State-Specific Coupled Cluster for Excited States

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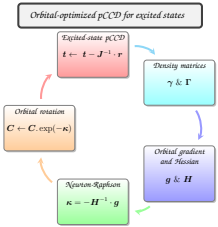
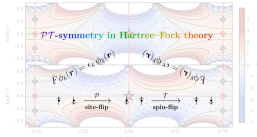
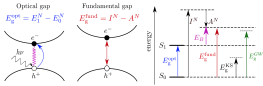
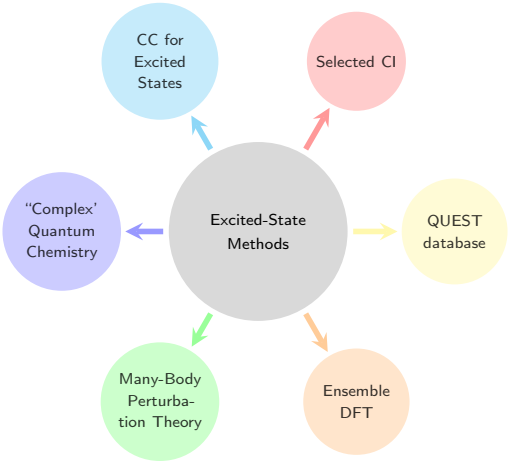
General Overview of our Research Group

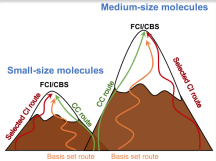


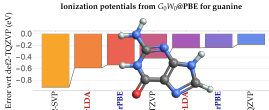


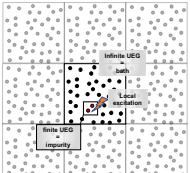




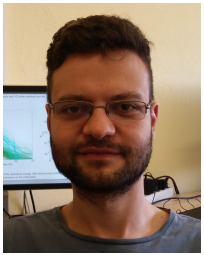
https://lcpq.github.io/PTEROSOR/







Collaborators



Fábris Kossoski
(Postdoc)

Antoine Marie
(PhD)

- Coupled-cluster (CC) wave function

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Psi_0\rangle \quad \text{where } \Psi_0 \text{ is a reference wave function} \tag{1}$$

- Exponential *ansatz*

$$e^{\hat{T}} = \hat{I} + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots \tag{2}$$

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n \quad \text{where } n \text{ is the number of electrons} \tag{3}$$

$$\hat{T}_1 |\Psi_0\rangle = \sum_i \sum_a \underbrace{t_i^a}_{\text{amplitudes}} |\Psi_i^a\rangle \qquad \hat{T}_2 |\Psi_0\rangle = \sum_{i<j} \sum_{a<b} t_{ij}^{ab} \underbrace{|\Psi_{ij}^{ab}\rangle}_{\text{excited determinants}} \tag{4}$$

- Schrödinger equation

$$\hat{H}\,|\Psi_{\rm CC}\rangle = E_{\rm CC}\,|\Psi_{\rm CC}\rangle \;\Rightarrow\; \hat{H}e^{\hat{T}}\,|\Psi_0\rangle = E_{\rm CC}\,e^{\hat{T}}\,|\Psi_0\rangle \;\Rightarrow\; \underbrace{e^{-\hat{T}}\hat{H}e^{\hat{T}}}_{\bar{H}\,=\,\text{similarity transform}}\,|\Psi_0\rangle = E_{\rm CC}\,|\Psi_0\rangle \quad (5)$$

- Variational CC energy (factorial complexity)

$$E_{\rm VCC} = \frac{\langle\Psi_{\rm CC}|\hat{H}|\Psi_{\rm CC}\rangle}{\langle\Psi_{\rm CC}|\Psi_{\rm CC}\rangle} = \frac{\langle\Psi_0(e^{\hat{T}})^\dagger|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0(e^{\hat{T}})^\dagger|e^{\hat{T}}\Psi_0\rangle} \geq E_{\rm exact} \quad (6)$$

- (Traditional) projected CC energy (polynomial complexity)

$$E_{\rm TCC} = \frac{\langle\Psi_0|\bar{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} = \frac{\langle\Psi_0 e^{-\hat{T}}|\hat{H}|e^{\hat{T}}\Psi_0\rangle}{\langle\Psi_0 e^{-\hat{T}}|e^{\hat{T}}\Psi_0\rangle} \quad (7)$$

- Unitary CC energy (very expensive unless you have a quantum computer)

$$E_{\rm UCC} = \frac{\langle\Psi_0(e^{\hat{\tau}})^\dagger|\hat{H}|e^{\hat{\tau}}\Psi_0\rangle}{\langle\Psi_0(e^{\hat{\tau}})^\dagger|e^{\hat{\tau}}\Psi_0\rangle} = \frac{\langle\Psi_0 e^{-\hat{\tau}}|\hat{H}|e^{\hat{\tau}}\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} \quad \text{where } \hat{\tau} = \hat{T} - \hat{T}^\dagger \text{ is anti-Hermitian} \quad (8)$$

Amplitude equations for TCC

- Amplitude equations for single amplitudes

$$\underbrace{r_i^a}_{\text{residual}} = \langle \Psi_i^a | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_i^a \tag{9}$$

- Amplitude equations for double amplitudes

$$r_{ij}^{ab} = \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_{ij}^{ab} \tag{10}$$

- Amplitude equations for k-tuple amplitudes

$$r_{ij\ldots}^{ab\ldots} = \langle \Psi_{ij\ldots}^{ab\ldots} | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_{ij\ldots}^{ab\ldots} \tag{11}$$

- We set $\hat{T} = \hat{T}_2$ (CCD) and we restrict the excitation manifold to electron pairs (p)

$$\hat{T} \left|\Psi_0\right\rangle = \sum_{ia} t_{i\bar{i}}^{a\bar{a}} \left|\Psi_{i\bar{i}}^{a\bar{a}}\right\rangle = \sum_{ia} t_i^a \left|\Psi_{i\bar{i}}^{a\bar{a}}\right\rangle \tag{12}$$

- TpCCD energy

$$E_{\text{TpCCD}} = \left\langle \Psi_0 | \hat{H} | \Psi_0 \right\rangle + \sum_{ia} t_i^a \left\langle ii|aa \right\rangle \tag{13}$$

- TpCCD residual

$$\begin{aligned} r_i^a = {} & \left\langle ii|aa \right\rangle + 2(f_a^a - f_i^i) t_i^a - 2 \sum_j \left\langle jj|aa \right\rangle t_j^a t_i^a - 2 \sum_b \left\langle ii|bb \right\rangle t_i^b t_i^a \\ & - 2(2 \left\langle ia|ia \right\rangle - \left\langle ia|ai \right\rangle) t_i^a + 2 \left\langle ii|aa \right\rangle t_i^a t_i^a \\ & + \sum_b \left\langle aa|bb \right\rangle t_i^b + \sum_j \left\langle ii|jj \right\rangle t_j^a + \sum_{jb} \left\langle jj|bb \right\rangle t_j^a t_i^b \end{aligned} \tag{14}$$

- Update amplitudes

$$t_i^a \leftarrow t_i^a - \frac{r_i^a}{2f_a^a - 2f_i^i} \quad \text{quasi-Newton algorithm} \tag{15}$$

Limacher et al. JCTC 9 (2013) 1394, Henderson et al. JCP 141 (2014) 244104, and many others.

Targeting excited states at the CC level

How to target excited states at the CC level?

Equation-of-motion (EOM) formalism

$$\bar{H} = \begin{pmatrix} E_{CC} & \langle \Psi_0 | \bar{H} | \Psi_i^a \rangle & \langle \Psi_0 | \bar{H} | \Psi_{ij}^{ab} \rangle \\ 0 & \langle \Psi_i^a | \bar{H} | \Psi_i^a \rangle & \langle \Psi_i^a | \bar{H} | \Psi_{ij}^{ab} \rangle \\ 0 & \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_i^a \rangle & \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_{ij}^{ab} \rangle \end{pmatrix}$$

This is biased towards the ground state!!

Stanton & Bartlett, JCP 98 (1993) 7029

"State-specific" formalism

$$r_i^a = \langle \Psi_i^a | \bar{H} | \Psi_0 \rangle = 0$$
$$r_{ij}^{ab} = \langle \Psi_{ij}^{ab} | \bar{H} | \Psi_0 \rangle = 0$$

There is more than one solution!!

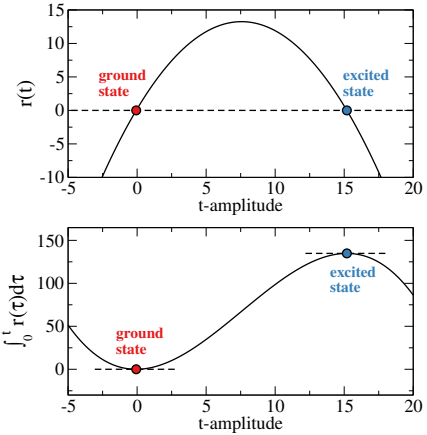
Piecuch & Kowalski, in Computational Chemistry: Reviews of Current Trends, Vol. 5 (2000) 1

We're looking for the roots of $r(t)$...

Residual and curvature

$$r(t) = \langle hh|ll\rangle + \left(2f_l^l - 2f_h^h - 4\langle hl|hl\rangle + 2\langle lh|hl\rangle + \langle ll|ll\rangle + \langle hh|hh\rangle\right) t - \langle ll|hh\rangle\, t^2 \tag{16}$$

$$r'(t) = 2f_l^l - 2f_h^h - 4\langle hl|hl\rangle + 2\langle lh|hl\rangle + \langle ll|ll\rangle + \langle hh|hh\rangle - 2\langle ll|hh\rangle\, t \tag{17}$$



$$t_i^a \leftarrow t_i^a - \sum_{jb} (\boldsymbol{J}^{-1})_{ia,jb} r_j^b \quad \text{Newton-Raphson algorithm} \tag{18}$$

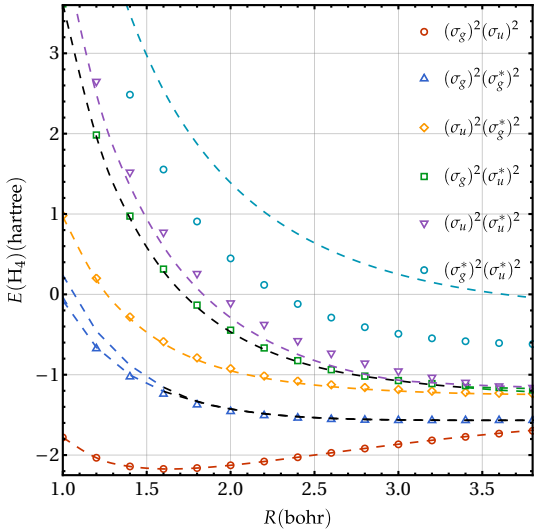
Elements of the exact Jacobian matrix for TpCCD

$$\begin{aligned} J_{ia,jb} = \frac{\partial r_i^a}{\partial t_j^b} = & \left[2f_a^a - 2f_i^i - 4\langle ia|ia\rangle + 2\langle ia|ai\rangle \right] \delta_{ij}\delta_{ab} \\ & + \left[\langle aa|bb\rangle - \langle jj|aa\rangle \, t_i^a + (1-2\delta_{ab}) \sum_{k\neq i} \langle kk|bb\rangle \, t_k^a \right] \delta_{ij} \\ & + \left[\langle ii|jj\rangle - \langle ii|bb\rangle \, t_i^a + (1-2\delta_{ij}) \sum_{c\neq a} \langle jj|cc\rangle \, t_i^c \right] \delta_{ab}. \end{aligned} \tag{19}$$

Kossoski et al. JCTC 17 (2021) 4756

NB: Same strategy works for VCC [Marie et al. JCP 155 (2021) 104105]

Stretching linear H_4/STO-6G: pCCD vs DOCI with HF ground-state reference



Orbital optimization

Orbital rotations via unitary transformation

$$\tilde{E}(\hat{T},\hat{\kappa}) = \langle \Psi_0 | \underbrace{(\hat{I}+\hat{Z})}_{\text{de-excitation operator}} e^{-\hat{T}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{T}} | \Psi_0 \rangle \tag{20}$$

NB: pCCD is not invariant wrt orbital rotations...

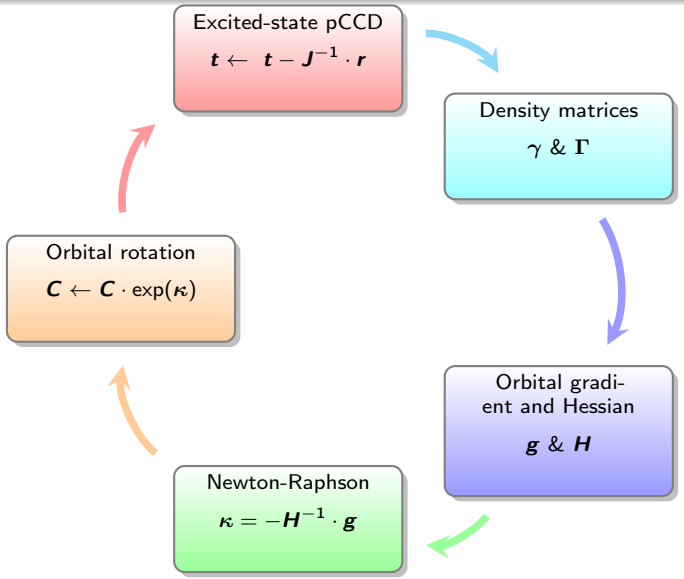
Updating the orbital coefficients

$$\tilde{E}(\boldsymbol{\kappa}) \approx \tilde{E}(0) + \boldsymbol{g}\cdot\boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{H}\cdot\boldsymbol{\kappa} \quad \Rightarrow \quad \boxed{\underbrace{\boldsymbol{C}}_{\text{new coefficients!}} \leftarrow \boldsymbol{C}\cdot e^{\boldsymbol{\kappa}} \quad \text{with} \quad \boldsymbol{\kappa} = -\boldsymbol{H}^{-1}\cdot\boldsymbol{g}} \tag{21}$$

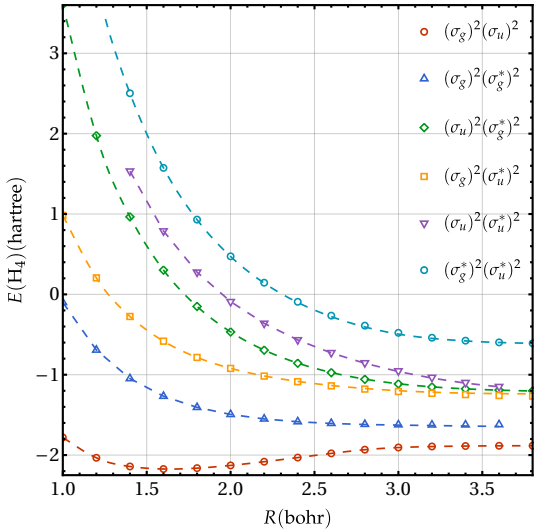
$$\text{Density matrices } \boldsymbol{\gamma} \text{ \& } \boldsymbol{\Gamma} \quad \Rightarrow \quad \underbrace{g_{pq}}_{\text{gradient}} = \left.\frac{\partial \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}}\right|_{\boldsymbol{\kappa}=0} \qquad \underbrace{H_{pq,rs}}_{\text{Hessian}} = \left.\frac{\partial^2 \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}\partial \kappa_{rs}}\right|_{\boldsymbol{\kappa}=0} \tag{22}$$

Henderson et al. JCP 141 (2014) 244104

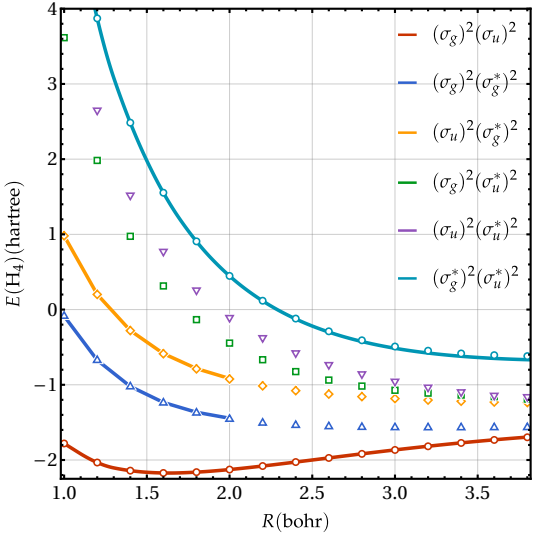
State-specific orbital-optimized TpCCD (oo-TpCCD) for excited states



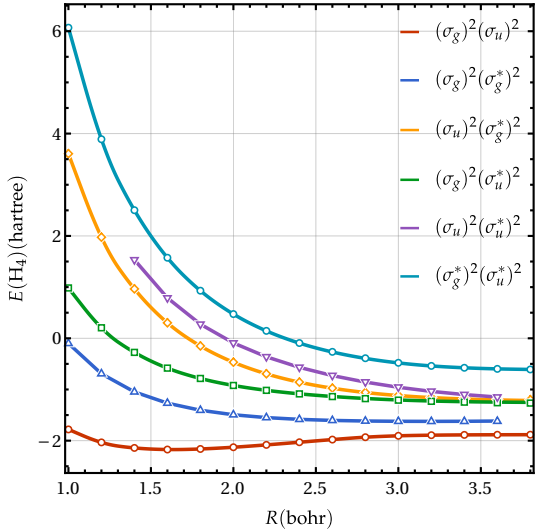
Stretching linear H_4/STO-6G: TpCCD vs DOCI with state-specific TpCCD reference



Stretching linear H_4/STO-6G: VpCCD vs DOCI with HF ground-state reference



Stretching linear H_4/STO-6G: VpCCD vs DOCI with state-specific VpCCD reference

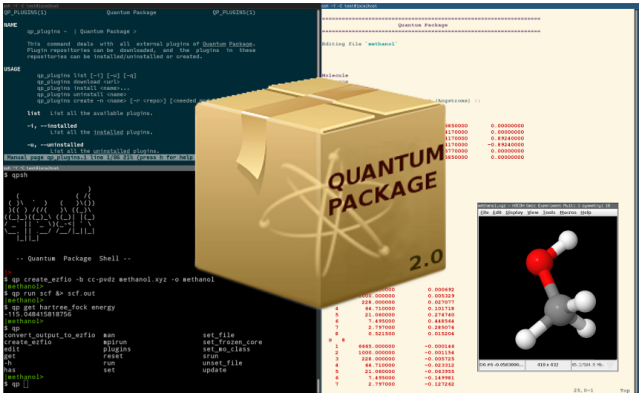


Doubly-excited states for molecules (6-31+G*)...

molecule	method	ΔE (eV)	$\Delta\Delta E$ (eV)
BH	Δoo-TpCCD	7.35	+0.24
	FCI	7.11	0
	EOM-CCSDTQ	7.12	+0.01
	EOM-CCSDT	7.15	+0.04
	CC3	7.30	+0.19
HNO	Δoo-TpCCD	4.49	−0.02
	FCI[1]	4.51	0
	EOM-CCSDTQ[1]	4.54	+0.03
	EOM-CCSDT[1]	4.81	+0.30
	CC3[1]	5.28	+0.77
H_3C-NO	Δoo-TpCCD	4.66	−0.20
	FCI[1]	4.86	0
	EOM-CCSDT[1]	5.26	+0.40
	CC3[1]	5.73	+0.87
$H_2C=O$	Δoo-TpCCD	11.26	+0.40
	FCI[1]	10.86	0
	EOM-CCSDTQ[1]	10.87	+0.01
	EOM-CCSDT[1]	11.10	+0.24
	CC3[1]	11.49	+0.63

[1] Results and geometries from JCTC 15 (2019) 1939

Quantum Package 2.0: https://github.com/QuantumPackage/qp2



"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs", Garniron et al., JCTC 15 (2019) 3591

Fábris' repo: https://github.com/kossoski/qp_plugins_kossoski

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- Fábris Kossoski
  [Kossoski et al. JCTC 17 (2021) 4756]
- Antoine Marie
  [Marie et al. JCP 155 (2021) 104105]
- Raul Quintero (Poster #739 on Fock-space CC)
- Enzo Monino (Poster #524 on *GW* methods)
  [Monino & Loos JCP 156 (2022) 231101]
- Yann Damour (SCI methods with optimized orbitals)
  [Damour et al. JCP 155 (2021) 134104]

https://lcpq.github.io/PTEROSOR

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