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Laboratoire de Chimie et Physique Quantiques

Exploiting the seniority number in calculations of molecular excited states

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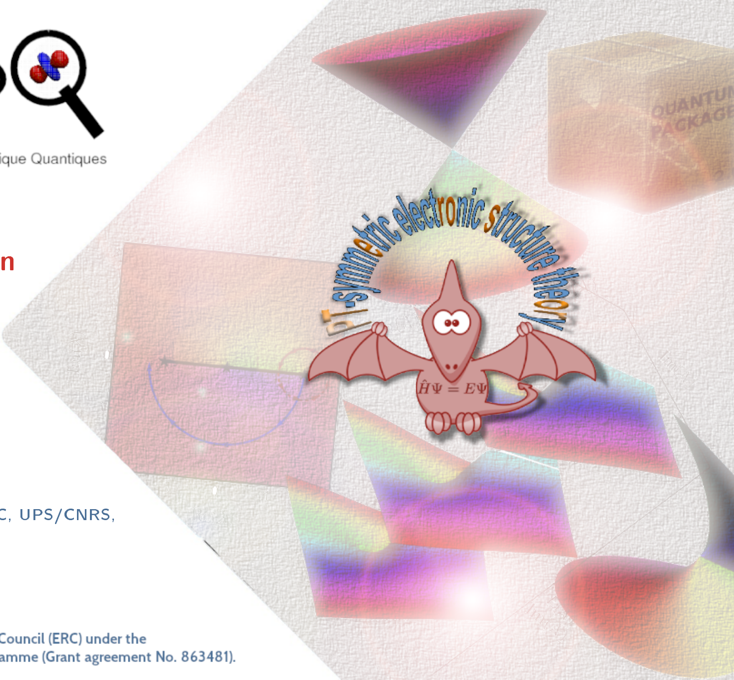
https://lcpq.github.io/pterosor



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Part 1: Targeting doubly-excited states with coupled cluster

Coupled-cluster

- One of the most successful approaches for the description of chemical systems.
- CC ansatz (exponential excitation operator of a single-determinant reference):

$$|\Psi\rangle = e^{\hat{T}}\,|\Phi\rangle\,, \tag{1}$$

- The cluster operator involves singles, doubles... excitations:

$$\hat{T}_n = \frac{1}{(n!)^2} \sum_{ij\ldots} \sum_{ab\ldots} t_{ij\ldots}^{ab\ldots} c_a^\dagger c_b^\dagger \ldots c_j c_i\,, \tag{2}$$

- The CC equations are solved by projection:

$$E_{\mathrm{CC}} = \langle \Phi | \bar{H} | \Phi \rangle \tag{3a}$$

$$0 = \langle \Phi_i^a | \bar{H} | \Phi \rangle\,, \tag{3b}$$

- where the effective (non-Hermitian) similarity-transformed Hamiltonian is

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}\,. \tag{4}$$

Excited states with coupled-cluster methods

Approach 1:

- Equation-of-motion formalism, starting from a ground-state coupled cluster wave function
- Well-defined, black box, established approach, though biased towards the ground state

Approach 2:

- Solve ground-state coupled cluster equations for higher-lying roots or starting from state-specific reference wave functions
- Demands much more care: choice of reference, unphysical solutions, algorithms. In principle more balanced and possibly cheaper

Paired coupled cluster doubles (pCCD)

pCCD: excitation manifold restricted to the paired double excitations

- pCCD and doubly-occupied configuration interaction (DOCI) ground state energies are very close (pCCD has polynomial scaling, DOCI has exponential)
- pCCD does a good job in recovering static correlation
- Minimal CC model for describing doubly-excited states

Goals

1. How to target excited states with pCCD?

System: helium atom

2. How do pCCD and DOCI compare for excited states?

System: symmetric stretching of the linear H_4 molecule

3. Can pCCD describe doubly-excited states without EOM?

System: larger molecules

F. Kossoski, A. Marie, A. Scemama, M. Caffarel, P.-F. Loos, J. Chem. Theory Comput. 17, 4756 (2021)

pCCD

- Usual exponential ansatz

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle$$

- the excitation operator is

$$\hat{T} = \sum_{ia} t_i^a P_a^\dagger P_i$$

- the singlet paired operators are

$$P_q^\dagger = c_{q\alpha}^\dagger c_{q\beta}^\dagger$$

- Substitution into the Schroedinger equation leads to

$$E = \langle\Phi|e^{-\hat{T}}He^{\hat{T}}|\Phi\rangle$$

$$0 = \langle\Phi|P_i^\dagger P_a e^{-\hat{T}}He^{\hat{T}}|\Phi\rangle$$

pCCD t-amplitudes

- Equation for the energy

$$E = \langle \Phi | H | \Phi \rangle + \sum_{ia} t_i^a v_{aa}^{ii}$$

- $k = n_O \times n_V$ polynomial equations for the t-amplitudes

$$\begin{aligned} r_i^a = & v_{ii}^{aa} + 2 \left(f_a^a - f_i^i - \sum_j v_{aa}^{jj} t_j^a - \sum_b v_{bb}^{ii} t_i^b \right) t_i^a \\ & - 2 \left(2 v_{ia}^{ia} - v_{ai}^{ia} - v_{aa}^{ii} t_i^a \right) t_i^a \\ & + \sum_b v_{bb}^{aa} t_i^b + \sum_j v_{ii}^{jj} t_j^a + \sum_{jb} v_{bb}^{jj} t_j^a t_i^b = 0 \end{aligned}$$

f_q^p is an element of the Fock operator and
$v_{rs}^{pq} = \langle \phi_p \phi_q | V_{ee} | \phi_r \phi_s \rangle$ is a two-electron integral.

pCCD z-amplitudes

- We introduce the de-excitation operator

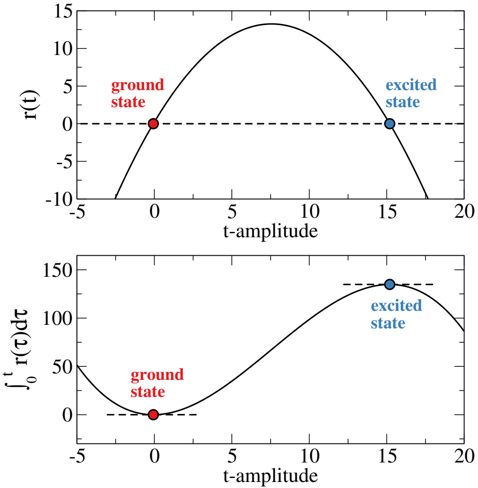
$$\hat{Z} = \sum_{ia} z_a^i P_i^\dagger P_a$$

- $\tilde{E} = \langle \Phi | (1 + \hat{Z}) e^{-\hat{T}} H e^{\hat{T}} | \Phi \rangle$ leads to k linear equations for the z-amplitudes

$$\begin{aligned} 0 = & v_{aa}^{ii} + 2 \left(f_a^a - f_i^i - \sum_j v_{aa}^{jj} t_j^a - \sum_b v_{bb}^{ii} t_i^b \right) z_a^i \\ & - 2 \left(2 v_{ia}^{ia} - v_{ai}^{ai} - v_{aa}^{ii} t_i^a \right) z_a^i - 2 v_{aa}^{ii} \left(\sum_j z_a^j t_j^a + \sum_b z_b^i t_i^b \right) \\ & + \sum_b v_{aa}^{bb} z_b^i + \sum_j v_{jj}^{ii} z_a^j + \sum_{jb} t_j^b \left(v_{bb}^{ii} z_a^j + v_{aa}^{jj} z_b^i \right) \end{aligned}$$

- $\partial \tilde{E} / \partial z_a^i = 0 \rightarrow$ eq. for the t-amplitudes; $\partial \tilde{E} / \partial t_i^a = 0 \rightarrow$ eq. for the z-amplitudes

He, 6-31G



- Residual equation and its integral, as a function of the single *t*-amplitude
- Usual algorithm cannot find the excited state solution
- Information about the curvature is required: Jacobian

Solving the CC equations

- Newton-Raphson algorithm:

$$t_i^a \leftarrow t_i^a - \sum_{jb} (\boldsymbol{J})^{-1}_{ia,jb} r_j^b$$

- For the ground state, a constant diagonal approximation is fine,

$$J_{ia,ia} = \frac{\partial r_i^a}{\partial t_i^a} \approx 2(f_a^a - f_i^i)$$

- But for excited states, the Jacobian is required. The (t-dependent) diagonal Jacobian usually works,

$$J_{ia,ia} = 2f_a^a - 2f_i^i - 4v_{ia}^{ia} + 2v_{ai}^{ia} + v_{aa}^{aa} + v_{ii}^{ii} - \sum_j v_{jj}^{aa} t_j^a - \sum_b v_{ii}^{bb} t_i^b$$

- Extra computational burden lies in memory, not so much in time.

Goals

1. How to target excited states with pCCD?

System: helium atom

Tailored algorithms are needed.

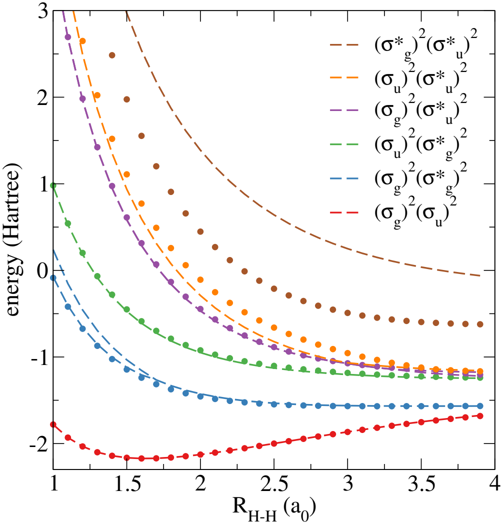
2. How do pCCD and DOCI compare for excited states?

System: symmetric stretching of the linear H_4 molecule

3. Can pCCD describe doubly-excited states without EOM?

System: larger molecules

H_4, STO-6G



- HF-pCCD (dashed) vs. DOCI(HF) (points)
- Results match for ground state, but not for excited states
- Two solutions for first and third doubly-excited states

Goals

1. How to target excited states with pCCD?

System: helium atom

Tailored algorithms are needed.

2. How do pCCD and DOCI compare for excited states?

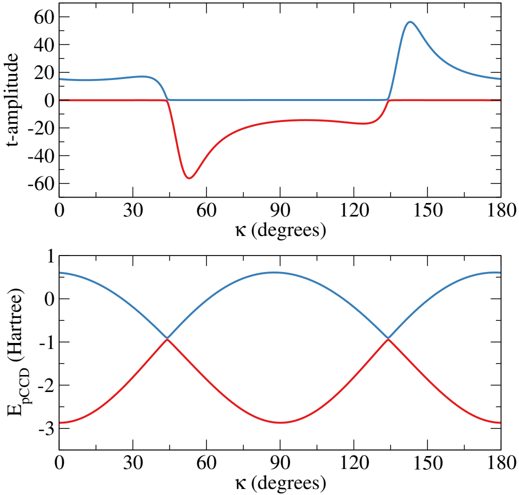
System: symmetric stretching of the linear H_4 molecule

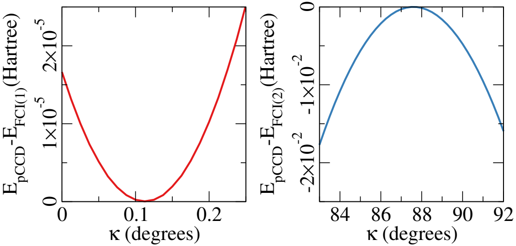
Very badly.

3. Can pCCD describe doubly-excited states without EOM?

System: larger molecules

He, 6-31G, orbital optimization





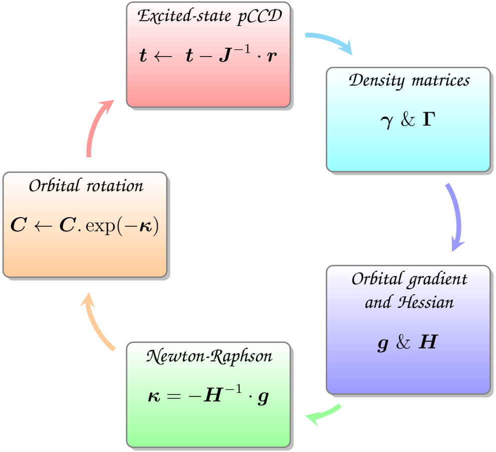
- Each state is variationally optimized with different references:
- Ground state: $\kappa = 0.12$ degrees
- Doubly-excited state: $\kappa = 87.8$ degrees

Orbital optimization

- The orbital rotations are introduced by $e^{\hat{\kappa}}$, where $\hat{\kappa}$ encompasses all unique rotations,
$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} (c^\dagger_{p\uparrow} c_{q\uparrow} - c^\dagger_{q\uparrow} c_{p\uparrow} + c^\dagger_{p\downarrow} c_{q\downarrow} - c^\dagger_{q\downarrow} c_{p\downarrow}).$$
- The energy can be expressed as a functional of the orbital rotation parameters κ_{pq},
$$\tilde{E}(\hat{\kappa}) = \langle \Phi | (1 + \hat{Z}) e^{-\hat{T}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{T}} | \Phi \rangle.$$
- Stationary points with respect to κ_{pq} can be found with the Newton-Raphson method. The energy is expanded to second order around $\kappa = \mathbf{0}$,
$$\tilde{E}(\boldsymbol{\kappa}) \approx \tilde{E}(\mathbf{0}) + \boldsymbol{g} \cdot \boldsymbol{\kappa} + \frac{1}{2} \boldsymbol{\kappa}^\dagger \cdot \boldsymbol{H} \cdot \boldsymbol{\kappa},$$
- and the orbital rotation vector is taken as
$$\boldsymbol{\kappa} = -\boldsymbol{H}^{-1} \cdot \boldsymbol{g}.$$

How to run oo-pCCD?

Orbital-optimized pCCD for excited states



Excited-state pCCD

$$\boldsymbol{t} \leftarrow \ \boldsymbol{t} - \boldsymbol{J}^{-1} \cdot \boldsymbol{r}$$

Density matrices

$$\boldsymbol{\gamma} \ \& \ \boldsymbol{\Gamma}$$

Orbital gradient and Hessian

$$\boldsymbol{g} \ \& \ \boldsymbol{H}$$

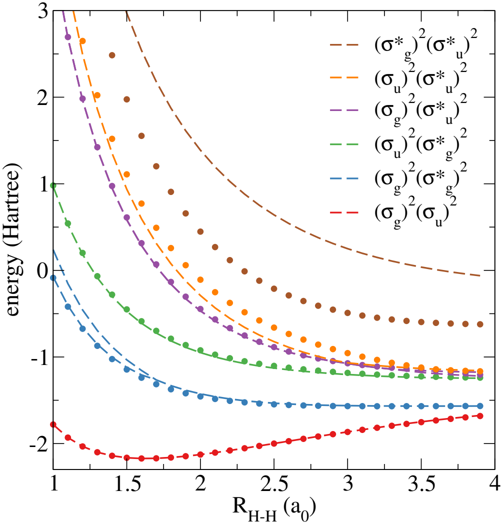
Newton-Raphson

$$\boldsymbol{\kappa} = -\boldsymbol{H}^{-1} \cdot \boldsymbol{g}$$

Orbital rotation

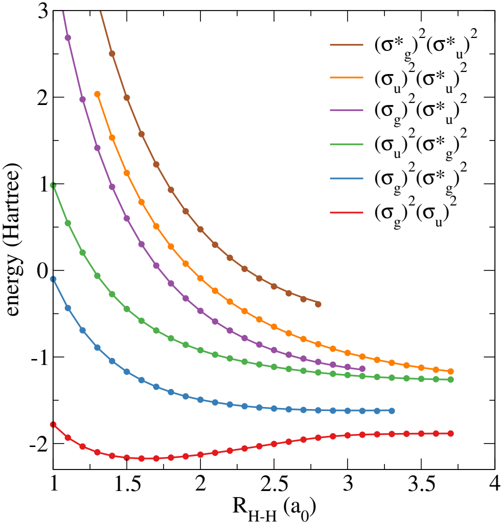
$$\boldsymbol{C} \leftarrow \boldsymbol{C}.\exp(-\boldsymbol{\kappa})$$

H_4, STO-6G



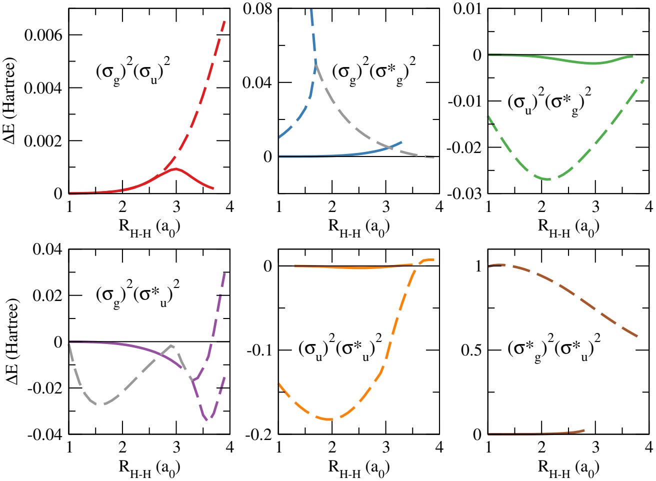
$(\sigma^*_g)^2(\sigma^*_u)^2$
$(\sigma_u)^2(\sigma^*_u)^2$
$(\sigma_g)^2(\sigma^*_u)^2$
$(\sigma_u)^2(\sigma^*_g)^2$
$(\sigma_g)^2(\sigma^*_g)^2$
$(\sigma_g)^2(\sigma_u)^2$
energy (Hartree)
3
2
1
0
-1
-2
1
1.5
2
2.5
3
3.5
4
$R_{H\text{-}H}$ (a_0)

H_4, STO-6G



- oo-pCCD (solid) vs. DOCI(oo-pCCD) (points)
- Results match for all states
- One single and real solution for each state
- In HF-pCCD, important higher-order connected excitations are missing (specially the connected quadruples)
- In oo-pCCD, they are mostly recovered with the optimized reference wave function
- Importance of orbital relaxation!

H_4, STO-6G



- Differences between pCCD and DOCI energies, computed with either HF (dashed) or state specific oo (solid)
- Massive improvement with orbital optimization
- DOCI and oo-pCCD do provide comparable excited states energies, as long as the references are suitable

Goals

1. How to target excited states with pCCD?

System: helium atom

Tailored algorithms are needed.

2. How do pCCD and DOCI compare for excited states?

System: symmetric stretching of the linear H_4 molecule

~~Very badly.~~

Very well, but only at the oo-pCCD level.

3. Can pCCD describe doubly-excited states without EOM?

System: larger molecules

Larger molecules

- Set of 5 molecules: CH^+, BH, nitroxyl, nitrosomethane, and formaldehyde
- 6-31+G(d) basis set, frozen core

Larger molecules

Vertical Excitation Energies (ΔE, in eV) for the First Doubly-Excited States

molecule	method	ΔE
CH^+	HF-pCCD	7.90
	Δoo-pCCD	8.32
	FCI	8.51
	EOM-CCSDTQ	8.51
	EOM-CCSDT	8.58
	CC3	8.74

molecule	method	ΔE
BH	HF-pCCD	10.83
	Δoo-pCCD	7.35
	FCI	7.11
	EOM-CCSDTQ	7.11
	EOM-CCSDT	7.14
	CC3	7.29

Larger molecules

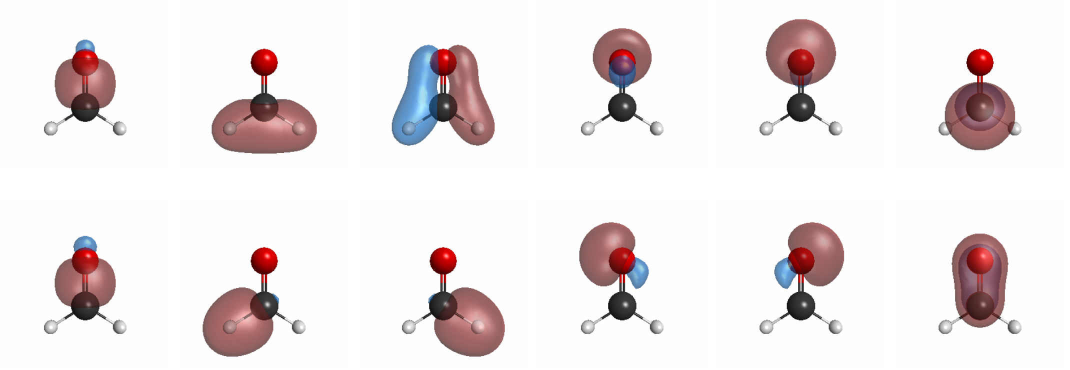
Vertical Excitation Energies (ΔE, in eV) for the First Doubly-Excited States

molecule	method	ΔE
HNO	HF-pCCD	5.53
	Δoo-pCCD	4.49
	FCI [a]	4.51
	EOM-CCSDTQ [a]	4.54
	EOM-CCSDT [a]	4.81
	CC3 [a]	5.28

molecule	method	ΔE
H_3C-NO	Δoo-pCCD	4.66
	FCI [a]	4.86
	EOM-CCSDT [a]	5.26
	CC3 [a]	5.73
$H_2C=O$	Δoo-pCCD	11.26
	FCI [a]	10.86
	EOM-CCSDTQ [a]	10.87
	EOM-CCSDT [a]	11.10
	CC3 [a]	11.49

[a] J. Chem. Theory Comput. 15, 1939 (2019)

Larger molecules

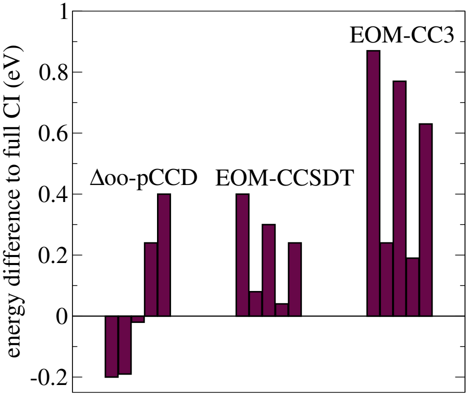


Variationally optimized orbitals at the pCCD level, for the ground (bottom) and the doubly-excited (top) states of formaldehyde.

Larger molecules

Root-mean square error (RMSE), maximum absolute error (MAE), and maximum signed error (MSE), with respect to FCI results.

method	RMSE	MAE	MSE
Δoo-pCCD	0.24	0.21	0.05
EOM-CCSDT	0.25	0.21	0.21
CC3	0.61	0.54	0.54



- Δoo-pCCD $\sim$ EOM-CCSDT $>$ CC3
- Alternative method for targeting doubly-excited states
- Correlations effects are more balanced in Δoo-pCCD

Goals

1. How to target excited states with pCCD?

System: helium atom

Tailored algorithms are needed.

2. How do pCCD and DOCI compare for excited states?

System: symmetric stretching of the linear H_4 molecule

Very well, but only at the oo-pCCD level.

3. Can pCCD describe doubly-excited states without EOM?

System: larger molecules

Yes, quite accurately, but only at the oo-pCCD level.

F. Kossoski, A. Marie, A. Scemama, M. Caffarel, P.-F. Loos, J. Chem. Theory Comput. 17, 4756 (2021)

Quantum Package

- `https://quantum-package.readthedocs.io/en/master/`
- `https://github.com/kossoski/qp_plugins_kossoski`
- An open-source environment for the development of new quantum chemistry methods
- Efficient selected configuration interaction algorithm, can provide near-exact absolute and excitation energies

Variational coupled cluster

Variational coupled cluster for ground and excited states

A. Marie, F. Kossoski, P.-F. Loos, J. Chem. Phys. 155, 104105 (2021).

Part 2: Configuration interaction with excitation degree and seniority number

CI with excitation degree

d	
0	
1	
2	
3	

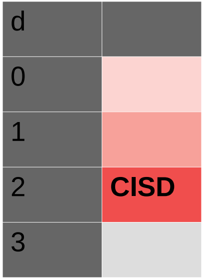
CI with excitation degree

d	
0	**HF**
1	
2	
3	

CI with excitation degree

d	
0	
1	**CIS**
2	
3	

CI with excitation degree



d	
0	
1	
2	**CISD**
3	

CI with excitation degree

d	
0	
1	
2	
3	**CISDT**

CI with seniority number

Ω	0	2	4	6

CI with seniority number

Ω	0	2	4	6
	CIΩ0			

CI with seniority number

Ω	0	2	4	6
		CIΩ2		

CI with seniority number

Ω	0	2	4	6
			CIΩ4	

CI with seniority number

Ω	0	2	4	6
	■	■	■	**CIΩ6**

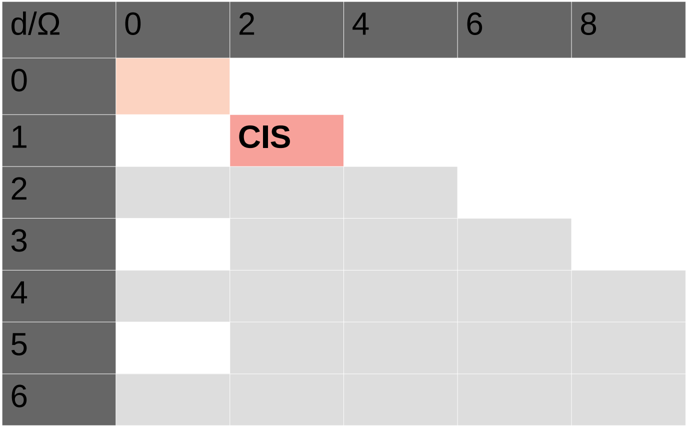
CI with excitation degree

d/Ω	0	2	4	6	8
0	▨				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree

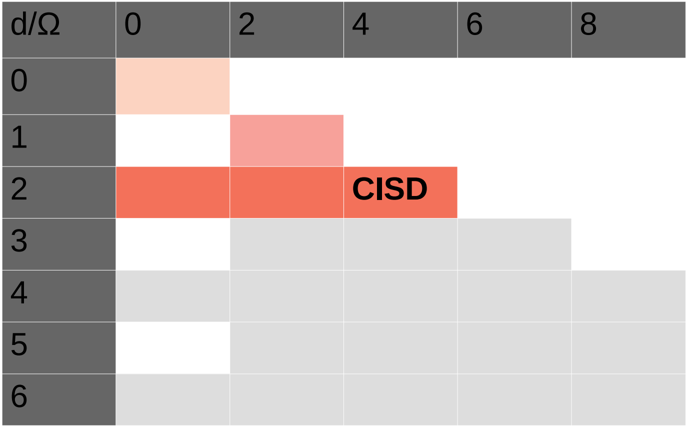
d/Ω	0	2	4	6	8
0	**HF**				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree



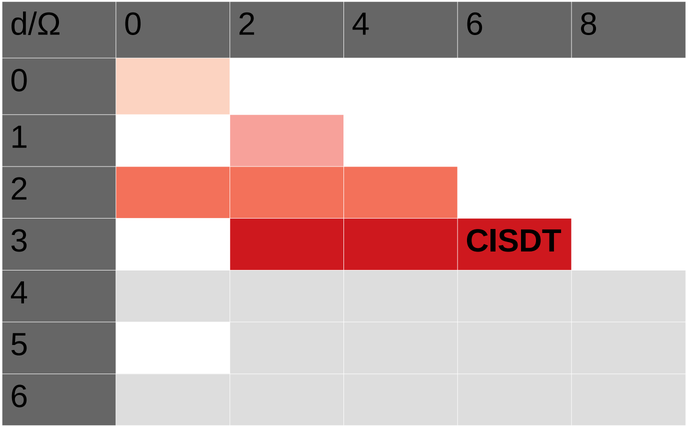
d/Ω	0	2	4	6	8
0	🟧				
1		**CIS**			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree



d/Ω	0	2	4	6	8
0	🟥				
1		🟥			
2	🟥	🟥	**CISD**		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree

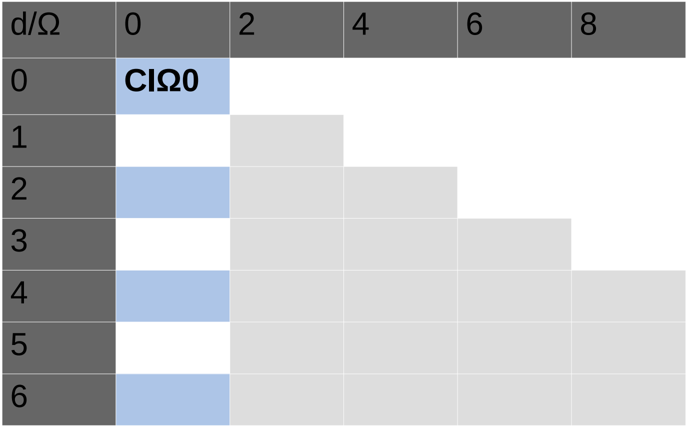


d/Ω	0	2	4	6	8
0	🟥				
1		🟥			
2	🟥	🟥	🟥		
3		🟥	🟥	**CISDT**	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with seniority number

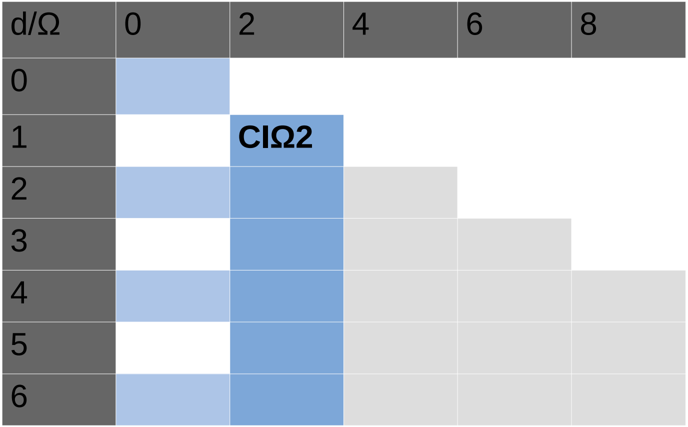
d/Ω	0	2	4	6	8
0	▨				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with seniority number



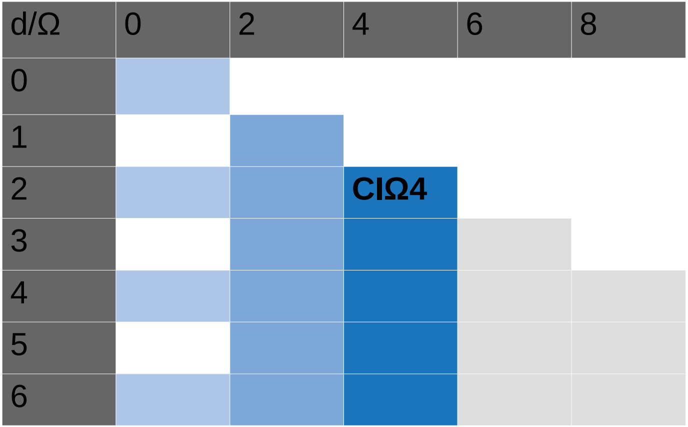
d/Ω	0	2	4	6	8
0	**CIΩ0**				
1		▨			
2	🟦	▨	▨		
3		▨	▨	▨	
4	🟦	▨	▨	▨	▨
5		▨	▨	▨	▨
6	🟦	▨	▨	▨	▨

CI with seniority number



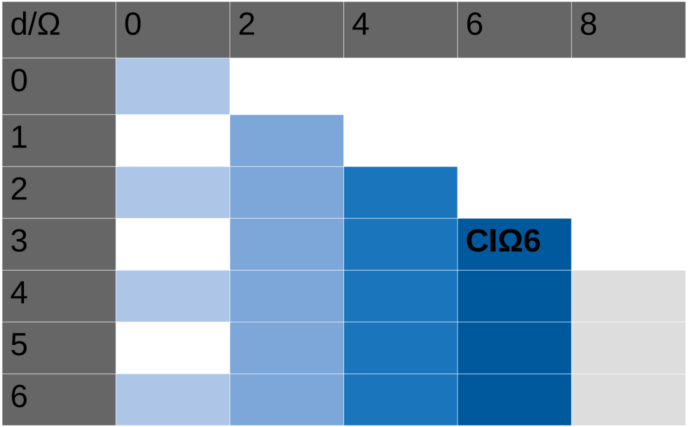
d/Ω	0	2	4	6	8
0	🟦				
1		**CIΩ2**			
2	🟦	🟦	⬜		
3		🟦	⬜	⬜	
4	🟦	🟦	⬜	⬜	⬜
5		🟦	⬜	⬜	⬜
6	🟦	🟦	⬜	⬜	⬜

CI with seniority number



d/Ω	0	2	4	6	8
0					
1					
2			**CIΩ4**		
3					
4					
5					
6					

CI with seniority number



d/Ω	0	2	4	6	8
0	🟦				
1		🟦			
2	🟦	🟦	🟦		
3		🟦	🟦	**CIΩ6**	
4	🟦	🟦	🟦	🟦	▨
5		🟦	🟦	🟦	▨
6	🟦	🟦	🟦	🟦	▨

CI with excitation degree and seniority number

A new CI hierarchy: CIo

$$o = \frac{d + \Omega/2}{2}$$

d: excitation degree
Ω: seniority number
o: order of the determinant

Motivation for new CI hierarchy

1st motivation: physical

CI with excitation degree quickly recovers dynamic correlation
CI with seniority number performs well for static correlation
CIo aims at accounting for most of both

2nd motivation: empirical

Any well-defined truncation scheme is valid.
Is CIo effective?

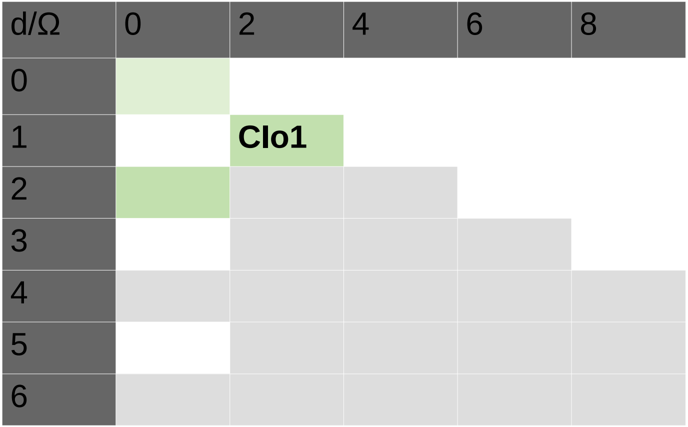
CI with excitation degree and seniority number

d/Ω	0	2	4	6	8
0	▨				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number

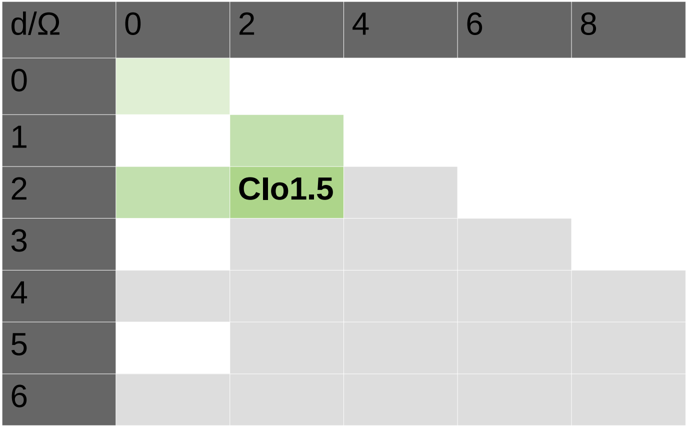
d/Ω	0	2	4	6	8
0	**HF**				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number



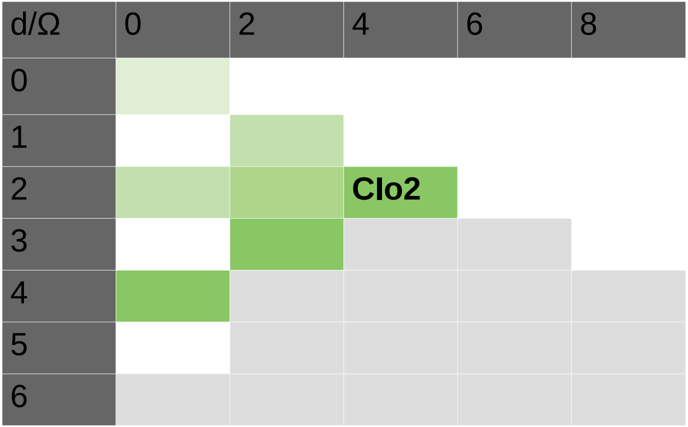
d/Ω	0	2	4	6	8
0	🟩				
1		**CIo1**			
2	🟩	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number



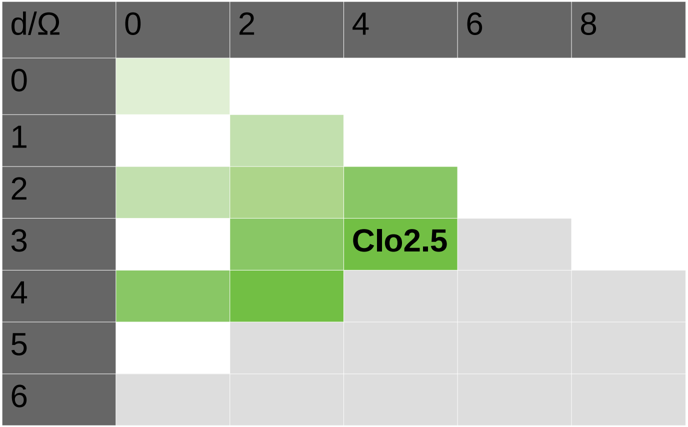
d/Ω	0	2	4	6	8
0	🟩				
1		🟩			
2	🟩	**CIo1.5**	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number



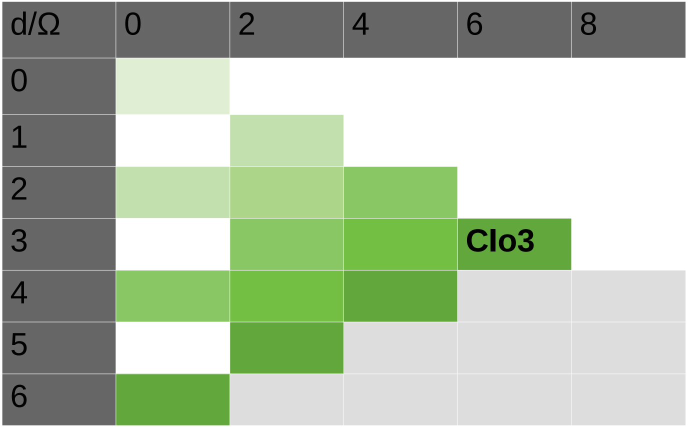
d/Ω	0	2	4	6	8
0	🟩				
1		🟩			
2	🟩	🟩	**CIo2**		
3		🟩	▨	▨	
4	🟩	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number



d/Ω	0	2	4	6	8
0	🟩				
1		🟩			
2	🟩	🟩	🟩		
3		🟩	🟩 **CIo2.5**	▨	
4	🟩	🟩	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number

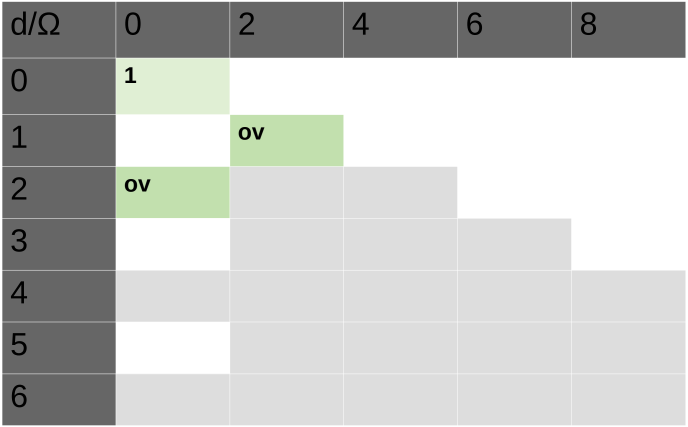


d/Ω	0	2	4	6	8
0	🟩				
1		🟩			
2	🟩	🟩	🟩		
3		🟩	🟩	**Clo3**	
4	🟩	🟩	🟩	▨	▨
5		🟩	▨	▨	▨
6	🟩	▨	▨	▨	▨

CI with excitation degree and seniority number

d/Ω	0	2	4	6	8
0	**1**				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number



d/Ω	0	2	4	6	8
0	**1**				
1		**ov**			
2	**ov**				
3					
4					
5					
6					

CI with excitation degree and seniority number

d/Ω	0	2	4	6	8
0	**1**				
1		**ov**			
2	**ov**	**ov(o+v)**	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

CI with excitation degree and seniority number

d/Ω	0	2	4	6	8
0	**1**				
1		**ov**			
2	**ov**	**ov(o+v)**	**o^2v^2**		
3		**o^2v^2**			
4	**o^2v^2**				
5					
6					

CI with excitation degree and seniority number

d/Ω	0	2	4	6	8
0	**1**				
1		**ov**			
2	**ov**	**ov(o+v)**	**o^2v^2**		
3		**o^2v^2**	**$o^2v^2(o+v)$**		
4	**o^2v^2**	**$o^2v^2(o+v)$**			
5					
6					

CI with excitation degree and seniority number

d/Ω	0	2	4	6	8
0	**1**				
1		**ov**			
2	**ov**	**$ov(o+v)$**	**o^2v^2**		
3		**o^2v^2**	**$o^2v^2(o+v)$**	**o^3v^3**	
4	**o^2v^2**	**$o^2v^2(o+v)$**	**o^3v^3**		
5		**o^3v^3**			
6	**o^3v^3**				

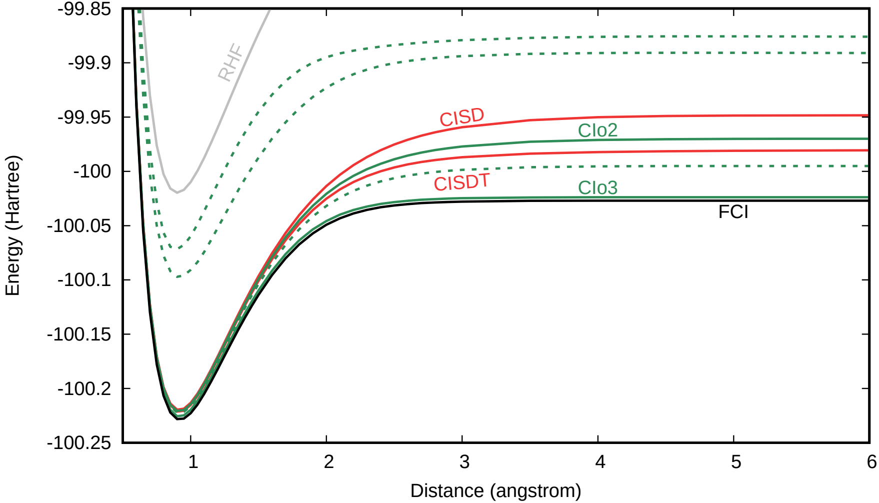
CI with excitation degree and seniority number

3rd motivation: computational

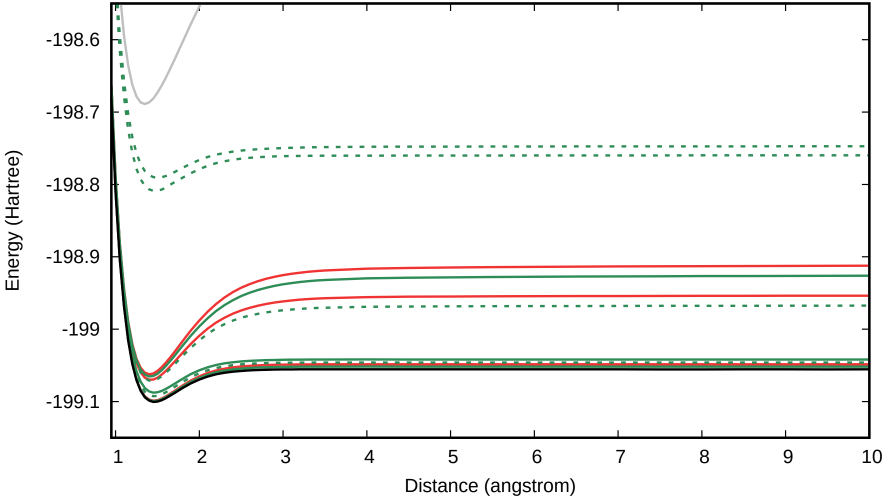
All types of determinants having the same scaling belong to the same CIo sector

CIS	CIo1	ov
-	CIo1.5	$ov(o+v)$
CISD	CIo2	o^2v^2
-	CIo2.5	$o^2v^2(o+v)$
CISDT	CIo3	o^3v^3

HF/cc-pvdz

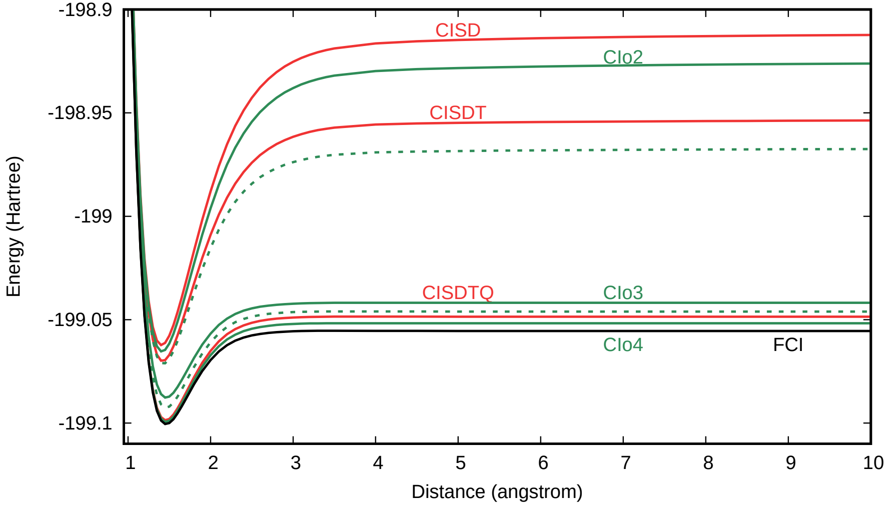

-99.85
-99.9
-99.95
-100
-100.05
-100.1
-100.15
-100.2
-100.25
Energy (Hartree)
1
2
3
4
5
6
Distance (angstrom)
RHF
CISD
CIo2
CISDT
CIo3
FCI

F_2/cc-pvdz

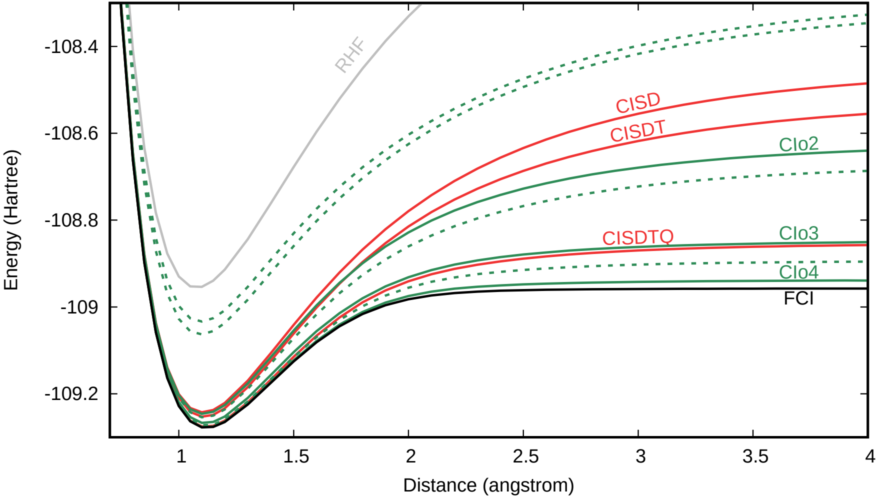


-198.6
-198.7
-198.8
-198.9
-199
-199.1
Energy (Hartree)
1
2
3
4
5
6
7
8
9
10
Distance (angstrom)

F_2/cc-pvdz

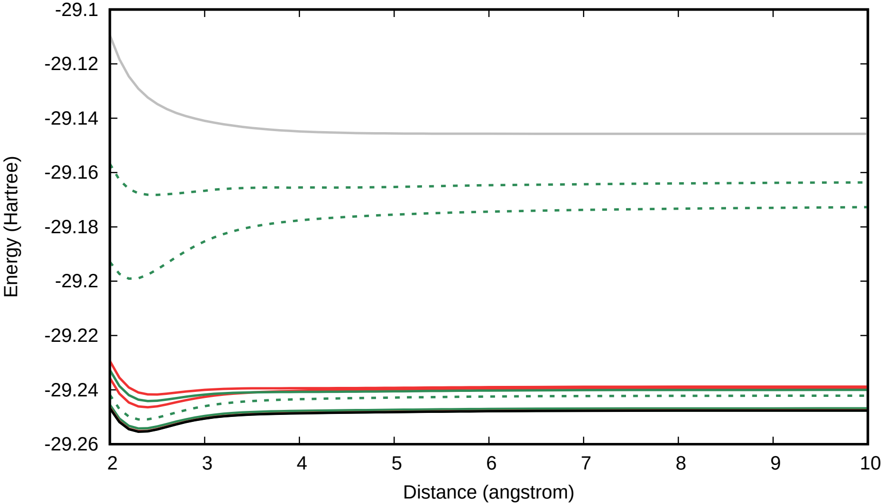

-198.9
-198.95
-199
-199.05
-199.1
Energy (Hartree)
1
2
3
4
5
6
7
8
9
10
Distance (angstrom)
CISD
CIo2
CISDT
CISDTQ
CIo3
CIo4
FCI

N_2/cc-pvdz

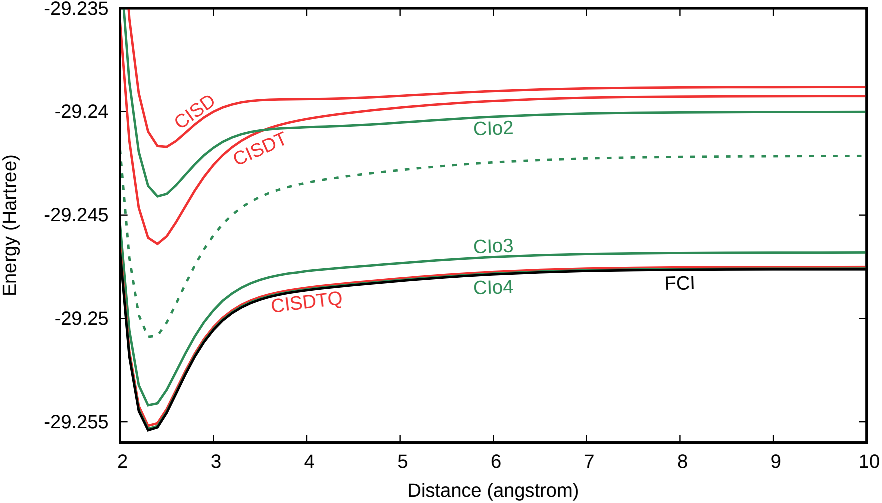


RHF
CISD
CISDT
CIo2
CISDTQ
CIo3
CIo4
FCI
Energy (Hartree)
-108.4
-108.6
-108.8
-109
-109.2
1
1.5
2
2.5
3
3.5
4
Distance (angstrom)

Be_2/cc-pvtz


-29.1
-29.12
-29.14
-29.16
-29.18
-29.2
-29.22
-29.24
-29.26
Energy (Hartree)
2
3
4
5
6
7
8
9
10
Distance (angstrom)

Be_2/cc-pvtz



Energy (Hartree)
-29.235
-29.24
-29.245
-29.25
-29.255
2
3
4
5
6
7
8
9
10
Distance (angstrom)
CISD
CISDT
CIo2
CIo3
CISDTQ
CIo4
FCI

Summary

Targeting doubly-excited states with coupled cluster

- Finding excited states require tailored algorithms
- Nice features of pCCD still holds for doubly-excited states
- Δoo-pCCD model provides accurate excitation energies of doubly-excited states

Configuration interaction with seniority number and excitation degree

- Novel CI hierarchy: CIo
- Physical, empirical, and computational motivations for CIo
- Promising results for ground state potential energy curves

Perspectives

- How about orbital optimized CIo? How much does it improve wrt to traditional CI?
- How about excited states? And avoided crossings?
- How about strongly correlated systems?
- How to extend these ideas to multireference CI and Coupled-cluster?

Thank you!