Q-CHEM™

A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

# Quantum Chemistry Methods for Valence and Core-Level Excited States: Coupled-Cluster and Equation-of-Motion Coupled-Cluster Family

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# Excited states

1. Excited states: What are they? Brief recap.
2. Excited-state methods in Q-Chem: From basic to advanced methods.
3. EOM-CC family.
4. Excited state properties and wave-function analysis.
5. Examples:
   - Excited states of formaldehyde (EOM-EE);
   - Core-level states of formaldehyde (CVS-EOM-IP/EE);
   - Singlet-triplet gap in methylene (EOM-SF);
   - Open-shell states by EOM-EA and EOM-DEA.

# Excited states

$H\Psi_L = E_L \Psi_L$ L=0: ground state, L>0: excited states.

For non-interacting electrons, excited states are just excited determinants and the excitation energies are orbital energy differences

$\Phi_0$ $\Phi_i^a$

$$E_{ex} = \epsilon_a - \epsilon_i$$

For interacting electrons: Need to include configuration interaction

The simplest approach: configuration interaction singles (CIS)

$$\Psi_{ex} = \Sigma_{ia} C_i^a \Phi_i^a$$

# Excited-state calculations

**WFT**

1. Perform SCF calculations: find Hartree-Fock orbitals.
$\Phi_0$: zero-order w.f. for the ground state.
2. Include correlation (MP2, CCSD,...): improve zero-order wave function.
3. Excited states: diagonalize H/ effective H:
  Hartree-Fock-> single excitations only (CIS)
  Correlated methods (CC): larger space.

**DFT**

1. Perform SCF calculations with $V_{xc}$: find Kohn-Sham orbitals.
$\Phi_0$: correlated density for the ground state.
2. Excited states: diagonalize Kohn-Sham H in the space of singles.

In both schemes excited states are described as linear combinations of **excited determinants**

# Excited states in Q-Chem

1. CIS: Hartree-Fock ground state; Single excitations from HF wfn.
2. TDDFT: Kohn-Sham ground state; Excited states are single excitations from the KS determinant.
3. CIS(D) and SOS-CIS(D)
4. EOM-CCSD: CCSD for the ground state and single and double excitations for the excited states.
5. ADC methods
6. Other methods: RASCI-SF, Delta-E, C-DFT, CASSCF, etc.
7. Properties and excited-state analysis; effect of the environment.
8. Special extensions:
   - Methods for open-shell species: radicals, diradicals, etc (EOM-EA/DEA/IP/SF);
   - Core-level states by using core-level separation (CVS-EOM, CVS-ADC);
   - Metastable states (resonances) by using CAPs and CBFs (CAP-EOM-CC).

# EOM-CC theory

$$\Psi = \mathrm{R}e^{T}\,\Phi_0$$

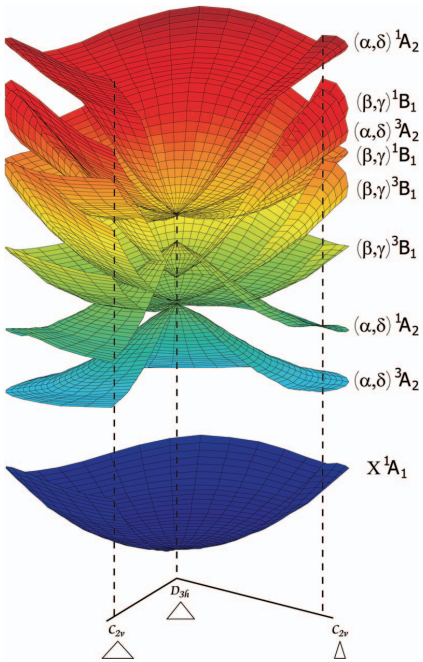
T: satisfies CCSD equations for the reference

$$R\Phi_0 = (R_0 + R_1 + R_2)\Phi_0$$

$$= r_0\Phi_0 + \sum_{ia} r_i^a \Phi_i^a + \frac{1}{4}\sum_{ijab} r_{ij}^{ab}\Phi_{ij}^{ab} + \ldots$$

$$\overline{H}R\Phi_0 = ER\Phi_0$$

$$\overline{H} = \exp(-T)H\exp(T)$$



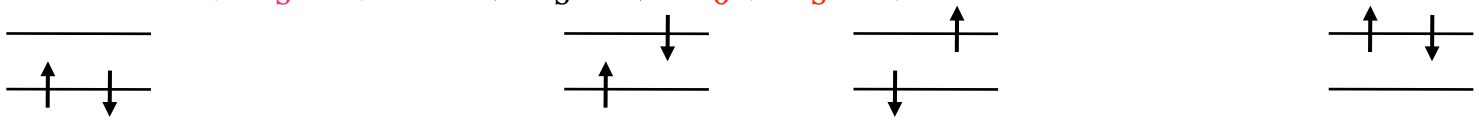

Specific EOM-CC model:

-choice of excitation level in T & R;

-choice of the reference and type of R.

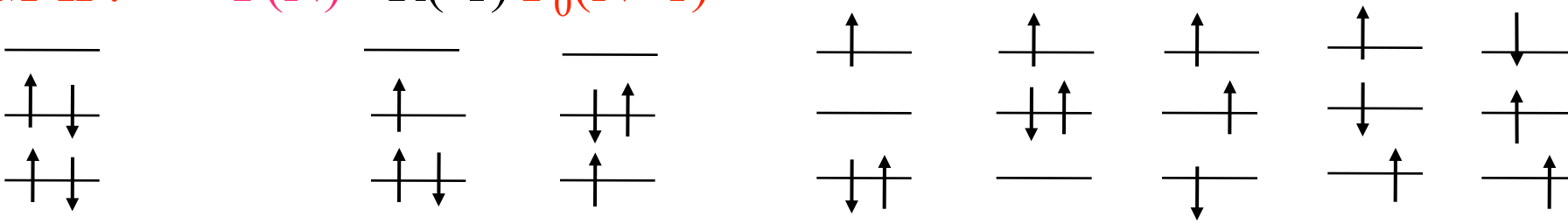
# EOM: Choice of R and $\Phi_0$

EOM-EE: $\Psi(M_s=0) = R(M_s=0)\Psi_0(M_s=0)$



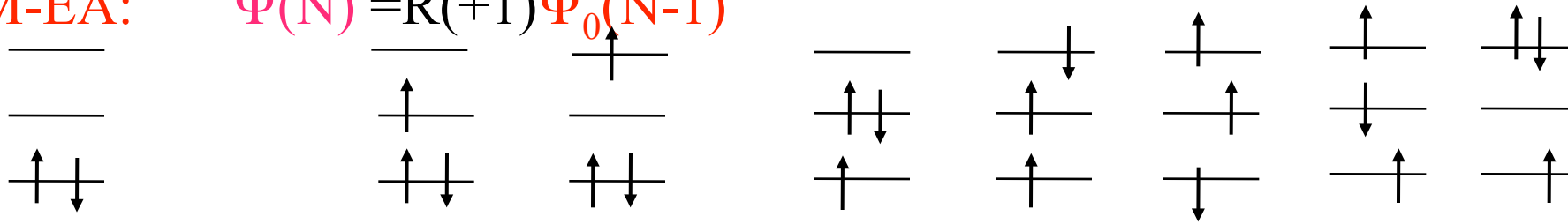
$\Psi_0$ $\Psi_i^a$ $\Psi_{ij}^{ab}$

EOM-IP: $\Psi(N) = R(-1)\Psi_0(N+1)$



$\Psi_0$ $\Psi_i$ $\Psi_{ij}^a$

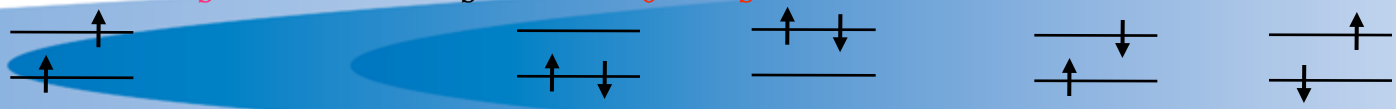
EOM-EA: $\Psi(N) = R(+1)\Psi_0(N-1)$



$\Psi_0$ $\Psi^a$ $\Psi_i^{ab}$

EOM-SF: $\Psi(M_s=0) = R(M_s=-1)\Psi_0(M_s=1)$

$\Psi_0$



$\Psi_i^a$

# How to set up EOM-CCSD calculations

- Decide which EOM model you need and set your reference state appropriately (charge and mutiplicity in $molecule).
- Specify type and number of target states:
- **EE_STATES**, IP_STATES, EA_STATES, SF_STATES
- Core-level states CVS_EE_STATES, …. (freeze core!)
- Mind the symmetry!
- Mind the basis (diffuse functions, uncontracted bases)
- If properties/gradients required: specify which EOM state you need properties for (or between which EOM states you want to compute transition properties).
- Performance-related keywords: MEM_TOTAL, FROZEN_CORE, FNO, use RI (AUX_BASIS) or CD (CD_THRESH), CC_BACKEND (VM, XM).

# Analysis of excited-state calculations

1. Determine spin-coupling (singlet or triplet), either from the amplitudes or from $<S^2>$.

2. Determine symmetry of the state (note symmetry of the <u>state</u> may not be the same as symmetry of the <u>transition</u>).

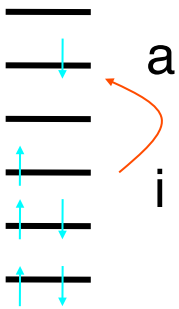
3. Look at dominant amplitudes. Which orbitals are involved? What is their character?

4. More rigorous methods: natural transition orbitals, Dyson orbitals.

5. Compute states' and interstate properties (need to specify in the input what you want).

# Types of excited states

- Valence, local excitations
- Rydberg states
- Charge-transfer states
- Mixed character
- Plasmons
- Core-level states

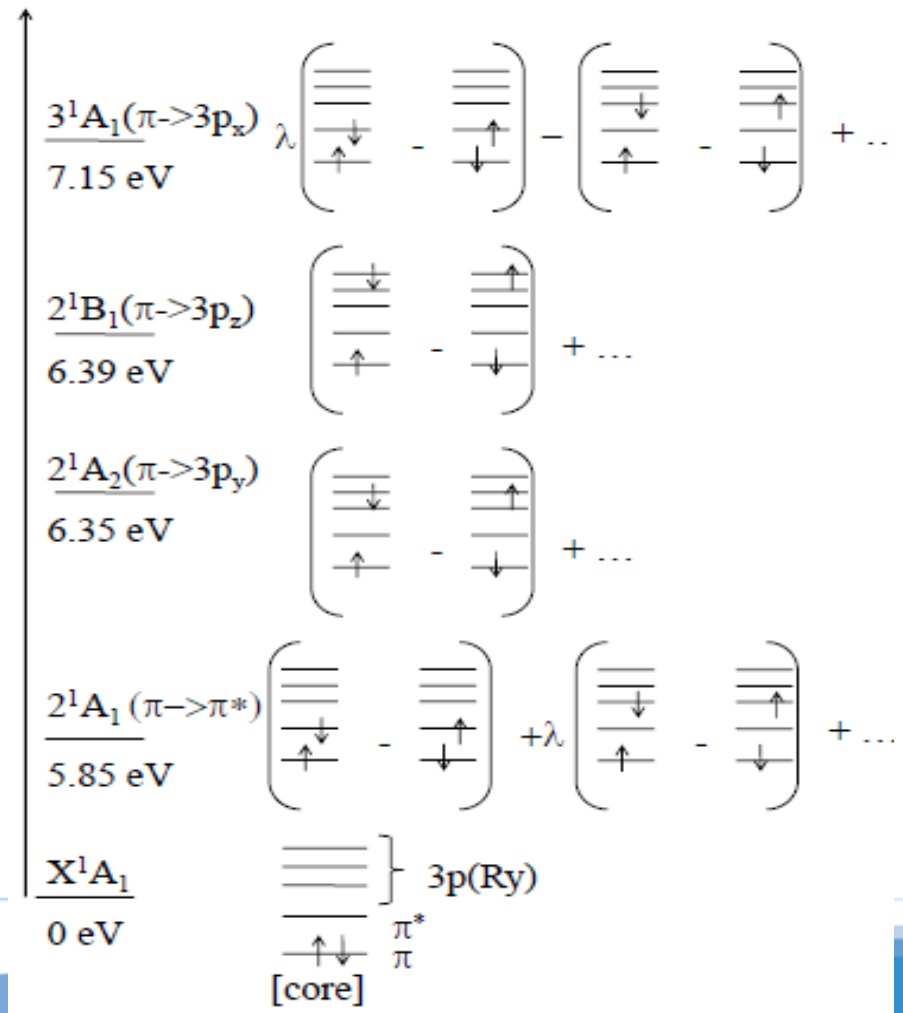


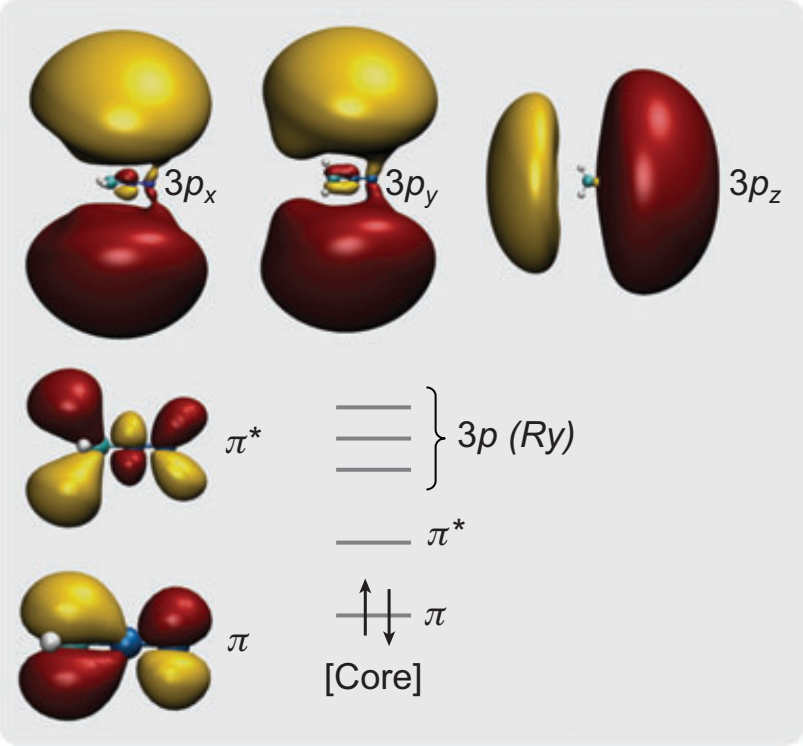

$$\Phi_i^a$$

Look at dominant amplitudes.
Which orbitals are involved?
What is their character?

# Rydberg versus valence states

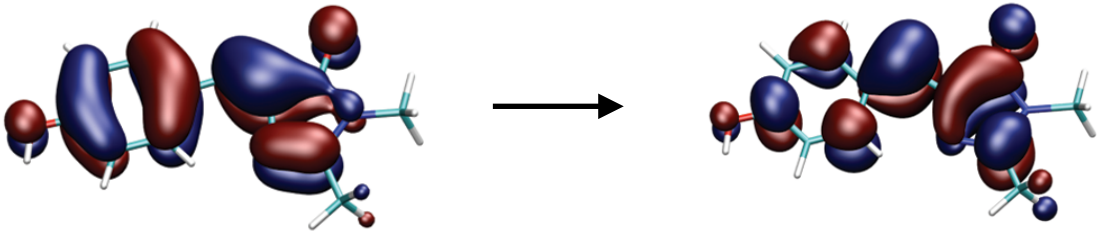
## Summary of EOM-EE calculations

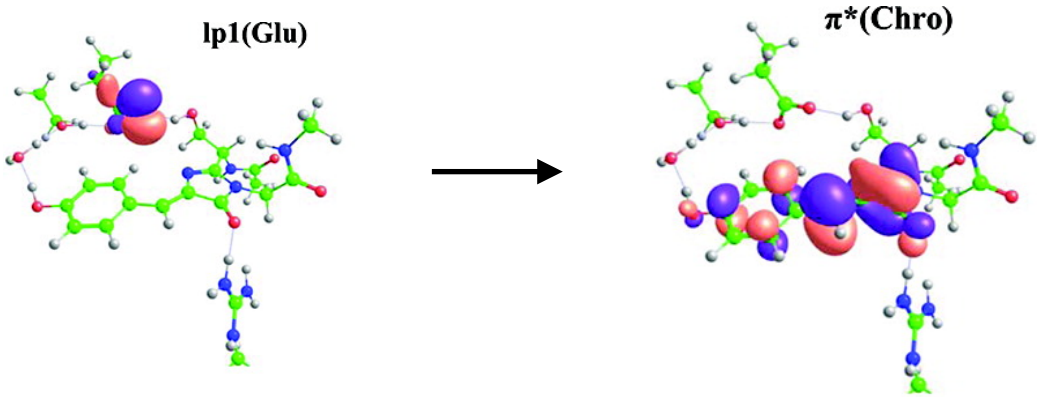


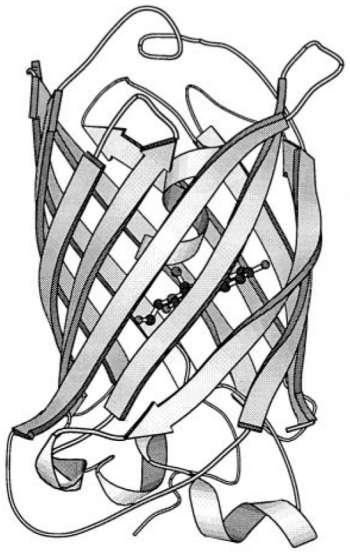




Fedorov, Koziol, Li, Parr, Krylov, Reisler *Theoretical* and experimental investigations of the electronic Rydberg states of diazomethane: Assignments and state interactions, JPCA **111** 4557 (2007)

# Excited states: LE vs CT



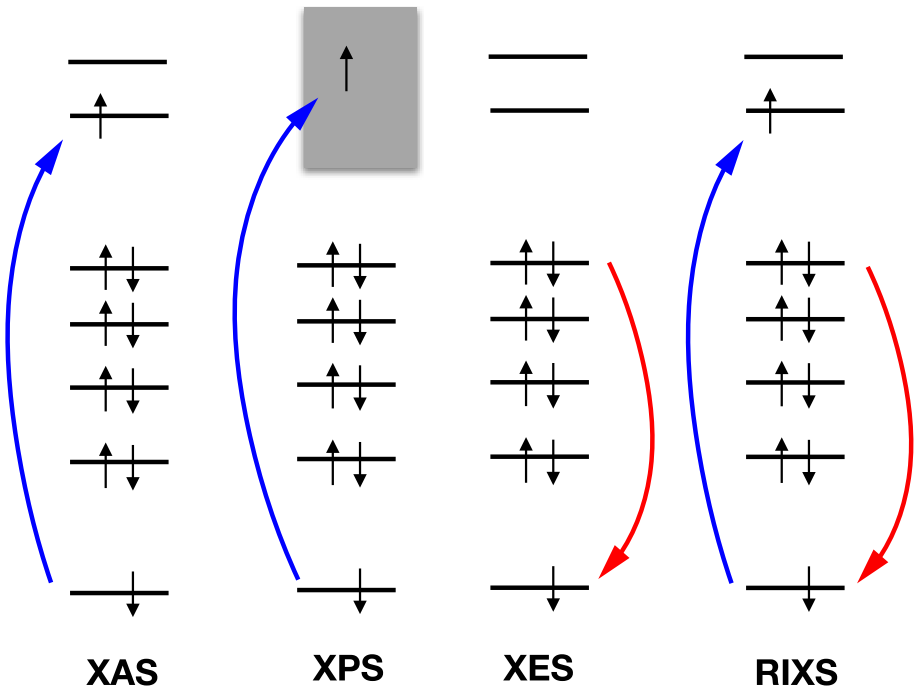


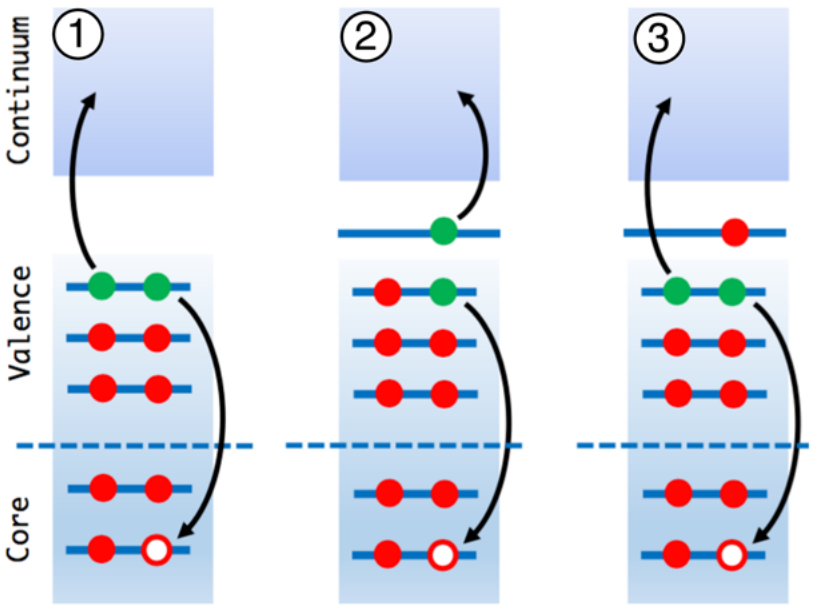



GFP

Locally excited and charge-transfer states in green fluorescent protein

# Core-level states



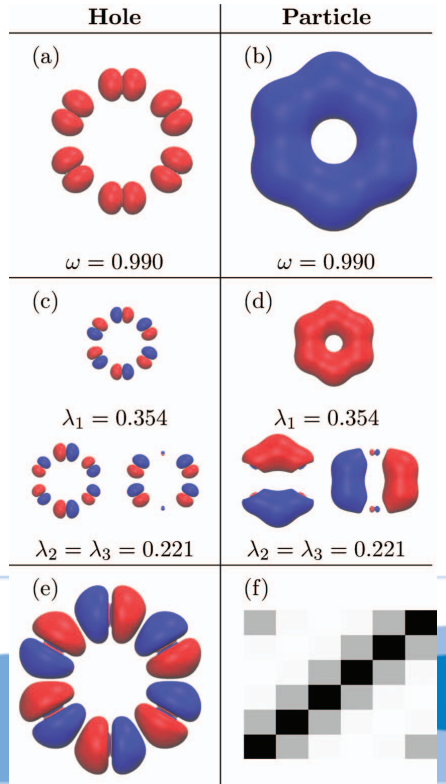




**Auger-Meitner process**

Various core-level spectra can be modeled using core-valence separation (CVS) extension of EOM-CC methods

# Excited-state analysis

1. Can compute and visualize NTOs, densities, attachment-detachment densities, spin densities, average particle-hole separation, and more.
2. Common set of tools for TD-DFT, CIS, EOM, and ADC methods.



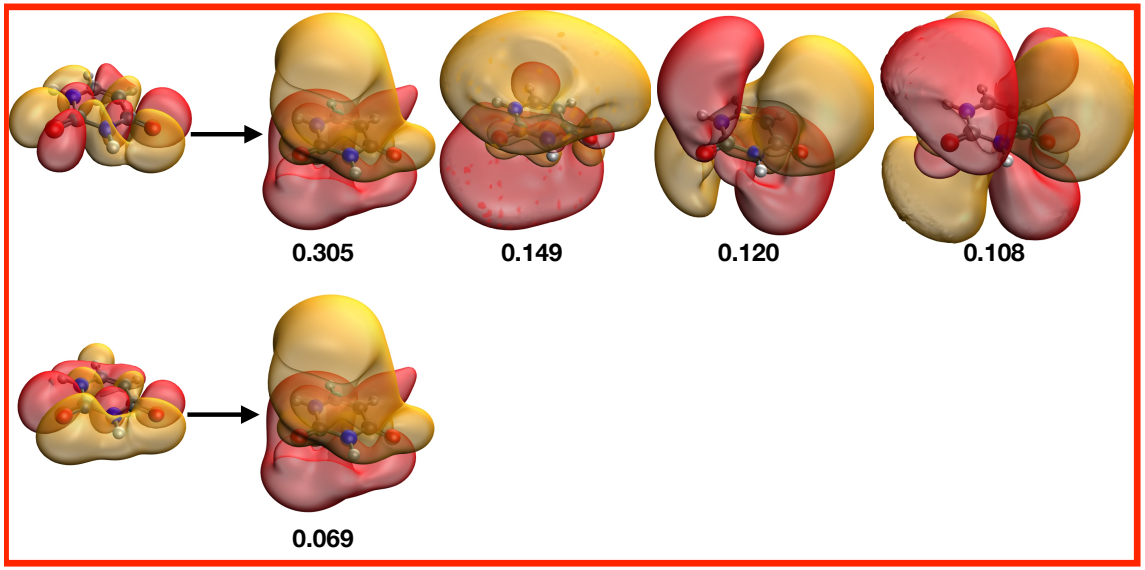

**Invoke with 'state_analysis=true'**
**Visualization: Jmol, Gabedit …**

Plasser, Krylov, Dreuw, libwfa: Wavefunction analysis tools for excited and open-shell electronic states, WIRES Comp. Mol. Sci. e1595 (2022);
Krylov, From orbitals to observables and back, JCP **153** 080901 (2020).

# Benefits of NTOs

**Uracil example (CIS/aug-cc-pVDZ calculation)**

Wave-function amplitudes in canonical MOs:



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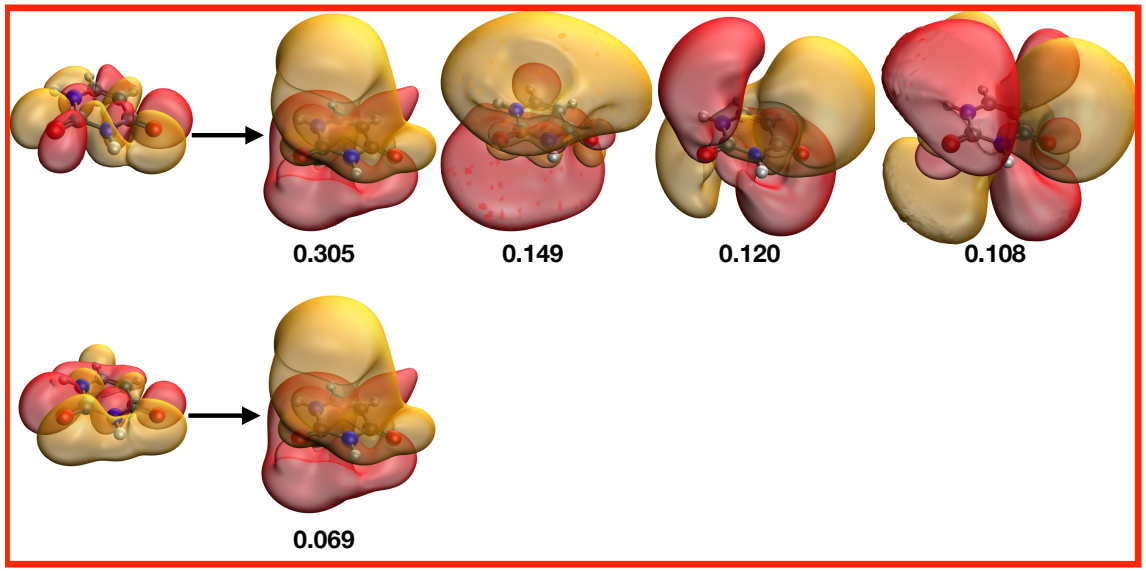
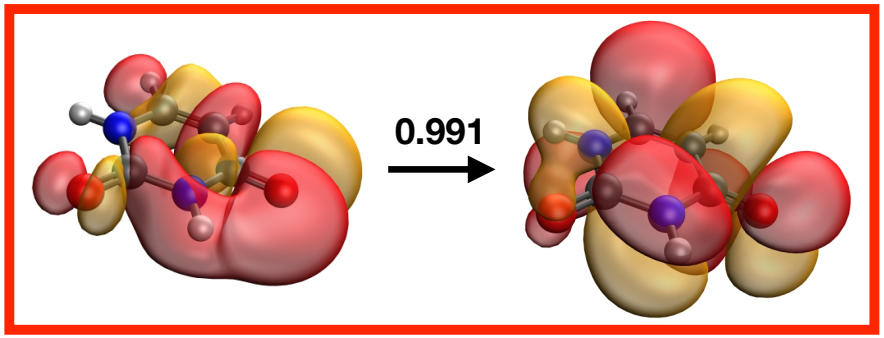



Amplitudes in the NTO representation:




lp(O)-> pi* character

# Excited-state properties

Gradients: CIS, TDDFT, EOM-CCSD
State dipole moments/transition dipole moments: All methods
SOCs: EOM-CCSD and CVS-EOM-CCSD, TDDFT/CIS, RAS-CI
NACs: CIS, DFT, SF-CIS, SF-DFT, EOM-CCSD
2PA: ADC, EOM-CCSD
ECD and OR: ADC, EOM-CCSD
XECD, X2PA: EOM-CCSD
RIXS: ADC, EOM-CCSD
Dyson orbitals: (CVS)-EOM-CC, ADC

**See manual**

# Summary

- Excited-state calculations follow hierarchy of methods starting from CIS
- Excited states are described by some type of linear expansion of excited configurations from a ground-state wave-function
- EOM-CCSD methods are based on coupled-cluster ansatz
- Different types of states can be accessed by different EOM methods
- Core-level states are accessible by CVS-EOM-CC
- Methods for metastable states (resonances) are available
- Broad variety of state and interstate properties are available
- NTOs and Dyson orbitals provide rigorous MO picture of excited/ionized states

$$\Psi = \mathrm{R}e^{T}\,\Phi_0$$

# Further reading

1. Krylov, The quantum chemistry of open-shell species, Reviews in Comp. Chem. **30** 151 (2017).

2. Dreuw, Head-Gordon, Single-reference ab initio methods for the calculation of excited states of large molecules, Chem. Rev. **105** 4009 (2005).

3. Krylov, Equation-of-motion coupled-cluster methods for electronically excited and open-shell species: The hitchhikers guide to Fock space, Ann. Rev. Phys. Chem. **59** 433 (2008).

4. Krylov, From orbitals to observables and back, J. Chem. Phys. **153** 080901 (2020).

5. Jagau, Bravaya, Krylov, Extending quantum chemistry of bound states to electronic resonances, Ann. Rev. Phys. Chem. **68** 525 (2017)

5. **Webinars on Q-Chem website, Q-Chem manual.**

# Examples

1. Excited states of formaldehyde (EOM-EE)
2. Core-level states of formaldehyde (CVS-EOM-IP/EE)
3. Singlet-triplet gap in methylene (EOM-SF)
4. Open-shell states by EOM-EA and EOM-DEA

- Download the structures from the provided link
- Lecture slides, inputs, outputs, and summaries are also available for download
- Remember to use MEM_TOTAL=4000 for all EOM-CC examples