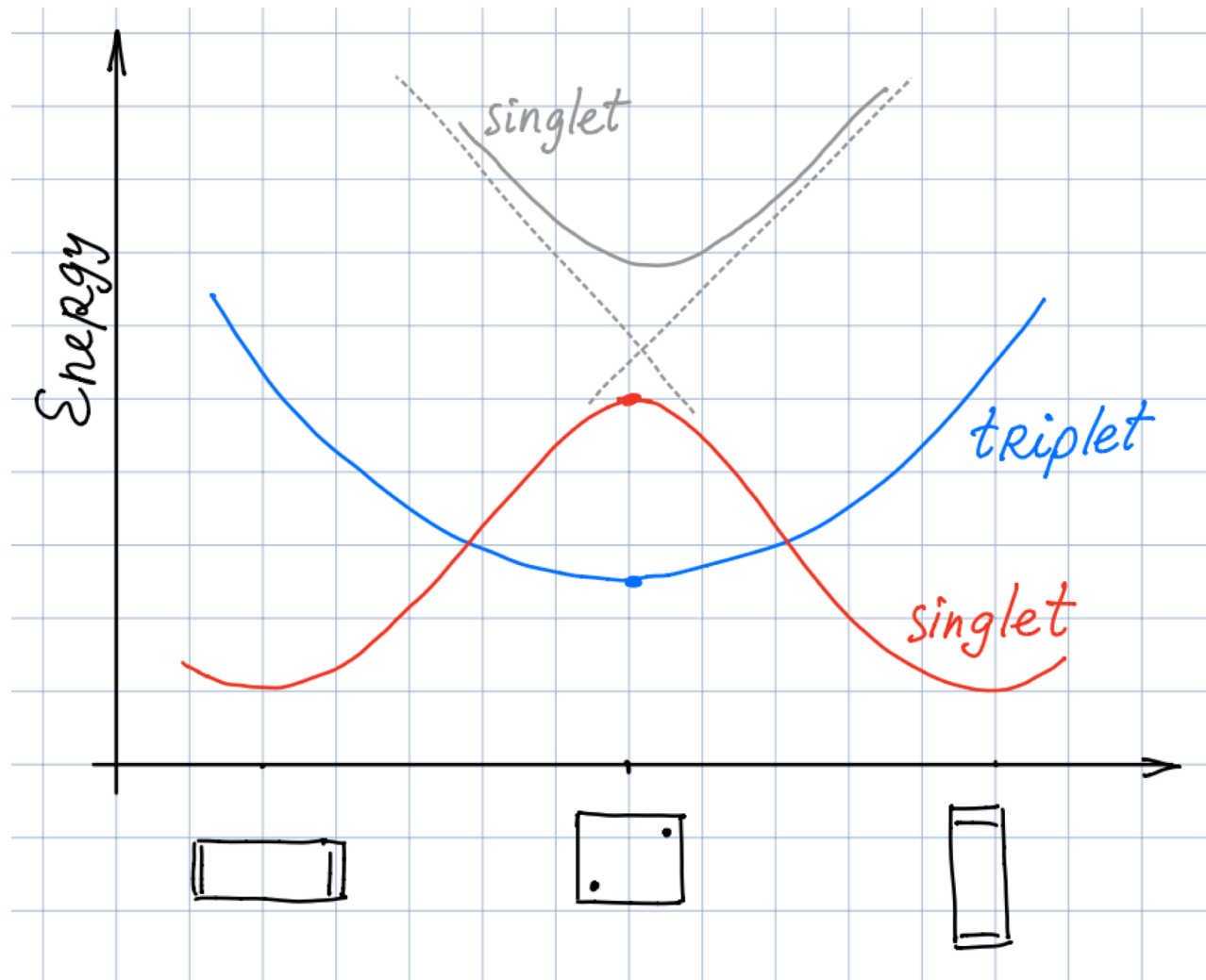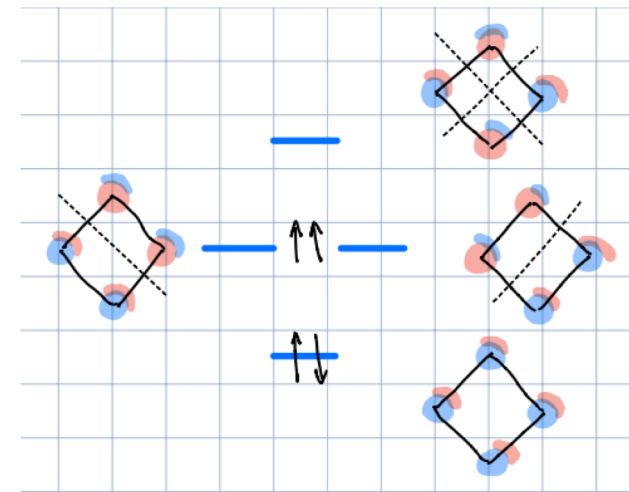
Singlet state:

One of the pair of degenerate orbitals is doubly occupied, another empty →
Jahn-Teller distortion will provide energy-lowering through symmetry breaking →
rectangular geometry

Example: cyclobutadiene

The ground state of cyclobutadiene is a rectangular singlet state

CASSCF with 4/4 active space

predicts that triplet is lower in energy

CASSCF with 10/10 active space: singlet is lower in energy

Why is CASSCF 4/4 wrong?
It omits $\sigma - \pi$ correlation!

How to perform MCSCF calculations?

- Always!!! start with Hartree-Fock calculation; examine the orbitals!
- Decide which orbitals should be in the active space. Typically bonding-antibonding pairs should be included
- Reorder the orbitals such that the active orbitals are the last occupied and the first virtual orbitals; use these orbitals as a guess for MCSCF
- Try MCSCF calculation; examine the orbitals!
- If MCSCF calculation did not converge or converged to a wrong active space, try some of the following:
  - Change MCSCF optimization parameters
  - Use MCSCF orbitals as a guess, reorder them accordingly
  - Use Hartree-Fock cationic state (+4, +6 etc) as a guess
  - Use localized Hartree-Fock orbitals as a guess
  - Try to converge MCSCF for larger or smaller active space, than use those orbitals as a guess

MCSCF: summary

- The goal of MCSCF is to provide correct zero-order wave function to account for non-dynamical correlation. MCSCF does not include dynamical correlation.
- In MCSCF, both CI coefficients and orbitals are optimized variationally. Typically harder to converge the wavefunction
- For accurate results, dynamical correlation should be included by other methods:
    - Perturbation theory – MRPT, CASPT2 etc
    - Configuration interaction – MRCI, CASCI, etc
- CASSCF is a FCI in an active space
- CASSCF in a full valence space is well defined; non-dynamical correlation – correlation of this wave function. But the computational cost is exponential
- Traditional approach – use a smaller active space based on physical considerations
- Cons:
    - MCSCF becomes "molecule-at-a-time" chemistry, due to the need to pick configurations (active space)
    - Not systematic, could be worse than HF if done poorly
    - Inherently unbalanced: all correlation within the active space, none in the inactive space