

# Excited states and symmetry considerations

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# Electronic Schrödinger equation

$$\hat{\mathbf{H}}\Psi(r_1, \dots, r_N) = E\Psi(r_1, \dots, r_N)$$

- Eigenvalue problem
- last time: how do we find the wave function with the lowest eigenvalue (energy)?
- this time: excited states
  - what are they?
  - how can they be computed?

# Excited states

- *formal*: Solutions to the electronic Schrödinger equation other than the ground state
- *physical*: rearrangement in the electronic structure compared to the ground state
  - electronic defect → electron-hole pair
- *quantum chemistry*: electron is taken from an occupied orbital („hole“) and put into a virtual orbital („electron“)

# Types of excited states

- valence states – occurring between bonding and anti-bonding valence MOs
  - $\pi\pi^*$  - typically the only possibility for bright states, i.e. photon absorption and emission occurs
  - $n\pi^*$  - often lower lying than  $\pi\pi^*$  but usually not directly accessible by light
  - $\pi\sigma^*$  - stable if bonds are elongated, may lead to dissociation
  - charge transfer – if donor and acceptor orbitals are spatially separated, may lead to complete charge separation
- Rydberg states - diffuse character, associated with higher quantum numbers
- core excited states – induced by X-rays

# Absorption and Emission

- 2 criteria for absorption (or stimulated emission)
  - photon energy corresponds to transition energy
  - the transition can interact with light (i.e. an oscillating electric field)

- Transition dipole moment

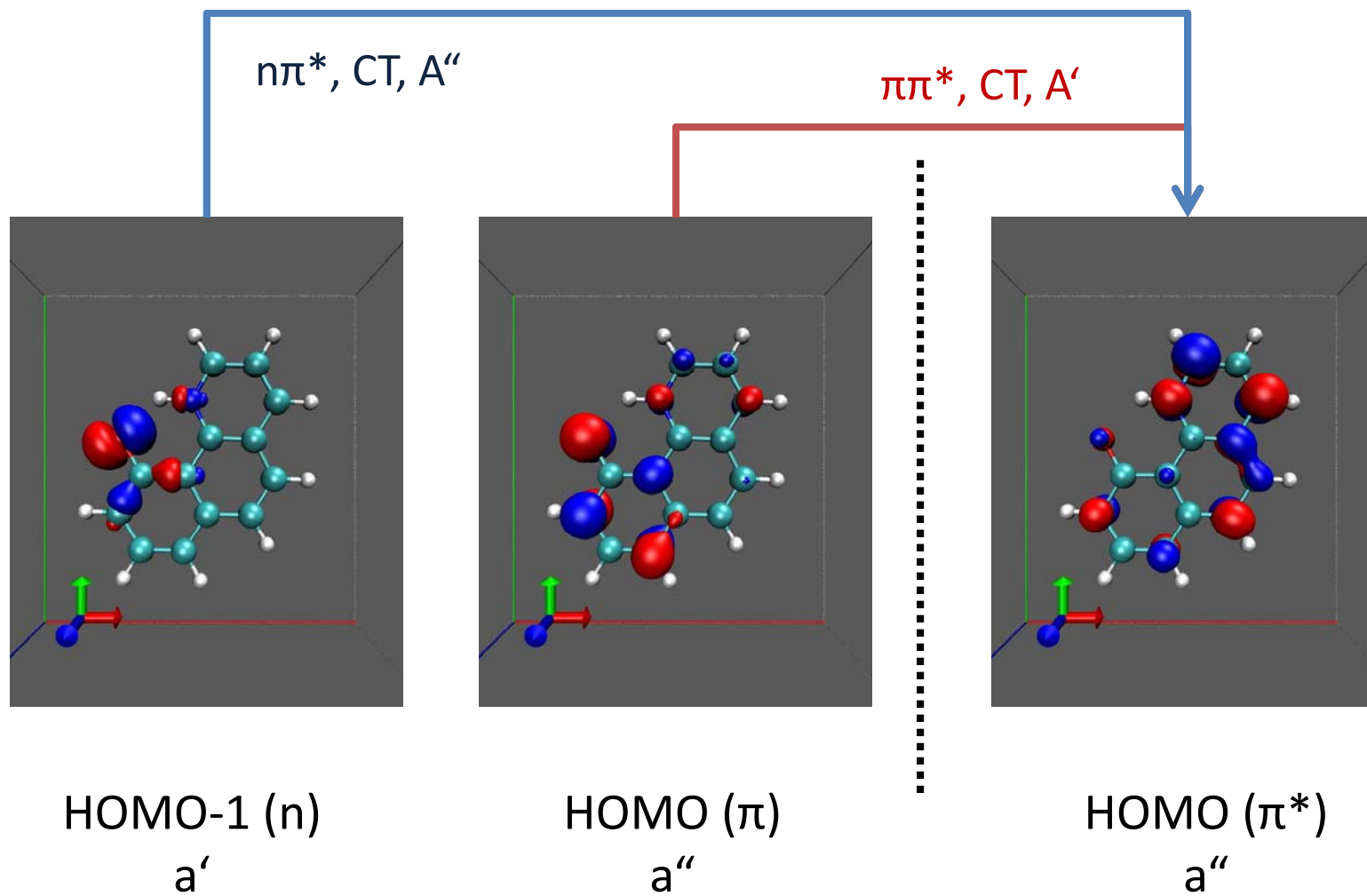
– estimation of the interaction with an electric field

*for a transition between states  $\Psi_i$  and  $\Psi_f$*

$$\mu_{trans} = \left\langle \Psi_i \left| \begin{pmatrix} x \\ y \\ z \end{pmatrix} \right| \Psi_f \right\rangle$$

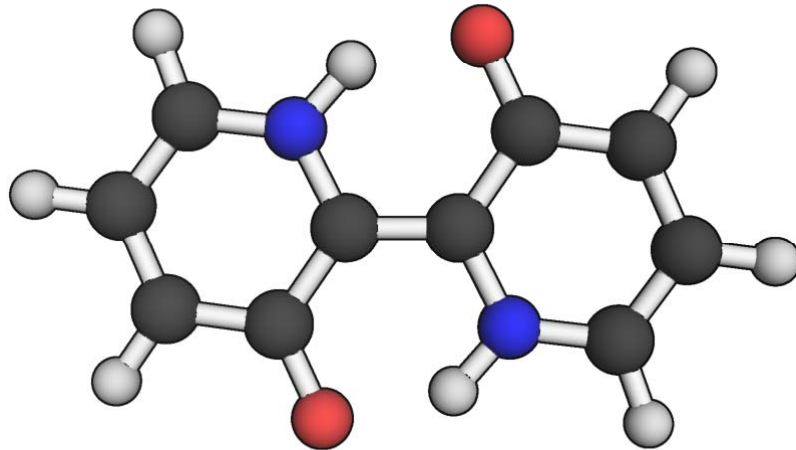
- Typically only  $\pi\pi^*$  states have high transition dipole moments and therefore give strong peaks
  - but other states may be enhanced by intensity borrowing and vibronic effects

# Examples



# Examples

- Which symmetry group?



$C_{2h}$  → irred. representations:  $A_g$ ,  $A_u$ ,  $B_g$ ,  $B_u$

g – „gerade“ – even function

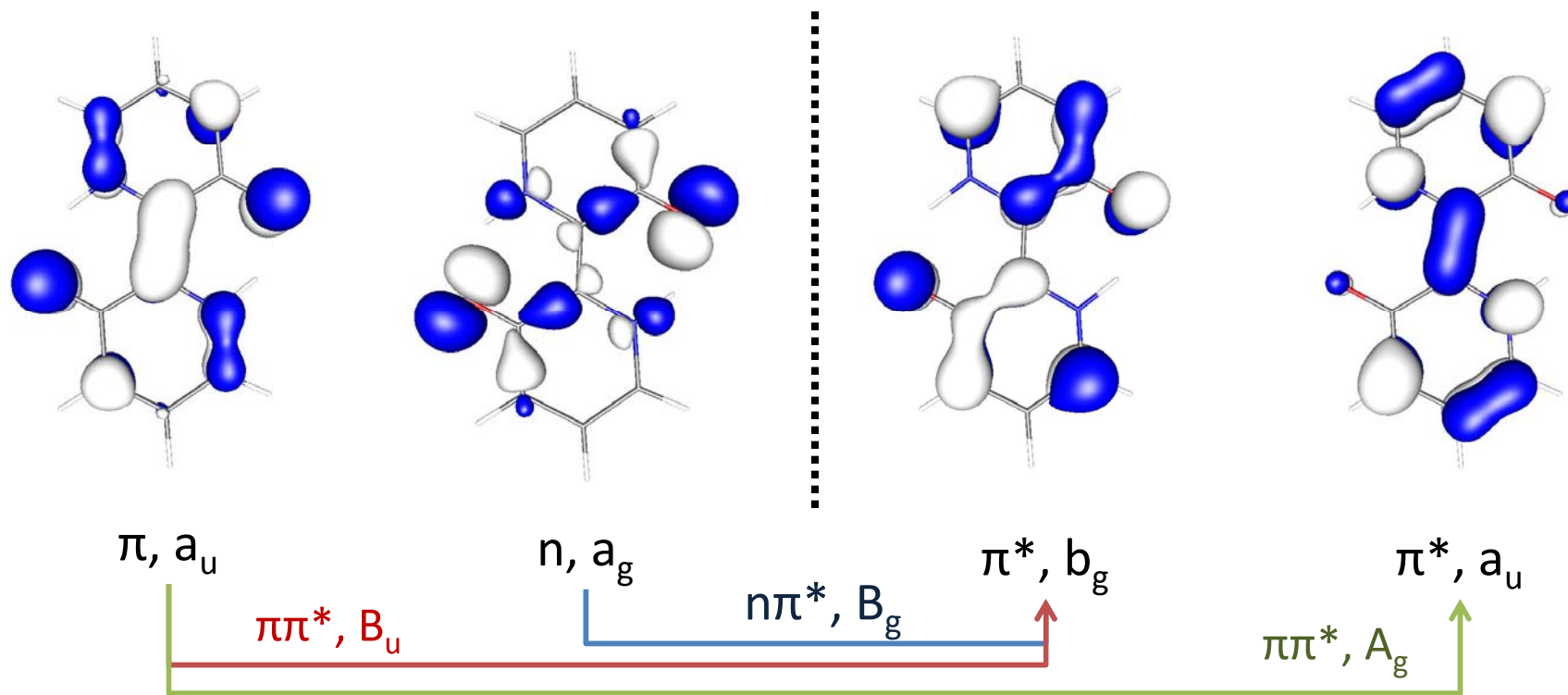
u – „ungerade“ – odd function

A – symmetric with  $C_2$  rotation

B – antisymmetric with  $C_2$  rotation

# Examples

- Label the orbitals
  - qualitative type + symmetry





# Symmetry

- Why use explicit symmetry?
  - Selection rules → information about which states may be spectroscopically active (UV, IR, Raman, ...) without any calculations
  - Significant computational speed-up → with symmetry it is a-priory known that a large fraction of the terms to be computed are zero (cf. last lecture)
  - Clear labels for the description of orbitals and states
    - possibility for analysis without having to manually check the character
    - steering possibilities in the calculation

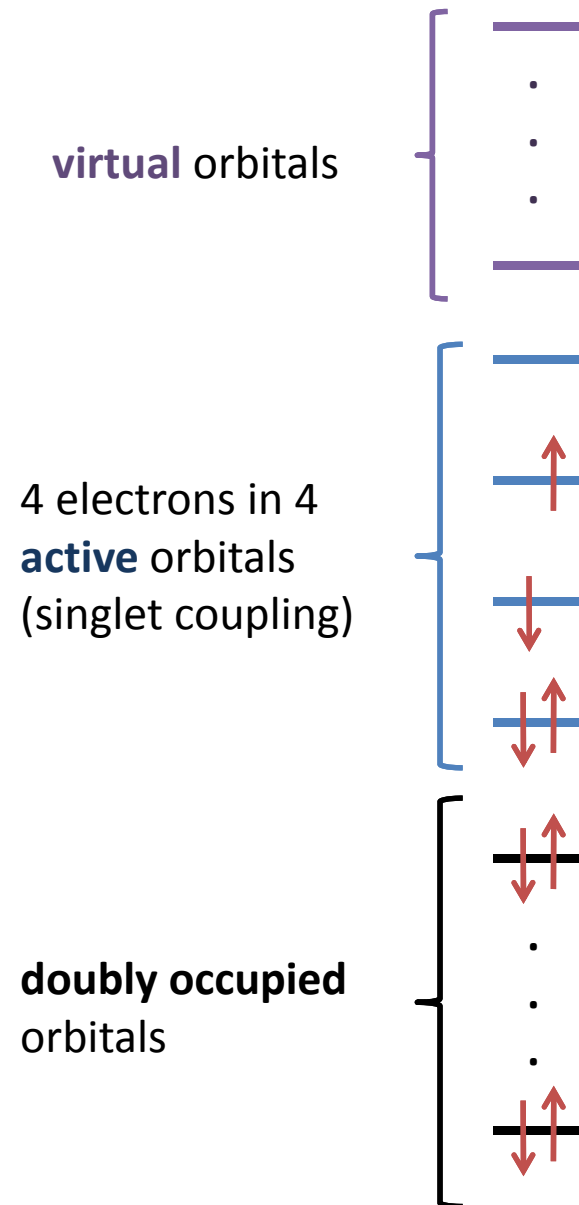
# Computation of excited states



- Configuration interaction (CI) based methods
  - direct computation of the states possible
  - obtained as higher roots of the CI matrix
  - (standard) single-reference CI, MCSCF, MR-CI
- Multi-configurational self-consistent field (MCSCF)
  - CI based method with optimization of the orbitals at the same time
  - smaller configuration space
  - useful for difficult cases
    - HF fails to describe the ground state (strong geometrical distortions, intersections, ...)
    - higher excitations present
- multi-reference (MR)-CI
  - CI on top of MCSCF

# Computation of excited states

- Example CASSCF
  - most popular MCSCF method
  - distribute  $m$  electrons in  $n$  orbitals according to all possible configurations  $CAS(m/n)$
  - simultaneous optimization of orbital and CI coefficients



# Computation of excited states



- Indirect approach
  - compute the light absorption properties of the ground state
    - absorption at poles of the frequency dependent polarizability
  - no construction of the excited states needed
  - applicable to HF, DFT, and CC
- No MP excited states!

# Computation of excited states



- HF, DFT
  - time-dependent (TD) formalism
  - TDHF, TDDFT
  - TDDFT widely used method because it gives good accuracy also on large systems
    - but there is no systematic way of testing and improving it

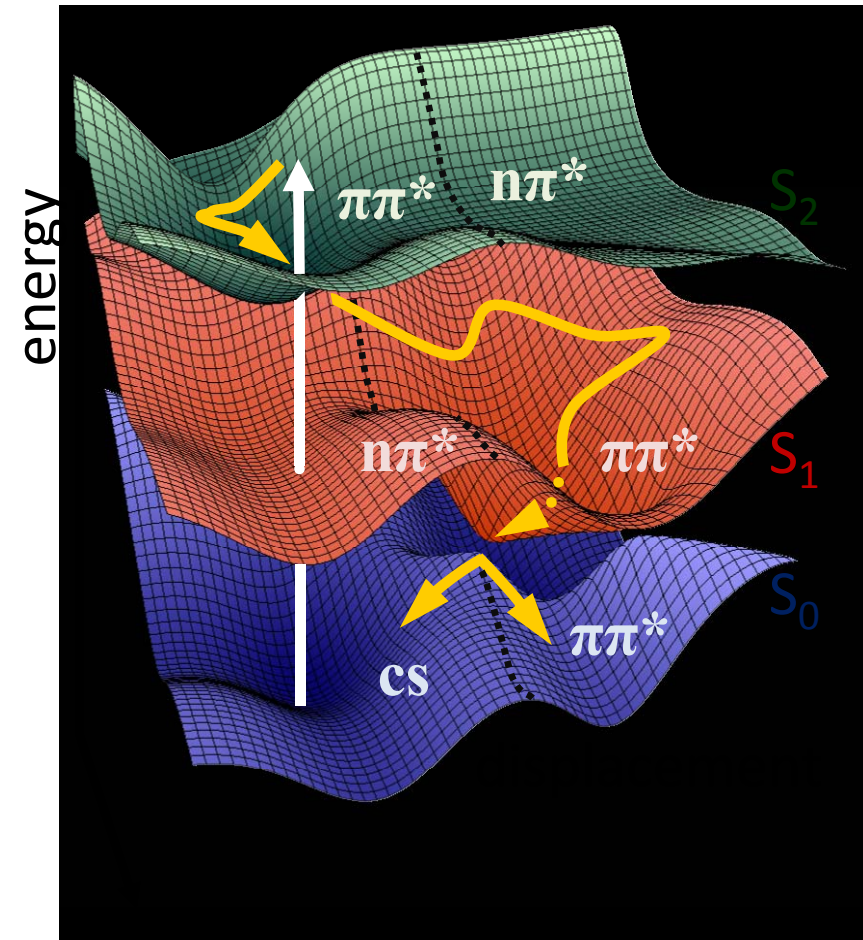
# Computation of excited states



- Coupled cluster (CC)
  - equation of motion (EOM) formalism available for non-perturbative methods
    - EOM-CCSD, EOM-CCSDT, ...
  - additional  $CC_n$  perturbative formalism for excited states
    - CC2, CC3, ...
    - similar ADC(2)
  - order of increasing computational cost (and accuracy)
    - CC2, ADC(2) < EOM-CCSD < CC3 < EOM-CCSDT
  - CC2, ADC(2) → methods for reliable results up to large system sizes
  - CCSD → significantly more expensive than CC2 but also widely applicable
  - CC3, EOM-CCSDT → for benchmark calculations

# Time dependent view

- Possibly several close lying excited states
- Photoabsorption
  - into bright excited state
  - possibly far from its minimum geometry
    - high vibrational energy
- Excited state dynamics
  - Propagation to „conical“ intersection *or*
  - relaxation and fluorescence
- Ground state dynamics
  - back to reactants *or*
  - formation of photoproducts



# Dynamics simulations

- Dynamics often necessary to describe ultrafast ( $< 1\text{ps}$ ) processes happening after photo-excitation
  - standard equilibrium approaches fail
- Different treatment of nuclei
  - classical motion
  - semi-classical coupling to electron dynamics
  - quantum-mechanical wave packets



# Dynamics example

- Dynamics after photoexcitation
  - double proton transfer in the first excited electronic state
  - ultrafast reaction
    - protons follow electrons shifted by the excitation

