Equation-of-Motion
Coupled-Cluster Theory

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Excited States

excited **states**	<=>	**solutions of the Schrödinger equation other than the ground state**

relevant for spectroscopy, photochemistry, ...

- – excitation energies $\qquad\qquad$ ΔE_{exc}

- – transition moments $\qquad\qquad$ $\langle \Psi_f | \, \mu \, | \Psi_i \rangle$

- – excited-state properties $\qquad\;$ $\partial E_{exc}/\partial x$

- – simulation of spectra
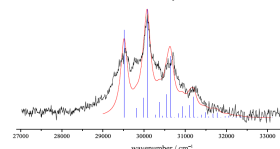
Coupled-Cluster Theory and Excited States

CC theory effectively ground-state theory

- **single-determinant reference**

- **difficulty to converge to higher-lying solutions**

but

- sometimes possible to converge to excited-state solutions

- **response theory (→ Olsen)**

    => excitation energies as poles of response function

- **equation-of-motion ansatz**

- **multireference CC treatments (→ Köhn)**

similar issues exist in HF, DFT, ...

I.

Equation-of-Motion Ansatz

Equation-of-Motion Ansatz

write excited-state wavefunction as

$$\left| \Psi_{exc} \right\rangle \;=\; \mathcal{R} \left| \Psi_{gs} \right\rangle$$

Equation-of-Motion Ansatz

write excited-state wavefunction as

$$|\Psi_{exc}\rangle \;=\; \mathcal{R}\,|\Psi_{gs}\rangle$$

excited-state wavefunction
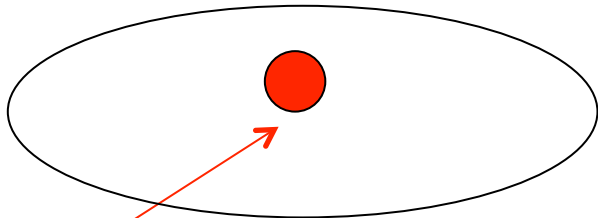
excitation operator

ground-state wavefunction

- **transforms ground-state into excited-state wavefunction**

- **describes differences in orbitals, correlation, ... upon excitation**

Motivation and Advantages

molecule

**local excitation
at chromophore**

**differences between
ground and excited state
more or less localized**

to be described by $\mathcal{R}$

---

usual approach to ΔE_{exc}

– get E **separately** for all states

– take difference to get ΔE_{exc}

– balanced description?

– computational efficiency?

– not generally applicable

'direct' approach to ΔE_{exc}

– get E_{exc} and Ψ_{exc} via **ground** state

– description of (local) **differences
less demanding**

– more **balanced**

– generally **applicable**

Equation-of-Motion Ansatz

equations for $\mathcal{R}$

- **insert equation-of-motion ansatz into Schrödinger equation**

$$H \, \mathcal{R} \, |\Psi_{gs}\rangle \;=\; E_{exc} \, \mathcal{R} \, |\Psi_{gs}\rangle$$

- **apply $\mathcal{R}$ to the ground-state Schrödinger equation**

$$\mathcal{R} \, H \, |\Psi_{gs}\rangle \;=\; E_{gs} \, \mathcal{R} \, |\Psi_{gs}\rangle$$

- **subtract**

$$(H \, \mathcal{R} \;-\; \mathcal{R} \, H) \, |\Psi_{gs}\rangle \;=\; \Delta E_{exc} \, \mathcal{R} \, |\Psi_{gs}\rangle$$

$$[H, \mathcal{R}] \, |\Psi_{gs}\rangle \;=\; \Delta E_{exc} \, \mathcal{R} \, |\Psi_{gs}\rangle$$

similarity to equation of motion for operators explains the name

II.

Equation-of-Motion CC Ansatz

Excited-State Wavefunction

EOM ansatz for excited-state wavefunction

$$|\Psi_{exc}\rangle = \mathcal{R} \, |\Psi_{CC}\rangle \longleftarrow$$

CC wavefunction
for ground state

$$= \mathcal{R} \, \exp(T) \, |0\rangle$$

excitation operator $\qquad \mathcal{R} = \mathcal{R}_0 + \mathcal{R}_1 + \mathcal{R}_2 + \dots$

$$\mathcal{R}_0 = r_0$$

$$\mathcal{R}_1 = \sum_i \sum_a r_i^a \, a_a^\dagger a_i$$

parameterization as
for the cluster operator

$$\mathcal{R}_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} r_{ij}^{ab} \, a_a^\dagger a_b^\dagger a_j a_i$$

unknown parameters
are the amplitudes of $\mathcal{R}$

$$\dots$$

exact parameterization of excited-state wavefunction

EOM-CC Equations

equations for $\mathcal{R}$
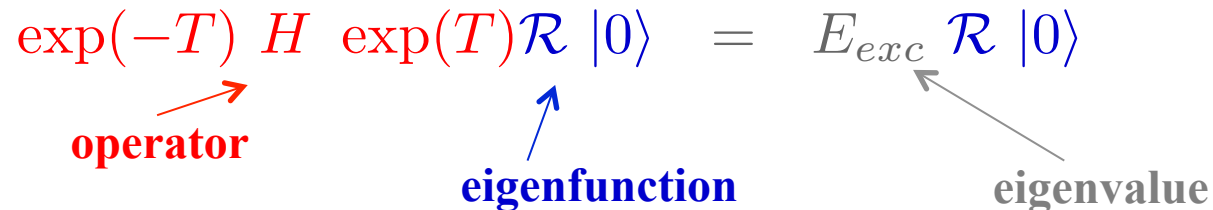
- **insert EOM-CC ansatz in Schrödinger equation**

$$H \; \mathcal{R} \; \exp(T) \; |0\rangle \;\; = \;\; E_{exc} \; \mathcal{R} \; \exp(T) \; |0\rangle$$

- **exploit that $\mathcal{R}$ and T commute**

$$H \; \exp(T) \; \mathcal{R} \; |0\rangle \;\; = \;\; E_{exc} \; \exp(T) \; \mathcal{R} \; |0\rangle$$

- **multiply from the left by exp(-T)**

$$\exp(-T) \; H \; \exp(T)\mathcal{R} \; |0\rangle \;\; = \;\; E_{exc} \; \mathcal{R} \; |0\rangle$$

operator   **eigenfunction**   **eigenvalue**

eigenvalue problem for a similarity-transformed Hamiltonian

EOM-CC Equations

further (optional) rewrite

- **excited-state eigenvalue equation**

$$\exp(-T)H\exp(T)\ \mathcal{R}\ |0\rangle\ =\ E_{exc}\ \mathcal{R}\ |0\rangle$$

- **apply $\mathcal{R}$ to ground-state CC equation**

$$\mathcal{R}\ \exp(-T)H\exp(T)\ |0\rangle\ =\ \mathcal{R}\ E_{gs}\ |0\rangle$$

- **subtract**

$$(\exp(-T)H\exp(T)\ \mathcal{R}\ -\ \mathcal{R}\ \exp(-T)H\exp(T))\ |0\rangle\ =\ \Delta E_{exc}\ \mathcal{R}\ |0\rangle$$

- **rewrite using commutators**

$$[\exp(-T)H\exp(T),\mathcal{R}]\ |0\rangle\ =\ \Delta E_{exc}\ \mathcal{R}\ |0\rangle$$

- **define effective Hamiltonian** $\qquad \bar{H}\ =\ \exp(-T)H\exp(T)$

$$\Rightarrow\qquad [\bar{H},\mathcal{R}]\ |0\rangle\ =\ \Delta E_{exc}\ \mathcal{R}\ |0\rangle \qquad \text{commutator expression}$$

EOM-CC Equations

cont´d

- **expand commutator**

$$(\bar{H}\mathcal{R} - \mathcal{R}\bar{H})\, |0\rangle \; = \; \Delta E_{exc}\, \mathcal{R}\, |0\rangle$$

resolution of identity

$$|0\rangle\langle 0| \; + \; \sum_{P\neq 0} |\Phi_P\rangle\langle\Phi_P|$$

- **insert resolution of identity**

$$(\bar{H} - \langle 0|\bar{H}|0\rangle)\, \mathcal{R}\, |0\rangle \; - \; \underbrace{\sum_{P\neq 0} \mathcal{R}\, |\Phi_P\rangle\langle\Phi_P|\, \bar{H}\, |0\rangle}_{=\,0} \; = \; \Delta E_{exc}\, \mathcal{R}\, |0\rangle$$

- **define**

$$\bar{H}_N \; = \; \bar{H} \; - \; \langle 0|\bar{H}|0\rangle$$

subtract CC ground-state energy

=> $$\bar{H}_N\, \mathcal{R}\, |0\rangle \; = \; \Delta E_{exc}\, \mathcal{R}\, |0\rangle$$

eigenvalue problem for excitation energy

Summary of EOM-CC Ansatz

- **excited-state wavefunction**

$$|\Psi_{exc}\rangle = \mathcal{R} \, \exp(T) \, |0\rangle$$

- **excitation operator**

$$\mathcal{R} = \mathcal{R}_0 + \mathcal{R}_1 + \mathcal{R}_2 + \ldots$$

- **equations for excitation energy and excitation operator**

$$\bar{H} \, \mathcal{R} \, |0\rangle = E_{exc} \, \mathcal{R} \, |0\rangle$$

or

$$\bar{H}_N \, \mathcal{R} \, |0\rangle = \Delta E_{exc} \, \mathcal{R} \, |0\rangle$$

- **without approximation equivalent to FCI**

Effective Hamiltonian in EOM-CC

- **effective Hamilton operator in EOM-CC**

$$\bar{H} \;=\; \exp(-T)\; H \;\exp(T)$$

  - **defined via a similarity transformation**

    similarity transformation $\qquad \bar{A} \;=\; B^{-1}\, A\, B \qquad$ eigenvalues are preserved

  - **non-Hermitian operator** **(operator exp(-T) is not unitary)**

    - **different left** and **right** eigenfunctions/vectors

    - **biorthogonality** instead of orthogonality

Left-Side Eigenvalue Problem of EOM-CC

left-side eigenvalue problem

$$\langle 0 | \; \mathcal{L} \; \bar{H} \; = \; \langle 0 \; | \mathcal{L} \; E_{exc}$$

same eigenvalues as
for right-side problem

with de-excitation operator

$$\mathcal{L} \; = \; \mathcal{L}_0 \; + \; \mathcal{L}_1 \; + \; \mathcal{L}_2 \; + \; \ldots$$

$$\mathcal{L}_0 \; = \; l_0$$

$$\mathcal{L}_1 \; = \; \sum_i \sum_a l_a^i \; a_i^\dagger a_a$$

$$\mathcal{L}_2 \; = \; \frac{1}{4} \sum_{i,j} \sum_{a,b} l_{ab}^{ij} \; a_i^\dagger a_j^\dagger a_b a_a$$

$$\ldots$$

parameterization as
for the Λ operator
in CC gradient theory

Biorthogonality in EOM-CC

biorthogonality requirement

i, j are state labels

$$\langle 0| \; \mathcal{L}^i \; \mathcal{R}^j \; |0\rangle \; = \; A \; \delta_{ij}$$

with A usually chosen to be one

orthogonality does not hold: $\quad \langle 0| \; \mathcal{R}^{i\dagger} \; \mathcal{R}^j \; |0\rangle \; \neq \delta_{ij}$

=> **EOM-CC energy expression**

$$E_{exc} \; = \; \langle 0| \; \mathcal{L} \; \bar{H} \; \mathcal{R} \; |0\rangle$$

$$= \; E_{cc} \; + \; \langle 0| \; \mathcal{L} \; \bar{H}_N \; \mathcal{R} \; |0\rangle$$

Ground-State Solution of EOM-CC

right-side solution

$$\mathcal{R} \;=\; 1 \qquad \longrightarrow$$

$$\langle \Phi_P | \; \exp(-T)H\exp(T) \;-\; E_{CC} \, |0\rangle \;=\; 0$$

CC equations

eigenvalue is coupled-cluster energy

left-side solution

$$\mathcal{L} \;=\; 1 \;+\; \Lambda \qquad \longrightarrow$$

$$\langle 0 | \; (1 \;+\; \Lambda) \; (\exp(-T)H\exp(T) \;-\; E_{CC}) \, |\Phi_P\rangle \;=\; 0$$

Λ equations from CC gradient theory

Matrix Representation of EOM-CC

projection onto excitation space

$$\langle \Phi_P | \; \bar{H} \; \mathcal{R} \; |0\rangle \;=\; E_{exc} \, \langle \Phi_P | \; \mathcal{R} \; |0\rangle \qquad P = 0, 1, \ldots$$

insert resolution of identity

$$\sum_Q \langle \Phi_P | \; \bar{H} \; |\Phi_Q\rangle \langle \Phi_Q | \; \mathcal{R} \; |0\rangle \;=\; E_{exc} \langle \Phi_P | \; \mathcal{R} \; |0\rangle$$

$$\overline{\mathbf{H}} \; \mathbf{r} \;=\; E_{exc} \; \mathbf{r}$$

eigenvalue problem for matrix $\bar{\mathbf{H}}$

$$\bar{H}_{PQ} \;=\; \langle \Phi_P | \; \bar{H} \; |\Phi_Q\rangle \qquad\qquad r_P \;=\; \langle \Phi_P | \mathcal{R} \; |0\rangle$$

matrix $\bar{\mathbf{H}}$ **eigenvector r**

Matrix Representation of EOM-CC

- **right-side eigenvalue problem**

$$\overline{\mathbf{H}} \; \mathbf{r} \; = E_{exc} \; \mathbf{r}$$

- **left-side eigenvalue problem**

$$\mathbf{l}^T \; \overline{\mathbf{H}} \; = \; \mathbf{l}^T \; E_{exc}$$

state labels

- **biorthogonality**

$$\mathbf{l^i}^T \; \mathbf{r^j} \; = \; \delta_{ij}$$

- **energy expression**

$$E_{exc} \; = \; \mathbf{l}^T \; \overline{\mathbf{H}} \; \mathbf{r}$$

Truncated EOM-CC Approaches

$$T \;=\; T_1 \;+\; T_2$$

$$\mathcal{R} \;=\; \mathcal{R}_0 \;+\; \mathcal{R}_1 \;+\; \mathcal{R}_2$$

=> **EOM-CCSD**

truncations in **cluster**
and **excitation** operator

projection on the space
of **singles and doubles**

EOM-CCSD:

diagonalization of the with **exp(T_1+T_2)**
similarity-transformed Hamiltonian
in the space of **singles and doubles**

issues:

diagonalization of untransformed Hamiltonian
in the space of singles and doubles

– **difference to CISD**

– **size consistency/extensivity/intensivity**

Superior Performance of EOM-CC

excitation space (i.e., Φ_i^a, Φ_{ij}^{ab})

diagonalization space

orthogonal complement

(i.e., $\Phi_{ijk}^{abc}, \Phi_{ijkl}^{abcd}, \ldots$)

coupling between P and Q block determines size of Q contributions

similarity transformation reduces coupling between P and Q space

CISD: $\langle \Phi_{ijk}^{abc} | H | \Phi_i^a \rangle = \langle bc || jk \rangle$

=> coupling is **first order**

EOM-CCSD: $\langle \Phi_{ijk}^{abc} | \bar{H} | \Phi_i^a \rangle = \underbrace{\bar{H}_{bcjk}}_{= 0} + \ldots$

=> coupling is **higher order**

EOM-CCSD should perform better than CISD

Size Intensivity

excitation at A

ground state at B

$r_{AB} \rightarrow \infty$

A size-consistent/extensive method provides the same excitation energies independent whether the excitation energies are computed for the sub-system A or for the non-interacting supersystem consisting of A and B

a) individual quantum-chemical calculations for A $\rightarrow$ $E_{exc}(A)$
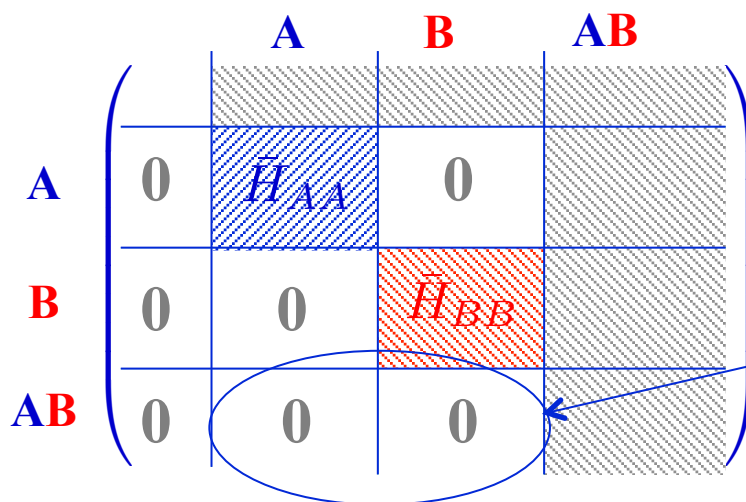
b) one quantum-chemical calculation for A+B $\rightarrow$ $E_{exc}(A)$

excitation energies are referred to as size intensive

Koch, Jensen, Jørgensen, Helgaker, 1990

Size Intensivity of EOM-CC Excitation Energies

block structure of $\overline{\mathrm{H}}$ for supersystem A+B

$$
\begin{array}{cc}
 & \begin{array}{ccc} \mathbf{A} & \mathbf{B} & \mathbf{AB} \end{array} \\
\begin{array}{c} \mathbf{A} \\ \mathbf{B} \\ \mathbf{AB} \end{array} &
\begin{pmatrix}
0 & \bar{H}_{AA} & 0 \\
0 & 0 & \bar{H}_{BB} \\
0 & 0 & 0
\end{pmatrix}
\end{array}
$$

AB-A, AB-B blocks **zero** because of **CC** amplitude equations

implies that

$$\overline{\mathbf{H}}(\mathbf{A})\,\mathbf{r}(\mathbf{A}) = \mathbf{E_{exc}}(\mathbf{A})\,\mathbf{r}(\mathbf{A})$$

$$=> \quad \overline{\mathbf{H}}(\mathbf{AB})\,\mathbf{r}(\mathbf{A}) = \overline{\mathbf{H}}_{\mathbf{AA}}(\mathbf{AB})\,\mathbf{r}(\mathbf{A})$$

$$= (\mathbf{E_{exc}}(\mathbf{A}) + \mathbf{E_{CC}}(\mathbf{B}))\,\mathbf{r}(\mathbf{A})$$

EOM-CC excitation energies are size intensive

III.

Computational Realization of EOM-CC

Solution of EOM-CC Eigenvalue Problem

- **full diagonalization of $\overline{\overline{H}}$ rarely possible and too expensive**

- **iterative determination of a few low-lying eigenvalues sufficient**

    - **Davidson scheme modified for non-Hermitian matrices**

    - cost-determining steps are

<div align="center">

for right side $\qquad \overline{\overline{H}} \cdot \mathbf{r} \; \hat{=} \; \sum_{P} \overline{H}_{QP} \, r_P \quad Q = 0, 1, \ldots$

for left side $\qquad \mathbf{l^T} \cdot \overline{\overline{H}} \; \hat{=} \; \sum_{P} l_P \, \overline{H}_{PQ} \quad Q = 0, 1, \ldots$

</div>

- **EOM-CC is a CI approach with H replaced by $\overline{\overline{H}}$**

Effective EOM-CCSD Hamiltonian

$$\bar{H} \;=\; \exp(-T)\,H\,\exp(T) \qquad T \;=\; T_1 \;+\; T_2$$
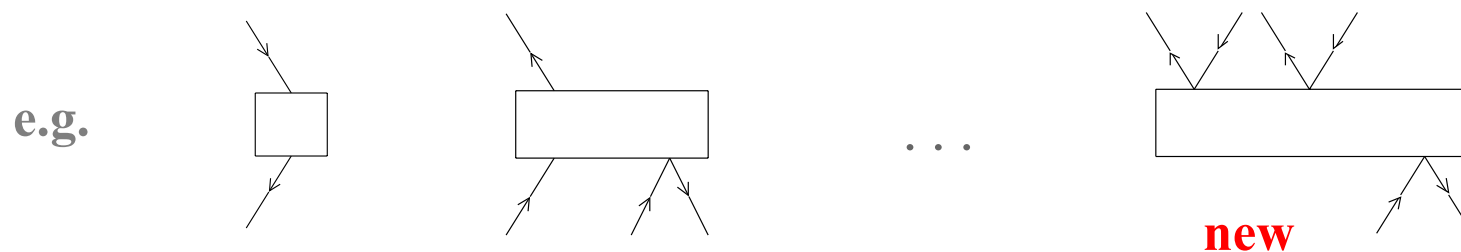
CCSD approximation

$$\bar{H} \;=\; \sum_{p,q} \mathcal{F}_{pq}\{a_p^\dagger a_q\} \;+\; \frac{1}{4}\sum_{p,q,r,s} \mathcal{W}_{pqrs}\{a_p^\dagger a_q^\dagger a_s a_r\} \;+\; \ldots$$

three-body terms

$$\mathcal{F}_{pq} \;=\; f_{qp} \;+\; \ldots \qquad\qquad \mathcal{W}_{pqrs} \;=\; \langle pq||rs\rangle \;+\; \ldots$$

leading terms are **Fock-matrix** elements and **two-electron integrals**

diagrammatic representation

e.g.

new

similar to H, use different symbol

Diagramms for EOM-CCSD Hamiltonian

same rules (i.e., consider open lines, excitation ranks, connectedness)

example:
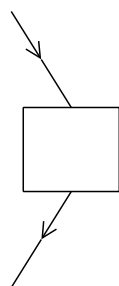
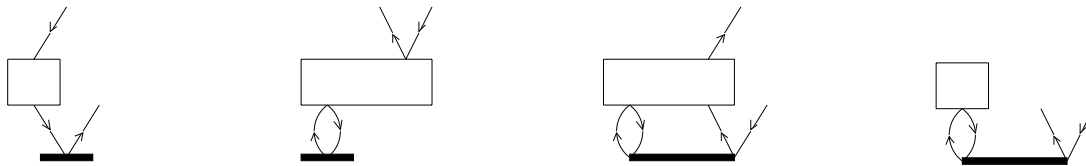**one virtual line above, one virtual line below**

overall excitation level is zero

f_N ~~W_N~~   ~~$(f_N T)_c$~~ $(W_N T_1)_c$ $(W_N T_2)_c$ $\dfrac{1}{2}(W_N T_1^2)_c$

X

$$\mathcal{F}_{ij} \;=\; f_{ai} \;+\; \sum_{m}\sum_{e}\langle im||je\rangle t_m^e \;+\; \frac{1}{2}\sum_{m}\sum_{e,f}\langle im||ef\rangle t_{jm}^{ef} \;+\; \frac{1}{2}\sum_{m}\sum_{e,f}\langle im||ef\rangle t_j^e t_m^f$$

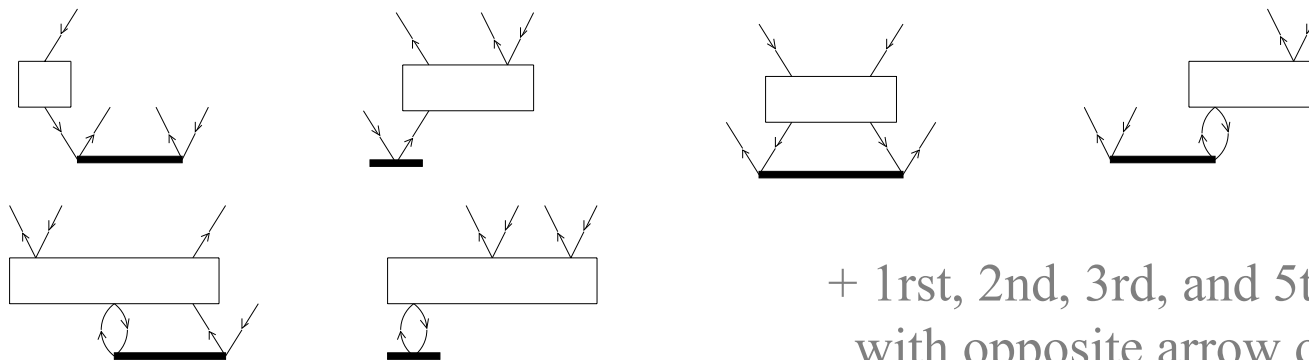**all other terms excluded because of overall excitation level**

Diagrammatic Representation of $\overline{H} \cdot r$

singles
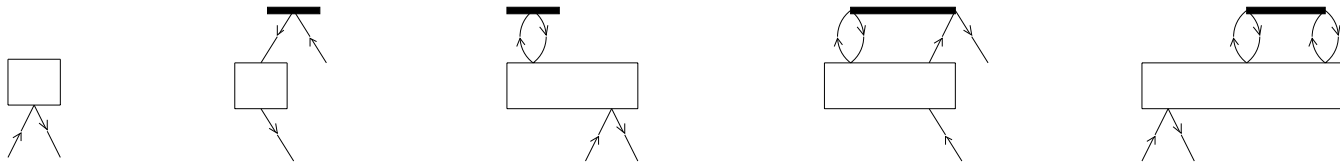

+ 1rst and 3rd diagram with opposite arrow directions

doubles

+ 1rst, 2nd, 3rd, and 5th diagram
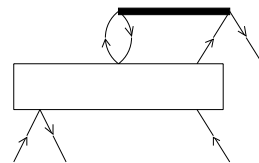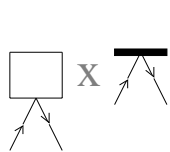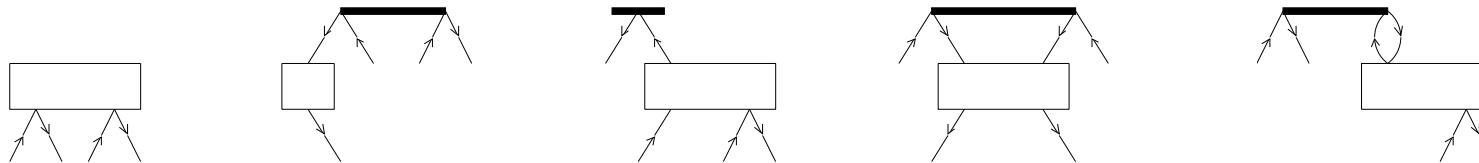with opposite arrow directions

Diagrammatic Representation of $\mathbf{l^T \cdot \bar{H}}$

singles

+ 2rst and 4th diagram with opposite arrow directions

doubles

+ 2nd, 3rd, 4th. and 7th diagram
with opposite arrow directions

Computational Requirements

one- and two-body terms

$$\text{storage} \sim N^4 \qquad\qquad \text{computational cost} \sim N^6$$

all terms are as in CISD

three-body terms

direct evaluation $\qquad$ storage $\sim N^6$ $\qquad$ cost $\sim N^7$ $\qquad$ **????**
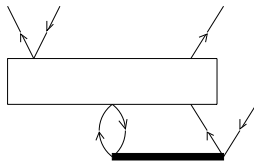
factorization
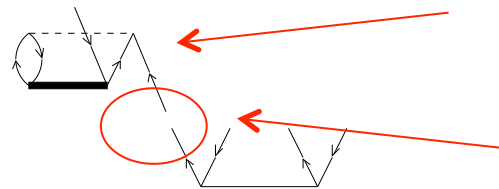
N^5

N^5

storage $\sim N^4$ $\qquad$ cost $\sim N^5$ $\qquad$ **!!!!**

Complex Eigenvalues

general real matrices have

      a) **real** eigenvalues

      b) **complex-conjugated pairs** of eigenvalues

complex eigenvalues usually not a problem

      – **except close to degeneracies (Köhn, Tatji, 2007)**

plausibility argument

$$\begin{pmatrix} a & c \\ d & \tilde{a} \end{pmatrix} \quad \Rightarrow \quad \lambda_{1,2} = \frac{a + \tilde{a}}{2} \pm \sqrt{\frac{(a - \tilde{a})^2}{4} + cd}$$

eigenvalues
of a 2x2 matrix

complex
eigenvalues   if   **small**   **negative**
possible

Standard EOM-CC Approaches

truncation of the cluster operator T and excitation operartor $\mathcal{R}$:

cluster operator	excitation operator	approximation	cost
$T=T_1+T_2$	$\mathcal{R}=\mathcal{R}_0+\mathcal{R}_1+\mathcal{R}_2$	EOM-CCSD	N^6
$T=T_1+T_2+T_3$	$\mathcal{R}=\mathcal{R}_0+\mathcal{R}_1+\mathcal{R}_2+\mathcal{R}_3$	EOM-CCSDT	N^8
$T=T_1+T_2+T_3+T_4$	$\mathcal{R}=\mathcal{R}_0+\mathcal{R}_1+\mathcal{R}_2+\mathcal{R}_3+\mathcal{R}_4$	EOM-CCSDTQ	N^{10}
…		…	…
$T=T_1+T_2+ \ldots +T_N$	$\mathcal{R}=\mathcal{R}_0+\mathcal{R}_1+ \ldots + \mathcal{R}_N$	FCI	

use always same truncation for T and $\mathcal{R}$, otherwise loss of size intensivity

EOM-CC versus CC Linear-Response Theory

linear-response theory
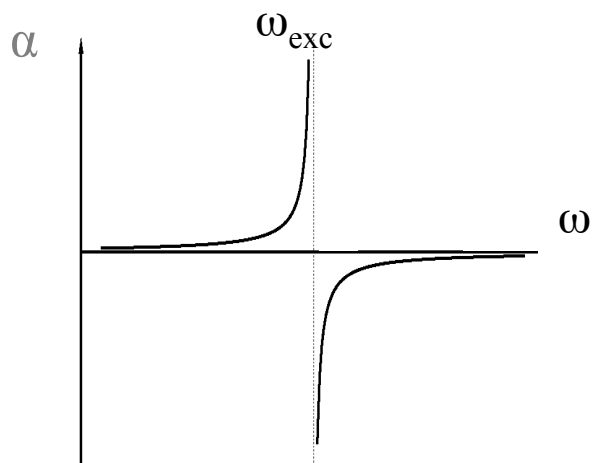
frequency-dependent properties

=> **response equations**

frequency   perturbation

$$\langle \Phi_P | (\bar{H}_N - \omega) T^x(\omega) | 0 \rangle = -\langle \Phi_P | V_x | 0 \rangle$$

response vector

excitation energies : poles of response function => resonances

$$\langle \Phi_P | (\bar{H}_N - \omega_{exc}) \mathcal{R} | 0 \rangle = 0$$

eigenvalue equation for **excitation frequency**

- **same eigenvalue equation as in EOM-CC (except for irrelevant r_0)**

- **conceptional differences, differences in transition moments**

Accuracy of EOM-CC Schemes

singlet excitation energies (in eV) of CH^+

	$^1\Pi$	$^1\Delta$	$1^1\Sigma$	$2^1\Sigma$
CCSD	3.26	7.87	9.10	13.59
CCSDT	3.22	6.99	8.62	13.53
CCSDTQ	3.23	6.95	8.54	13.53
AEL	1.03	2.00	1.96	1.06

approximate excitation level

calculations with 'DZP+diffuse' basis set

Singly and Doubly Excited States in EOM-CCSD

$^1\Pi$ state   ground state $^1\Delta$ state

single excitation

error $\approx 0.1 - 0.3$ eV

double excitation

error $>$ 0.5 eV

easy

difficult

$\mathcal{R}_1 =>$ excitation

$\mathcal{R}_2 =>$ relaxation effects

$\mathcal{R}_2 =>$ excitation

$\mathcal{R}_3$ needed for relaxation effects
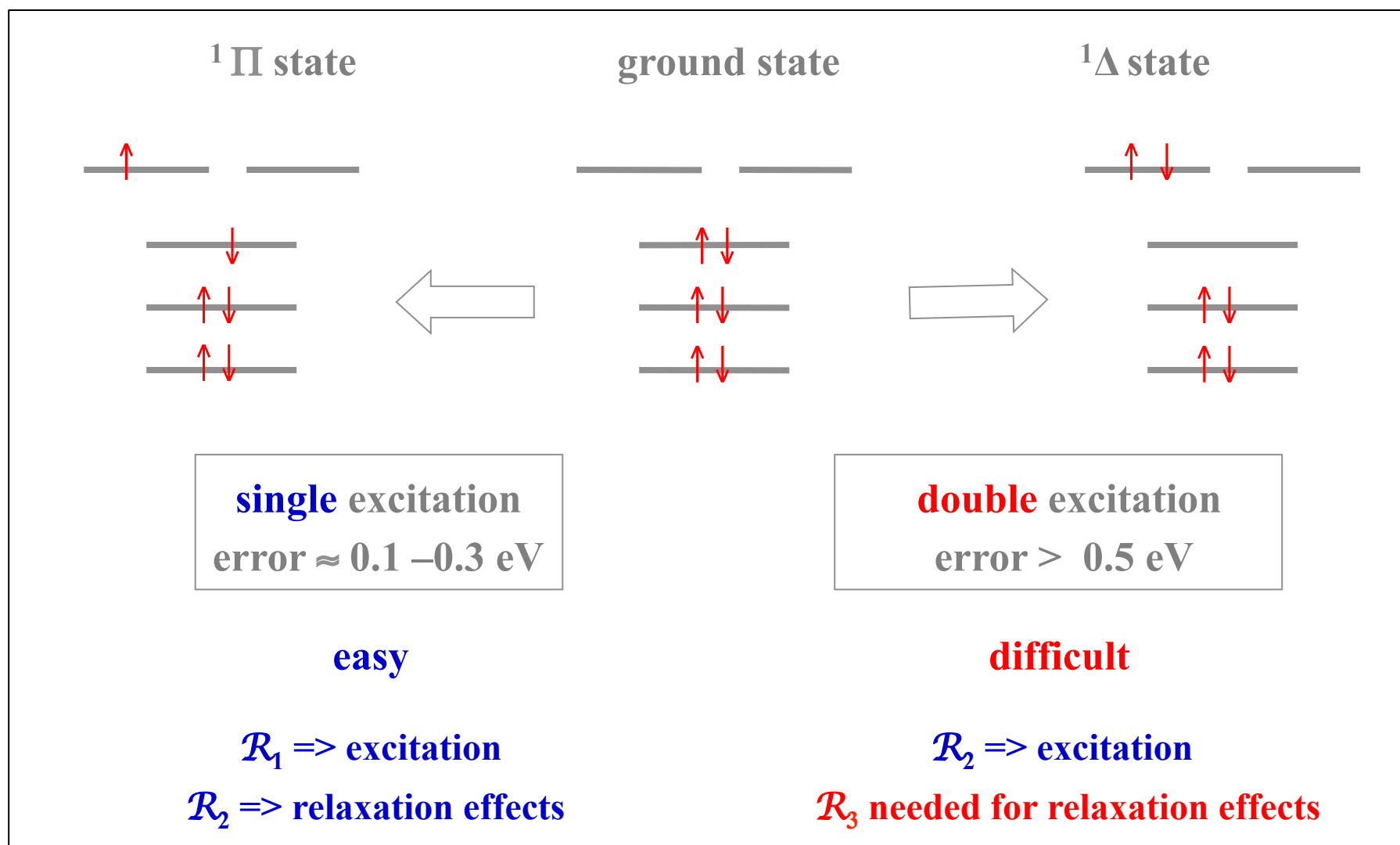
Historical Remarks

– **EOM-CC and CC response theory**

Monkhorst, 1977
Paldus et al., 1978
Nakatsuji, 1978
Emrich, 1981
Mukherjee et al., 1982
Sekino, Bartlett, 1984

– **CCSD linear-response implementation**

Koch et al., 1990

– **EOM-CCSD implementation**

Stanton, Bartlett, 1993

– **EOM-CCSDT implementations**

Kowalski, Piecuch, 2001
Kucharski et al., 2001

– **general EOM-CC implementation**

Hirata et al., 2000 (via FCI)
Hald et al., 2001 (via FCI)
Kállay, Gauss, 2005

III.

EOM-CC Transition Moments
and the Importance of Connectedness

EOM-CC Transition Moments

transition moment between
excited and **ground** state

$$T_{i0} \;=\; \langle \Psi^i_{exc}| \; \mu \; |\Psi_{gs}\rangle$$

in EOM-CC

$$T_{i0}^{EOM} \;=\; \langle 0|\mathcal{L}^i \; \exp(-T) \; \mu \; \exp(T) \; |0\rangle$$

transition moment between
ground and **excited** state

$$T_{0i} \;=\; \langle \Psi_{gs}| \; \mu \; |\Psi^i_{exc}\rangle$$

in EOM-CC

$$T_{0i}^{EOM} \;=\; \langle 0| \; (1+\Lambda) \; \exp(-T) \; \mu \; \exp(T) \; \mathcal{R}^i \; |0\rangle$$

EOM-CC transition moments are different $\qquad T_{i0}^{EOM} \;\neq\; T_{0i}^{EOM}$

physically relevant quantity $\qquad |\mu|^2 \;=\; T_{0i}^{EOM} \; T_{i0}^{EOM} \qquad$ **well defined**

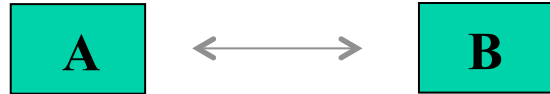# Size Consistency and Extensivity

if

$$E_{AB}^{\text{Method}} = E_{A}^{\text{Method}} + E_{B}^{\text{Method}}$$

a method is size consistent

size extensivity: correct linear scaling with system size

→ **connectedness of equations, ...**

Why is Connectedness important?

A ⟷ B

$r_{AB} \rightarrow \infty$

product of operators

two operators

$$X = X^A + X^B$$

$$Y = Y^A + Y^B$$

$$X\,Y = X^A\,Y^A + X^B\,Y^B$$

$$+ X^A\,Y^B + X^B\,Y^A$$

unwanted, not connected

connected: common indices via contraction(s)

Why is Connectedness important?

A ⟷ B

two operators

$r_{AB} \rightarrow \infty$

$$X = X^A + X^B$$

$$Y = Y^A + Y^B$$

connected: common indices via contraction(s)

commutator of two connected operators is **connected**

$$[X, Y] = [X^A, Y^A] + [X^B, Y^B]$$

$\rightarrow$ **size extensivity ...**

Size Extensivity of CC Theory

CC equations

$$\langle \Phi_P | \, \exp(-T) H \exp(T) \, |0\rangle \; = \; 0$$

BCH formula → commutator expansion
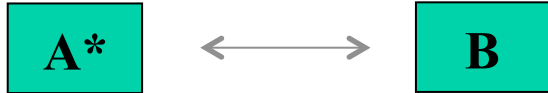
fully connected

→ size extensivity of CC theory

Size Extensivity in EOM-CC Theory

- **energy expression is not connected**

$$E_{exc} = \langle 0| \, \mathcal{L} \, \exp(-T)H\exp(T) \, \mathcal{R} \, |0\rangle$$

- $\mathcal{R}$ and $\mathcal{L}$ are linear parameterization of wavefunction

→ **incorrect multiplicative behaviour of wavefunction**

Multiplicative Behaviour in EOM-CC

A* $\longleftrightarrow$ B

$r_{AB} \rightarrow \infty$

excitation at A

ground state at B

right-hand side wavefunction

$$\mathcal{R}^{A\otimes B} = \mathcal{R}^A \otimes 1^B$$

not a problem

left-hand side wavefunction

$$\mathcal{L}^{A\otimes B} = \mathcal{L}^A \otimes (1+\Lambda)^B$$

truncation is a problem !

$\mathcal{L}$ **is not connected**

to consider in the following:

$\mathcal{R}^A \quad \mathcal{L}^A, \mathcal{L}^{AB}$

EOM-CC Excitation Energies

$$E \ = \ \langle 0| \ \mathcal{L} \exp(-T)(H^A \ + \ H^B) \exp(T) \ \mathcal{R}|0\rangle$$

$$\overline{H}^A + \overline{H}^B$$

$$= \ \langle 0| \ \mathcal{L}^A(\overline{H}^A + \overline{H}^B)\mathcal{R}^A|0\rangle + \langle 0| \ \mathcal{L}^{AB}\overline{H}^B\mathcal{R}^A|0\rangle$$

$$\langle 0|\mathcal{L}^{AB} \ \mathcal{R}^A \ \overline{H}^B|0\rangle$$

vanishes due to CC equations

$$= \ E_{exc}^A \ + \ E_{CC}^B$$

EOM-CC excitation energies are size intensive

EOM-CC Transition Moments

excited state on the left, **ground state** on the right

$$T_{i0}^{EOM} = \langle 0|\mathcal{L}^i \, \exp(-T) \, \mu \, \exp(T) \, |0\rangle$$

$$= \langle 0|\mathcal{L}^i \, \bar{\mu} \, |0\rangle$$

size-consistency analysis

no contribution

$$T_{i0}^{EOM\,AB} = \langle 0|\mathcal{L}^{iA} \, (\bar{\mu}^A + \bar{\mu}^B) \, |0\rangle$$

o.k.

$$+ \langle 0| \, \mathcal{L}^{iAB}(\bar{\mu}^A + \bar{\mu}^B) \, |0\rangle$$

vanishes

EOM-CC Transition Moments

ground state on the left, **excited state** on the right

$$T_{0i}^{EOM} = \langle 0| \ (1+\Lambda) \ \exp(-T) \ \mu \ \exp(T) \ \mathcal{R}^i \ |0\rangle$$

$$= \langle 0| \ (1+\Lambda) \ \bar{\mu} \ \mathcal{R}^i \ |0\rangle$$

size-consistency analysis

no contribution

$$T_{0i}^{EOM \ AB} = \langle 0| \ (1+\Lambda^A) \ (\bar{\mu}^A + \bar{\mu}^B) \ \mathcal{R}^{iA} |0\rangle$$

$$+ \ \langle 0| \ \mathcal{L}^{AB}(\bar{\mu}^A + \bar{\mu}^B) \ \mathcal{R}^{iA} |0\rangle$$

non-vanishing contribution
problem!

no contribution

Connectedness in EOM-CC Theory

problem due to

$$\langle 0|\mathcal{L}\ \overline{X}\ \mathcal{R}|0\rangle$$

$\mathcal{L}$ **not connected**

product not connected

but no problem for CC properties

$$\langle 0|(1\ +\ \Lambda)\ \overline{X}\ |0\rangle$$

not connected

connected

IV.

Approximate Treatment of Higher Excitations

Need for Higher Excitations

higher excitations (triples) important for

high-accuracy prediction of excitation energies

adequate description of doubly excited states

full inclusion of triples via EOM-CCSDT too expensive

=> iterative approximations to EOM-CCSDT

=> CCn hierarchy

=> perturbative corrections on top of EOM-CCSD

Iterative Approximations to EOM-CCSDT

main idea

$$\mathcal{R} = \mathcal{R}_0 + \mathcal{R}_1 + \mathcal{R}_2 + \mathcal{R}_3$$

plus approximations in $\bar{\bar{H}}$ consistent with CCSDT-n

define

$$\left(\bar{H}_{\text{CCSDT-n}}\right)_{IJ} \equiv \frac{\partial}{\partial t_J} \langle \Phi_I | (H \exp(T))_{c,\text{CCSDT-n}} | 0 \rangle$$

CCSDT-n amplitude equation

− **consistent with Λ equations for gradients and with CC-LR theory**

− **EOM-CC scheme with O(N^7) cost and no storage of triples**

=> **EOM-CCSDT-n, n=1,2,3**

Watts, Bartlett (1995,1997)

Accuracy of EOM-CCSDT-3

singlet excitation energies (in eV) of CH^+

	$^1\Pi$	$^1\Delta$	$1\,^1\Sigma$
CCSD	3.26	7.87	9.10
CCSDT-3	3.24	7.27	8.78
CCSDT	3.22	6.99	8.62
AEL	1.03	2.00	1.96

approximate excitation level

calculations with 'DZP+diffuse' basis set

Accuracy of EOM-CCSDT-3

singlet excitation energies (in eV) of CH^+

deviations from CCSDTQ

	$^1\Pi$	$^1\Delta$	$1^1\Sigma$
CCSD	0.03	0.95	0.56
CCSDT-3	0.01	0.32	0.24
CCSDT	-0.01	0.04	0.08

improved treatment of doubly excited states

accuracy of doubly excited states in EOM-CCSDT-3 similar
to those (0.1-0.3 eV) for singly excited states in EOM-CCSD

CCn Hierarchy

- iterative approximations usually based on standard PT arguments

  i.e., T_2 first order, T_1 second order, ...

- response theory/excitation energy not consistent with standard PT

  e.g., for a singly excited state, $\mathcal{R}_1$ zeroth order !!

  => CCn hierarchy with n=2,3,...

  (treat single excitations as zeroth order)

CC2: approximation to CCSD, widely used for „cheap" excitation energies

CC3: approximation to CCSDT, economical triples treatment

Jørgensen and co-workers, 1995

Accuracy of EOM-CC3

singlet excitation energies (in eV) of CH^+

deviations from CCSDTQ

	$^1\Pi$	$^1\Delta$	$1^1\Sigma$
CCSD	0.03	0.95	0.56
CCSDT-3	0.01	0.32	0.24
CC3	0.01	0.31	0.24
CCSDT	-0.01	0.04	0.08

similar performance of CC3 and CCSDT-3

Perturbative Triples to EOM-CCSD

idea

$$\mathcal{R}_{ijk}^{abc} = \frac{\langle \Phi_{ijk}^{abc} | \, \bar{H} \, (\mathcal{R}_1 + \mathcal{R}_2 \, |0\rangle}{D_{ijk}^{abc} \, + \, \Delta E_{exc}^{CCSD}}$$

lowest-order correction to $\mathcal{R}_3$

denominator

$$\Delta E \, = \, \langle 0| \, (\mathcal{L}_1 + \mathcal{L}_2) \, \bar{H} \, \mathcal{R}_3 \, |0\rangle$$

energy correction

issues:

approximations for denominator

typically via orbital-energy differences

approximations for $\bar{H}$

as in CCSDT-1, CCSDT-3, CC3

EOM-CCSD(T)   **derives from CCSDT-1**

EOM-CCSD(T̃)   **derives from CCSDT-3**

Watts, Bartlett, 1995, 1997

see also CCSDR(3) from CC-LR, Christiansen, Koch, Jørgensen (1996)

Accuracy of Non-Iterative Triples

singlet excitation energies (in eV) of CH^+

	$^1\Pi$	$^1\Delta$	$1^1\Sigma$
CCSD	3.26	7.89	9.11
CCSD(T)	3.24	7.25	8.75
CCSD($\tilde{T}$)	3.22	7.24	8.75
CCSDT-3	3.24	7.28	8.78

similar performance as CCSDT-3

cost-efficient treatment of triples

(unfortunately) no commonly accepted standard

V.

Analytic Derivatives in EOM-CC Theory

EOM-CC Lagrangian

EOM-CC is bivariational wrt to $\mathcal{R}$ and $\mathcal{L}$

but EOM-CC is not variational wrt to T

=> EOM-CC Lagrangian

biorthonormality

$$L_{EOM-CC} = \langle 0|\mathcal{L}\exp(-T)H\exp(T)\mathcal{R}|0\rangle - \varepsilon\,(\langle 0|\mathcal{L}\mathcal{R}|0\rangle - 1)$$

EOM-CC energy

$$+ \sum_I \mathcal{Z}_I\,\langle\Phi_I|\exp(-T)H\exp(T)|0\rangle$$

Lagrange multipliers

CC equations as constraints

for simplicity orbital relaxation is ignored

Stationarity Conditions

wrt to $\mathcal{R}$- and $\mathcal{L}$-amplitudes

      => EOM-CC eigenvalue equations with $\varepsilon = E_{EOM\text{-}CC}$

wrt to $\mathcal{Z}$-amplitudes   **=> CC equations**

wrt to t-amplitudes
$$\frac{\partial L_{EOM\text{-}CC}}{\partial t_I} = 0$$

$$\Rightarrow \quad 0 = \langle 0 | \mathcal{L} \, [\bar{H}, \tau_I] \, \mathcal{R} | 0 \rangle \; + \; \langle 0 | \mathcal{Z} \, [\bar{H}, \tau_I] \, | 0 \rangle$$

linear equations for $\mathcal{Z}$
$$\mathcal{Z} = \sum_I \mathcal{Z}_I \, \tau_I$$

stationarity => (2n+1) rule for T-, $\mathcal{R}$- and (2n+2) for $\mathcal{L}$- and $\mathcal{Z}$-amplitudes

$\mathcal{Z}$-Equations in EOM-CC

$$\langle 0| \, \mathcal{L} \, [\bar{H}, \tau_I] \, \mathcal{R} \, |0\rangle \; + \; \langle 0| \, \mathcal{Z} \, [\bar{H}, \tau_I] \, |0\rangle \; = \; 0$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{\langle 0| \, \Xi \, |\Phi_I\rangle}$$

$$\Rightarrow \qquad \langle 0| \, \Xi \, |\Phi_I\rangle \; + \; \langle 0| \, \mathcal{Z} \, (\bar{H} \; - \; E_{CC}) \, |\Phi_I\rangle \; = \; 0$$

similar to Λ equations for CC ground state

diagrammatic representation of Ξ

(e.g., Ξ_1, two open lines pointing downwards, at least one of them connected to $\bar{H}$)

$$\Xi_1 \quad \hat{=} \qquad \Box \quad \mathbf{x} \quad \left(\; + \; \right) \qquad + \qquad \qquad + \quad \dots$$

$$= 1$$

disconnected
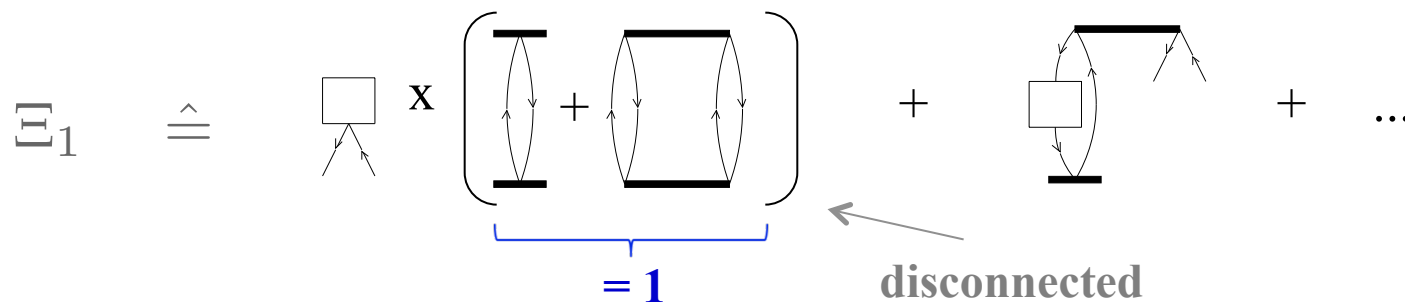
Implementation of EOM-CC Gradients

- solve CC equations
- solve eigenvalue equation for $\mathcal{R}$

- **solve linear equation for $\mathcal{L}$**
- **solve linear equation for $\mathcal{Z}$**
- **compute density matrices and gradient**

cost about twice of EOM-CC energy computation

historical remarks:

Stanton (theory) 1993; Stanton and Gauss (CCSD implementation) 1994;
Kállay and Gauss (general CC implementation) 2004

Accuracy of EOM-CC Geometries

excited singlet states of CH$^+$, distances in Å

	$^1\Pi$	$^1\Delta$	$1^1\Sigma$
CCSD	1.2409	1.1953	1.2491
CCSDT	1.2511	1.2163	1.2780
CCSDTQ	1.2517	1.2191	1.2758
AEL	1.03	2.00	1.96

approximate excitation level

calculations with 'DZP+diffuse' basis set

VI.

EOM-CC for IPs, EAs, ...

Ionization and Electron Attachment
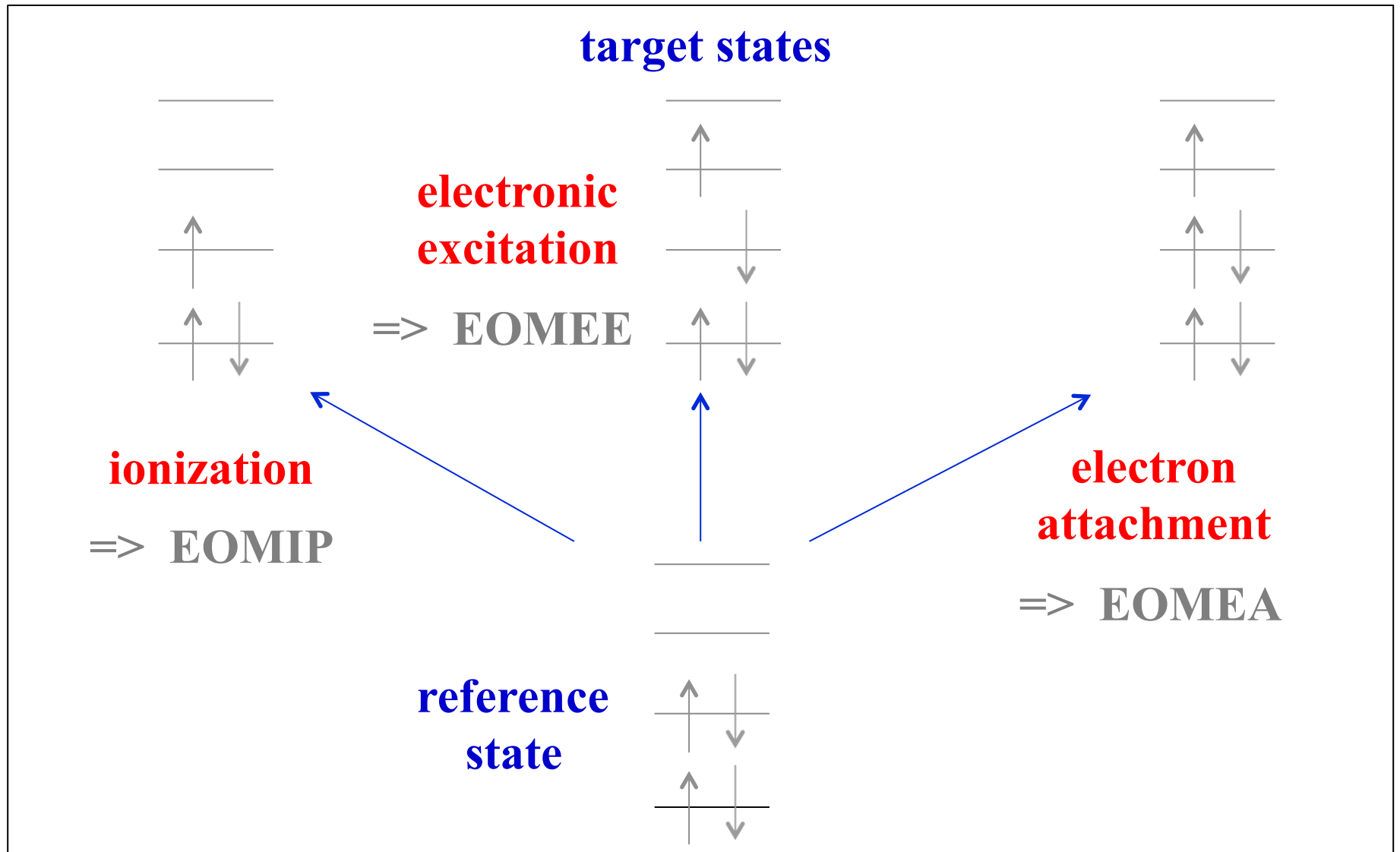
EOMIP-CC Ansatz
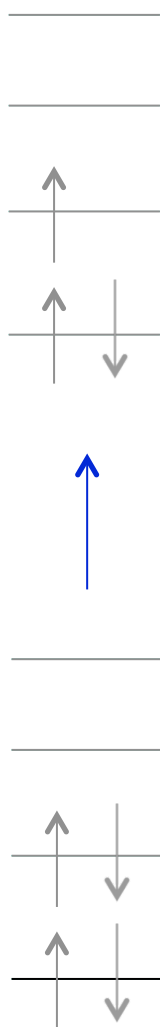
wavefunction for ionized state

$$|\Psi_{ion}\rangle \;=\; \mathcal{R}\,|\Psi_{CC}\rangle$$

ionization operator

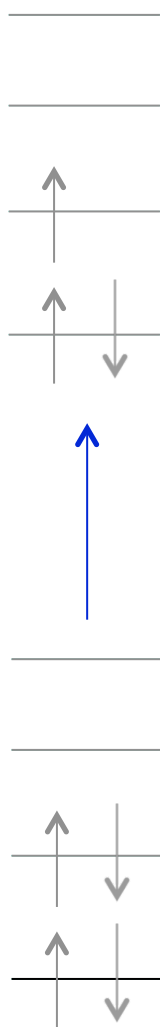$$\mathcal{R} \;=\; \mathcal{R}_1 \;+\; \mathcal{R}_2 \;+\; \ldots$$

$$\mathcal{R}_1 \;=\; \sum_i r_i\, a_i$$

$$\mathcal{R}_2 \;=\; \frac{1}{2}\sum_{i,j}\sum_a r_{ij}^a\, a_a^\dagger a_i a_j$$

$$\ldots$$

diagrammatic representation

EOMIP-CC Equations

usual EOM procedure

$$\bar{H}\ \mathcal{R}\ |0\rangle\ =\ E_{ion}\ \mathcal{R}\ |0\rangle$$

or

$$\bar{H}_N\ \mathcal{R}\ |0\rangle\ =\ \Delta E_{ion}\ \mathcal{R}\ |0\rangle$$

projection on ionized states (e.g., CCSD: Φ_i, Φ_{ij}^a)

$$\overline{\mathbf{H}}\ \mathbf{r}\ =\ E_{ion}\ \mathbf{r}$$

initial work by Mukherjee and co-workers, 1979;
Mattie and Bartlett, 1994; Stanton and Gauss, 1994

equivalent to the (0,1) sector of Fock-space CC (Lindgren, 1979)
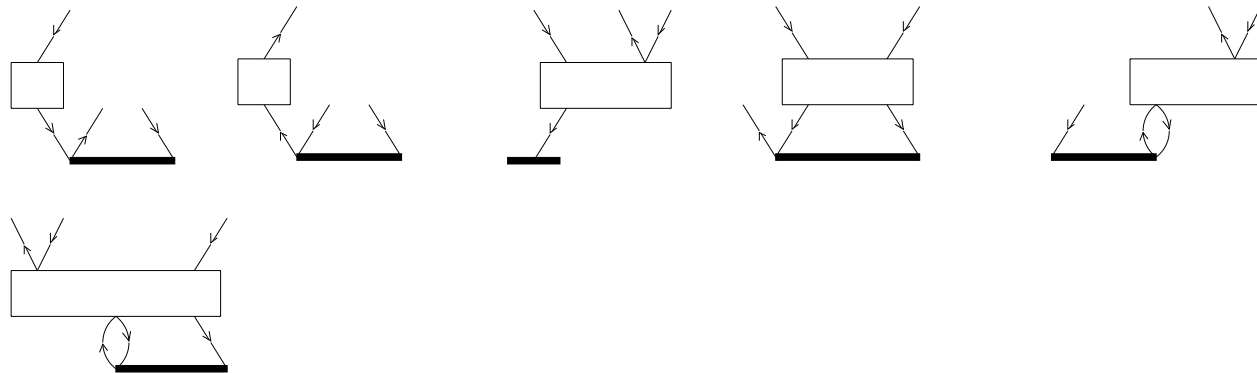and CC Green's function approach (Nooijen and Snijders, 1993)

EOMIP-CCSD Eigenvalue Problem

- **solution of the eigenvalue problem using the Davidson procedure**

- **diagrammatic representation of $\bar{H} \cdot r$ contraction**

singles
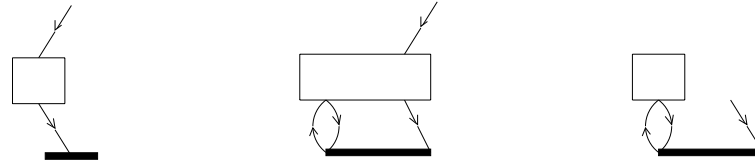
doubles

- **computational cost of EOMIP-CCSD step of $O(N^5)$**
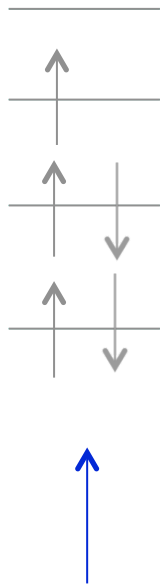
- **left eigenvalue problem is treated similarly**

Accuracy of EOMIP-CC Schemes

ionization potentials (in eV) of N_2

	$^2\Sigma^+_u$	$^2\Pi_u$	$^2\Sigma^+_g$
CCSD	18.47	16.93	15.18
CCSDT	18.36	16.64	15.10
CCSDTQ	18.28	16.63	15.06
FCI	18.28	16.63	15.06

frozen-core calculations with cc-pVDZ basis set

EOMEA-CC Ansatz

wavefunction for electron-attached state

$$|\Psi_{ea}\rangle = \mathcal{R}\,|\Psi_{CC}\rangle$$

attachment operator
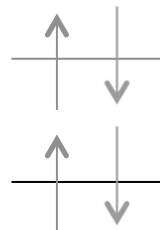
$$\mathcal{R} = \mathcal{R}_1 + \mathcal{R}_2 + \dots$$

$$\mathcal{R}_1 = \sum_a r^a\, a_a^\dagger$$

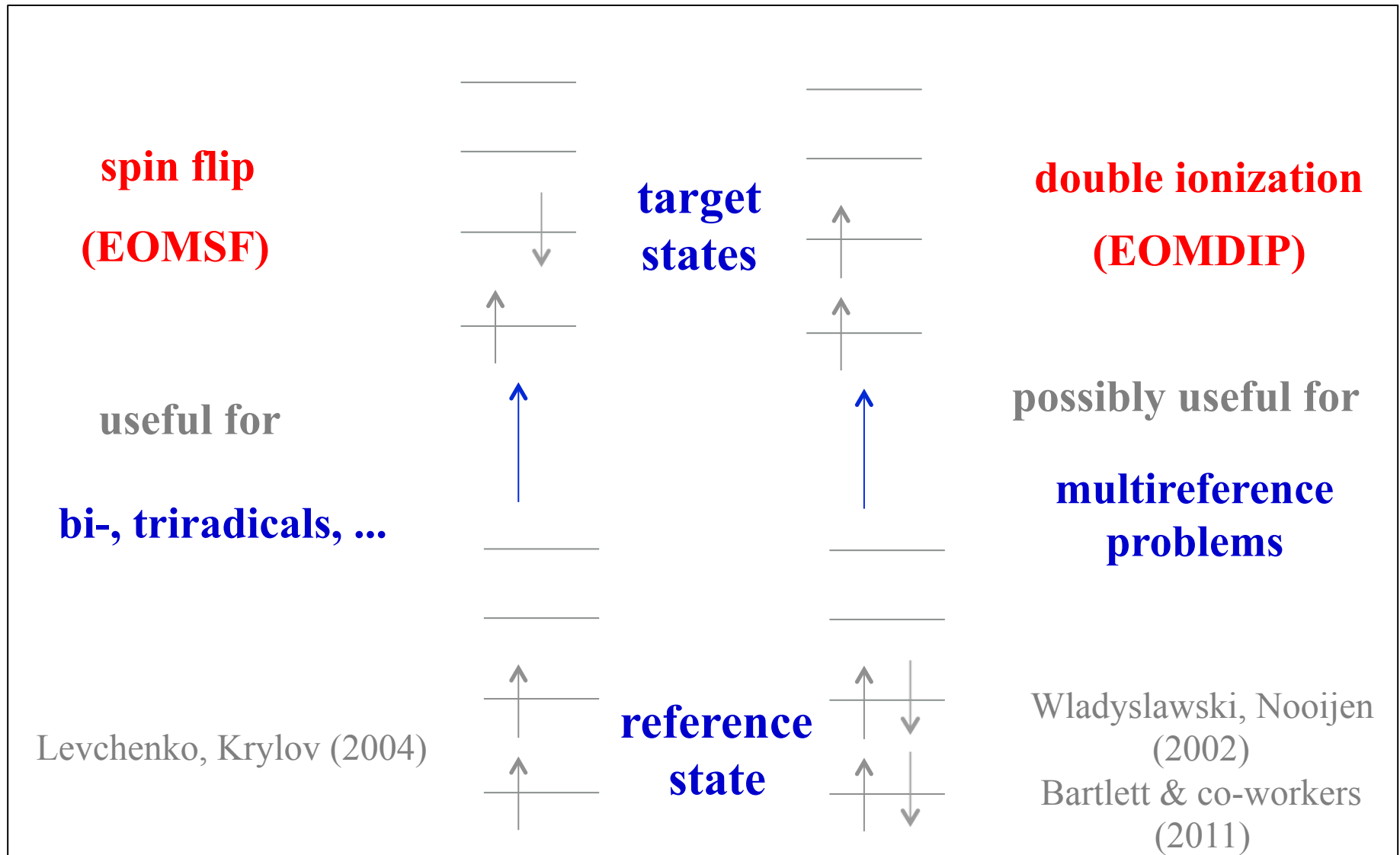$$\mathcal{R}_2 = \frac{1}{2}\sum_i\sum_{a,b} r_i^{ab}\, a_a^\dagger a_i a_b^\dagger$$

$$\dots$$

very similar to EOMIP-CC

cost for EOMEA-CCSD is O(N^5)

Nooijen, Bartlett (1996); equivalent to the (1,0) sector of Fock-space CC

Other Flavours of EOM-CC

spin flip (EOMSF)

double ionization (EOMDIP)

target states

reference state

useful for

bi-, triradicals, ...

possibly useful for

multireference problems

Levchenko, Krylov (2004)

Wladyslawski, Nooijen (2002)

Bartlett & co-workers (2011)

Summary and Outlook

- **EOM-CC** enables the treatment of **other states** than the ground state

- **EOMEE-CC** standard for computation of **excitation energies**

- **EOMIP-CC** option for **open-shell** systems

- **EOMSF-CC, ...** option for (some) **multireference** systems

- close relationship to **CC linear-response theory**

not discussed

- **higher-order EOM-CC properties and transition moments**

- **simulation of spectra based on EOM-CC computations**

- **...**