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Excited States From State Specific Orbital Optimized Pair Coupled Cluster

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09/04/2021

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<https://lcpq.github.io/pterosor>



PTEROSOR has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).



<https://arxiv.org/abs/2104.03746>



- ▶ 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 (addition by subtraction)
- ▶ Minimal CC model for describing doubly-excited states



How to target excited states with pCCD? → helium atom

How does pCCD and DOCI compare for excited states? → linear H_4 molecule

Can pCCD describe doubly-excited states without EOM? → larger molecules



Usual exponential ansatz,

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

where the excitation operator is

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

and singlet paired operators

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

Substitution into the Schroedinger equation leads to

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

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



Equations for the energy

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

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

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

where 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.



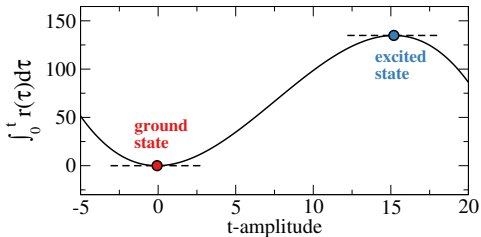
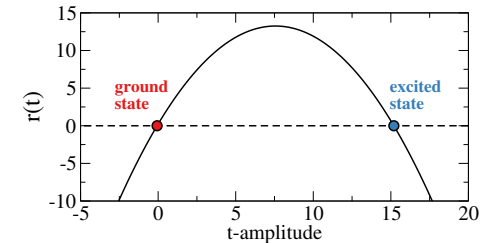
We introduce the de-excitation operator,

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

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

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

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



- ▶ Helium atom, 6-31G basis set
- ▶ 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:

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

- ▶ 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.
- ▶ Empolying 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.
- ▶ Equation for the z -amplitudes are linear, thus Newton-Raphson is exact.



Orbital optimization

The orbital rotations are introduced by an exponential unitary operator, $e^{\hat{\kappa}}$, which acts on right and left-hand wavefunctions. The $\hat{\kappa}$ operator encompasses all unique rotations,

$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} (c_{p\uparrow}^\dagger c_{q\uparrow} - c_{q\uparrow}^\dagger c_{p\uparrow} + c_{p\downarrow}^\dagger c_{q\downarrow} - c_{q\downarrow}^\dagger c_{p\downarrow})$$

The energy can be expressed as a functional of the orbital rotation parameters κ_{pq} ,

$$\tilde{E}(\hat{\kappa}) = \langle \Phi | (1 + \hat{Z}) e^{-\hat{T}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{T}} | \Phi \rangle.$$



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Stationary points with respect to κ_{pq} can be found with the Newton-Raphson method. The energy is expanded to second order around $\kappa = \mathbf{0}$,

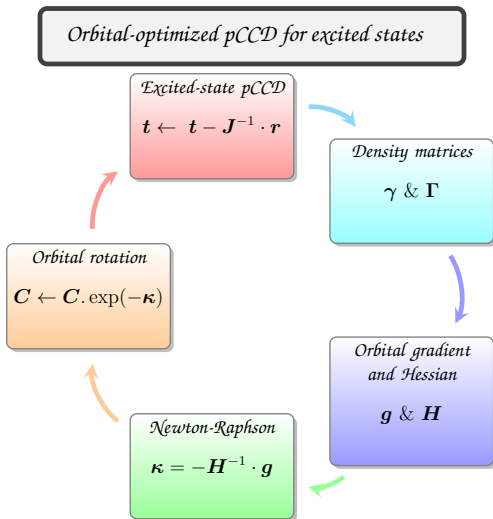
$$\tilde{E}(\kappa) \approx \tilde{E}(\mathbf{0}) + \mathbf{g} \cdot \kappa + \frac{1}{2} \kappa^\dagger \cdot \mathbf{H} \cdot \kappa,$$

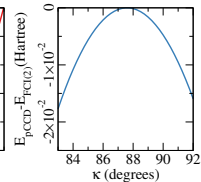
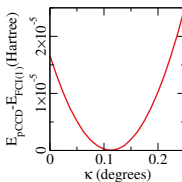
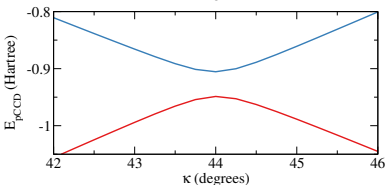
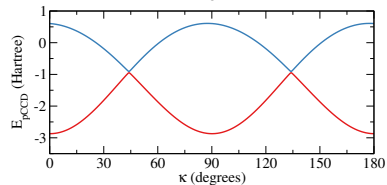
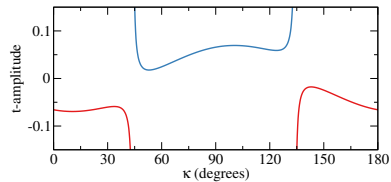
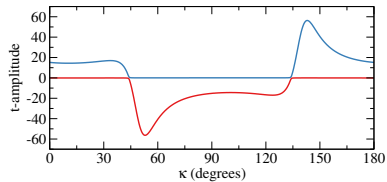
And the orbital rotation vector is taken as

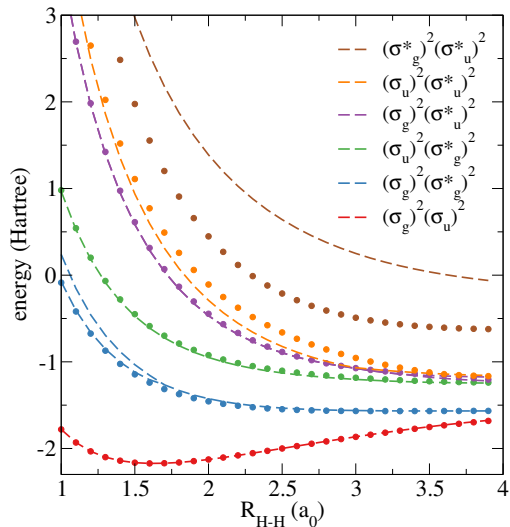
$$\kappa = -\mathbf{H}^{-1} \cdot \mathbf{g}$$



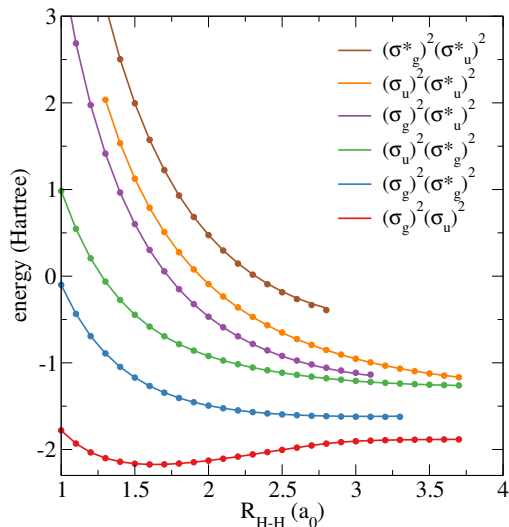
How to run oo-pCCD?



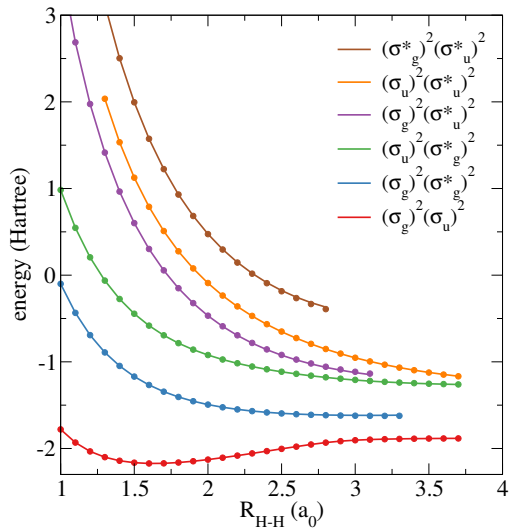
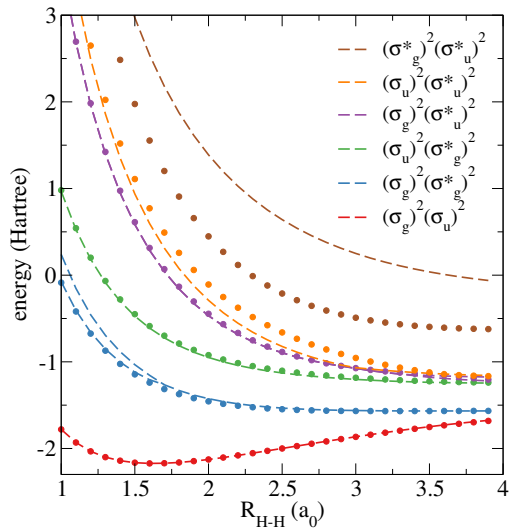




- ▶ HF-pCCD (dashed) vs. DOCI(HF) (points)
- ▶ Results match for ground state, but not for excited states
- ▶ Two solutions for first and third doubly-excited states



- ▶ oo-pCCD (solid) vs. DOCI(oo-pCCD) (points)
- ▶ Results match for all states
- ▶ One single and real solution for each state
- ▶ Lack of higher-order connected excitations in HF-pCCD, which are less important in oo-pCCD

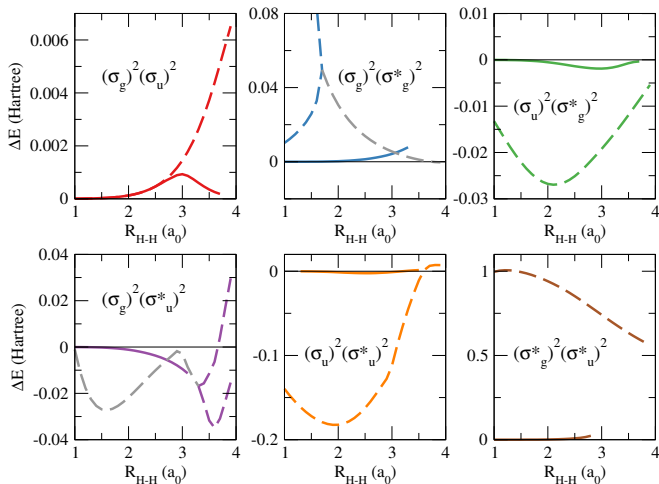




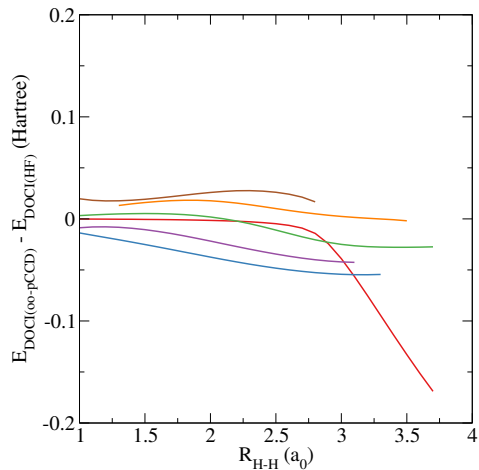
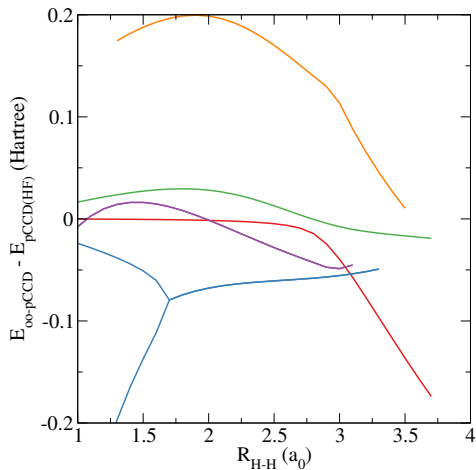
Number of negative Hessian eigenvalues for oo-pCCD:

- ▶ Ground state: 1 ($1.4 a_0 - 2.7 a_0$), 0 elsewhere
- ▶ 1st excited state: 2
- ▶ 2nd excited state: 3 ($\leq 2.3 a_0$), 2 ($\geq 2.4 a_0$)
- ▶ 3rd excited state: 3
- ▶ 4th excited state: 3
- ▶ 5th excited state: 6 ($\leq 1.9 a_0$), 5 ($\geq 2.0 a_0$)

Spatial symmetry-broken vs. symmetry-preserving solutions



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





- ▶ Set of 5 molecules: CH^+ , BH, nitroxyl, nitrosomethane, and formaldehyde
- ▶ 6-31+G(d) basis set, frozen core
- ▶ For CH^+ , additional basis set employed in previous calculations
- ▶ oo-pCCD and DOCI calculations performed with Quantum Package
- ▶ Additional CC3, EOM-CCSDT, and EOM-CCSDTQ calculations performed with CFOUR



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

molecule	method	ΔE	molecule	method	ΔE
CH ⁺ ^a	HF-pCCD	7.74	CH ⁺	HF-pCCD	7.90
	Δ oo-pCCD	8.36		Δ oo-pCCD	8.32
	FCI ^a	8.55		FCI	8.51
	EOM-CCSDT ^b	8.62		EOM-CCSDTQ	8.51
	EOM-oo-pCCD-LCCSD ^c	8.84		EOM-CCSDT	8.58
	EOM-pCCD-LCCSD ^c	7.61		CC3	8.74
	CC3 ^d	8.78	BH	HF-pCCD	10.83
		Δ oo-pCCD		7.35	
		FCI		7.11	
		EOM-CCSDTQ		7.11	
		EOM-CCSDT		7.14	
		CC3		7.29	

^a Chem. Phys. Lett. 154, 380 (1989);
^b Chem. Phys. Lett. 347, 237 (2001);
^c J. Chem. Theory Comput. 15, 18 (2019);
^d J. Chem. Phys. 103, 7429 (1995).



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

molecule	method	ΔE
nitroxyl	HF-pCCD	5.53
	Δ_{oo} -pCCD	4.49
	FCI ^e	4.51
	EOM-CCSDTQ ^e	4.54
	EOM-CCSDT ^e	4.81
	CC3 ^e	5.28
nitrosomethane	Δ_{oo} -pCCD	4.66
	FCI ^e	4.86
	EOM-CCSDT ^e	5.26
	CC3 ^e	5.73
formaldehyde	Δ_{oo} -pCCD	11.26
	FCI ^e	10.86
	EOM-CCSDTQ ^e	10.87
	EOM-CCSDT ^e	11.10
	CC3 ^e	11.49

^e J. Chem. Theory Comput. 15, 1939 (2019)



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

method	RMSE	MAE	MSE
$\Delta_{\text{oo-pCCD}}$	0.24	0.21	0.05
EOM-CCSDT	0.25	0.21	0.21
CC3	0.61	0.54	0.54

- ▶ pCCD-HF way off, $\Delta_{\text{oo-pCCD}}$ rather accurate
- ▶ $\Delta_{\text{oo-pCCD}} \sim \text{EOM-CCSDT} > \text{CC3}$
- ▶ For the 3 larger molecules, $\Delta_{\text{oo-pCCD}} > \text{EOM-CCSDT}$?
- ▶ MSE is much smaller: correlations effects are more balanced (Is this desirable?)
- ▶ Alternative method for targeting doubly-excited states



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DOCI and pCCD provide very close energies as long as state specific reference wavefunctions are employed

Δ_{oo} -pCCD provides accurate excitation energies for doubly-excited states



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- ▶ How to generalize pCCD to target singly-excited states?



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- ▶ How to generalize pCCD to target singly-excited states?
- ▶ What about strongly correlated systems?