# Traditional and Variational Coupled Cluster for Ground and Excited States

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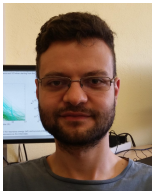
# Collaborators



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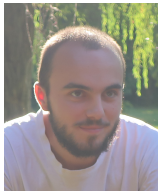

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- Coupled-cluster (CC) wave function

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

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n \quad \text{where } n \text{ is the number of electrons} \tag{2}$$

- Exponential *ansatz*

$$\begin{aligned} e^{\hat{T}} &= \hat{I} + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \ldots \\ &= \hat{I} + \hat{T}_1 + \left( \underbrace{\hat{T}_2}_{\text{connected}} + \frac{1}{2} \underbrace{\hat{T}_1^2}_{\text{disconnected}} \right) + \left( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6}\hat{T}_3 \right) \\ &+ \left( \hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{1}{2} \underbrace{\hat{T}_2^2}_{\text{two pairs of electrons}} + \frac{1}{2}\hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \underbrace{\hat{T}_4}_{\text{four electrons}} \right) + \ldots \end{aligned} \tag{3}$$

# Excitation operators

- Singles

$$\hat{T}_1\Psi_0 = \sum_i \sum_a \underbrace{t_i^a}_{\text{amplitudes}} \Psi_i^a \tag{4}$$

- Doubles

$$\hat{T}_2\Psi_0 = \sum_{i<j} \sum_{a<b} t_{ij}^{ab} \underbrace{\Psi_{ij}^{ab}}_{\text{excited determinants}} \tag{5}$$

- FCI wave function

$$\Psi_{\text{CI}} = (\hat{I} + \hat{T})\Psi_0 = (\hat{I} + \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n)\Psi_0 \tag{6}$$

- Schrödinger equation

$$\hat{H}\,|\Psi_{\rm CC}\rangle = E_{\rm CC}\,|\Psi_{\rm CC}\rangle \;\Rightarrow\; \hat{H}e^{\hat{T}}\,|\Psi_0\rangle = E_{\rm CC}\,e^{\hat{T}}\,|\Psi_0\rangle \;\Rightarrow\; \underbrace{e^{-\hat{T}}\hat{H}e^{\hat{T}}}_{\bar{H}\,=\,\text{similarity transform}}\,|\Psi_0\rangle = E_{\rm CC}\,|\Psi_0\rangle \quad (7)$$

- (Projected) Traditional CC energy (polynomial complexity)

$$\boxed{E_{\rm TCC} = \langle\Psi_0|\bar{H}|\Psi_0\rangle = \frac{\langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle}{\langle\Psi_0|e^{-\hat{T}}e^{\hat{T}}|\Psi_0\rangle} = \langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle} \quad (8)$$

- Variational CC energy (factorial complexity)

$$\boxed{E_{\rm VCC} = \frac{\langle\Psi_{\rm CC}|\hat{H}|\Psi_{\rm CC}\rangle}{\langle\Psi_{\rm CC}|\Psi_{\rm CC}\rangle} = \frac{\langle\Psi_0|e^{\hat{T}^\dagger}\hat{H}e^{\hat{T}}|\Psi_0\rangle}{\langle\Psi_0|e^{\hat{T}^\dagger}e^{\hat{T}}|\Psi_0\rangle} \geq E_{\rm FCI}} \quad (9)$$

Van Voorhis & Head-Gordon, JCP 113 (2000) 8873

# Amplitude equations for TCC

- Amplitude equations for single amplitudes

$$\underbrace{r_i^a}_{\text{residual}} = \langle \Psi_i^a | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_i^a \tag{10}$$

- Amplitude equations for double amplitudes

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

- Amplitude equations for $k$-tuple amplitudes

$$r_{ij\ldots}^{ab\ldots} = \langle \Psi_{ij\ldots}^{ab\ldots} | \bar{H} | \Psi_0 \rangle = 0 \quad \Rightarrow \quad t_{ij\ldots}^{ab\ldots} \tag{12}$$

# Amplitude equations for VCC

- Amplitude equations for single amplitudes

$$\frac{\partial E_{\mathrm{VCC}}}{\partial t_i^a} = \underbrace{r_i^a}_{\text{residual} \equiv \text{gradient}} = 0 \quad \Rightarrow \quad t_i^a \tag{13}$$

- Amplitude equations for double amplitudes

$$\frac{\partial E_{\mathrm{VCC}}}{\partial t_{ij}^{ab}} = r_{ij}^{ab} = 0 \quad \Rightarrow \quad t_{ij}^{ab} \tag{14}$$

- Amplitude equations for $k$-tuple amplitudes

$$\frac{\partial E_{\mathrm{VCC}}}{\partial t_{ij\ldots}^{ab\ldots}} = r_{ij\ldots}^{ab\ldots} = 0 \quad \Rightarrow \quad t_{ij\ldots}^{ab\ldots} \tag{15}$$

# Traditional pair CCD (TpCCD)

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

$$\hat{T} \left|\Psi_0\right\rangle = \sum_{ia} t_{i\bar{i}}^{a\bar{a}} \left|\Psi_{i\bar{i}}^{a\bar{a}}\right\rangle = \sum_{ia} t_i^a \left|\Psi_{i\bar{i}}^{a\bar{a}}\right\rangle \tag{16}$$

- TpCCD energy

$$E_{\text{TpCCD}} = \langle\Psi_0|\hat{H}|\Psi_0\rangle + \sum_{ia} t_i^a \langle ii|aa\rangle \tag{17}$$

- TpCCD residual

$$\begin{aligned} r_i^a = {} & \langle ii|aa\rangle + 2(f_a^a - f_i^i) t_i^a - 2\sum_j \langle jj|aa\rangle\, t_j^a t_i^a - 2\sum_b \langle ii|bb\rangle\, t_i^b t_i^a \\ & - 2(2\langle ia|ia\rangle - \langle ia|ai\rangle) t_i^a + 2\langle ii|aa\rangle\, t_i^a t_i^a \\ & + \sum_b \langle aa|bb\rangle\, t_i^b + \sum_j \langle ii|jj\rangle\, t_j^a + \sum_{jb} \langle jj|bb\rangle\, t_j^a t_i^b \end{aligned} \tag{18}$$

- Update amplitudes

$$t_i^a \leftarrow t_i^a - \frac{r_i^a}{2f_a^a - 2f_i^i} \quad \text{quasi-Newton algorithm} \tag{19}$$

Henderson et al. JCP 141 (2014) 244104; Limacher et al. JCTC 9 (2013) 1394

# TpCCD vs DOCI: Ground state with HF reference [Henderson et al. JCP 141 (2014) 244104]

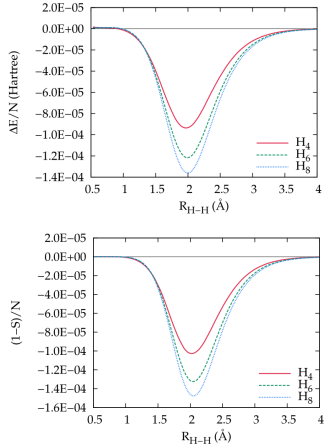



FIG. 3. Dissociation of equally spaced hydrogen chains. Top panel: Differences between DOCI and pCCD energies ($\Delta E$, defined in Eq. (27)) per electron pair. Bottom panel: Deviations in the overlap ($1 - S$, with $S$ defined in Eq. (28)) per electron pair.

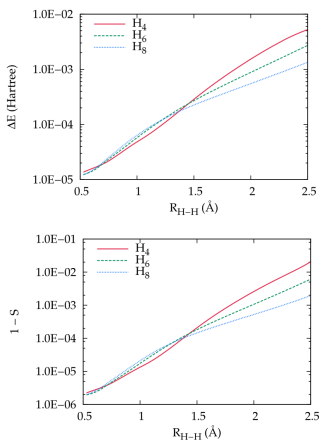



FIG. 4. Dissociation of equally spaced hydrogen chains in the canonical RHF basis rather than the pCCD-optimized basis used elsewhere. Top panel: Differences between DOCI and pCCD energies ($\Delta E$, defined in Eq. (27)). Bottom panel: Deviations in the overlap ($1 - S$, with $S$ defined in Eq. (28)).

**Does the similarity between TpCCD and DOCI still hold for excited states?**

## Equation-of-motion (EOM) formalism

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

Krylov, Annu Rev Phys 59 (2008) 433

## "Ground state" formalism

There is more than one solution!!

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

or

$$r_i^a = \frac{\partial E_{\mathrm{VCC}}}{\partial t_i^a} = 0$$
$$r_{ij}^{ab} = \frac{\partial E_{\mathrm{VCC}}}{\partial t_{ij}^{ab}} = 0$$

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

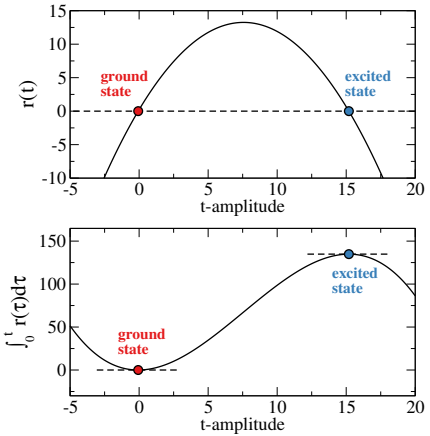
# Example: TpCCD for He/6-31G with $h$ = HOMO and $l$ = LUMO

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

## Residual and curvature

$$r(t) = \langle hh|ll\rangle + \left(2f_l^l - 2f_h^h - 4\langle hl|hl\rangle + 2\langle lh|hl\rangle + \langle ll|ll\rangle + \langle hh|hh\rangle\right) t - \langle ll|hh\rangle\, t^2 \tag{20}$$

$$r'(t) = 2f_l^l - 2f_h^h - 4\langle hl|hl\rangle + 2\langle lh|hl\rangle + \langle ll|ll\rangle + \langle hh|hh\rangle - 2\langle ll|hh\rangle\, t \tag{21}$$



$$t_i^a \leftarrow t_i^a - \sum_{jb} (\boldsymbol{J}^{-1})_{ia,jb} r_j^b \quad \text{Newton-Raphson algorithm} \tag{22}$$

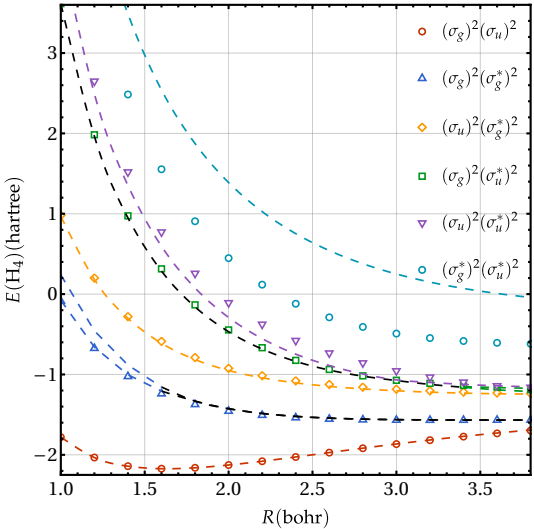
## Elements of the exact Jacobian matrix for TpCCD

$$\begin{aligned} J_{ia,jb} = \frac{\partial r_i^a}{\partial t_j^b} = & \left[ 2f_a^a - 2f_i^i - 4\langle ia|ia\rangle + 2\langle ia|ai\rangle \right] \delta_{ij}\delta_{ab} \\ & + \left[ \langle aa|bb\rangle - \langle jj|aa\rangle\, t_i^a + (1-2\delta_{ab}) \sum_{k\neq i} \langle kk|bb\rangle\, t_k^a \right] \delta_{ij} \\ & + \left[ \langle ii|jj\rangle - \langle ii|bb\rangle\, t_i^a + (1-2\delta_{ij}) \sum_{c\neq a} \langle jj|cc\rangle\, t_i^c \right] \delta_{ab}. \end{aligned} \tag{23}$$

Kossoski et al. JCTC (in press) arXiv:2104.03746

**NB:** Same strategy works for VCC [Marie et al. JCP (submitted) arXiv:2106.11305]

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



# Orbital optimization

## Orbital rotations via unitary transformation

$$\tilde{E}(\hat{T},\hat{\kappa}) = \langle \Psi_0 | \underbrace{(\hat{I}+\hat{Z})}_{\text{de-excitation operator}} e^{-\hat{T}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{T}} | \Psi_0 \rangle \tag{24}$$

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

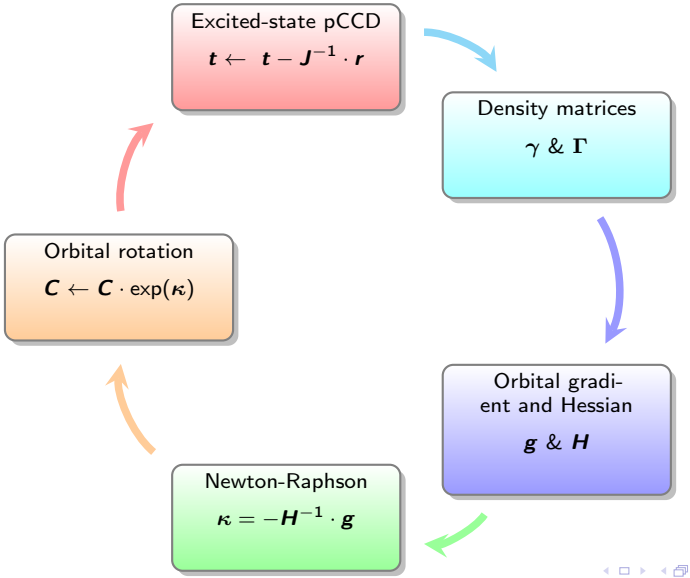
## Updating the orbital coefficients

$$\tilde{E}(\boldsymbol{\kappa}) \approx \tilde{E}(0) + \boldsymbol{g}\cdot\boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{H}\cdot\boldsymbol{\kappa} \quad \Rightarrow \quad \boxed{\underbrace{\boldsymbol{C}}_{\text{new coefficients!}} \leftarrow \boldsymbol{C}\cdot e^{\boldsymbol{\kappa}} \quad \text{with} \quad \boldsymbol{\kappa} = -\boldsymbol{H}^{-1}\cdot\boldsymbol{g}} \tag{25}$$

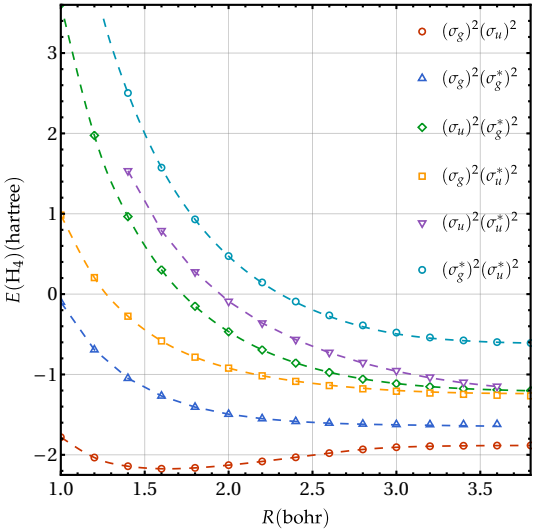
$$\text{Density matrices } \boldsymbol{\gamma} \ \& \ \boldsymbol{\Gamma} \quad \Rightarrow \quad \underbrace{g_{pq}}_{\text{gradient}} = \left.\frac{\partial \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}}\right|_{\boldsymbol{\kappa}=0} \qquad \underbrace{H_{pq,rs}}_{\text{Hessian}} = \left.\frac{\partial^2 \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}\partial \kappa_{rs}}\right|_{\boldsymbol{\kappa}=0} \tag{26}$$

Henderson et al. JCP 141 (2014) 244104

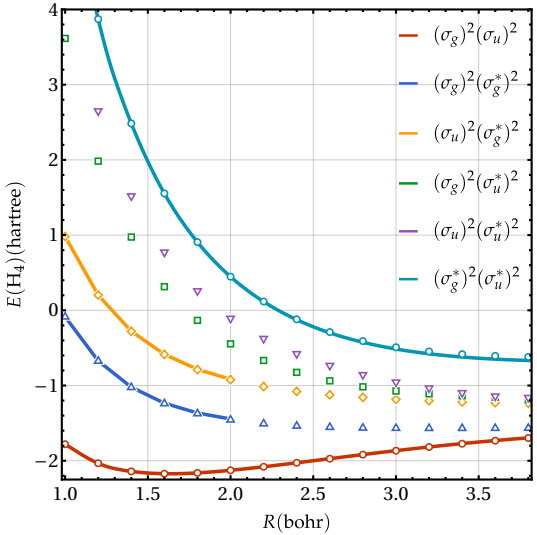
# State-specific orbital-optimized TpCCD (oo-TpCCD) for excited states



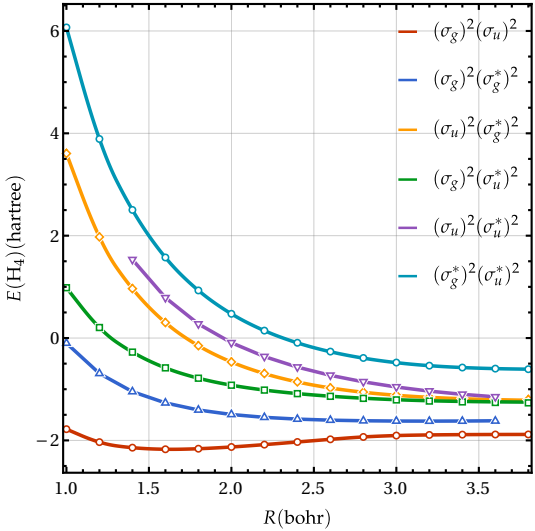
# Stretching linear $H_4$/STO-6G: TpCCD vs DOCI with state-specific TpCCD reference



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

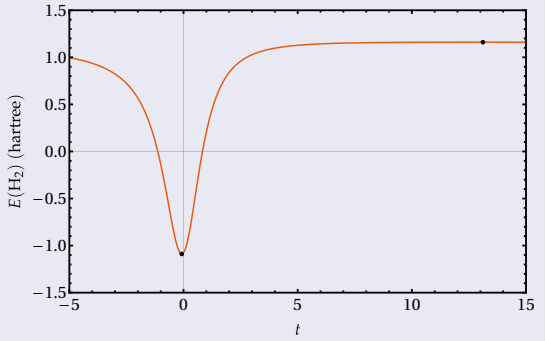


# Stretching linear $H_4$/STO-6G: VpCCD vs DOCI with state-specific VpCCD reference

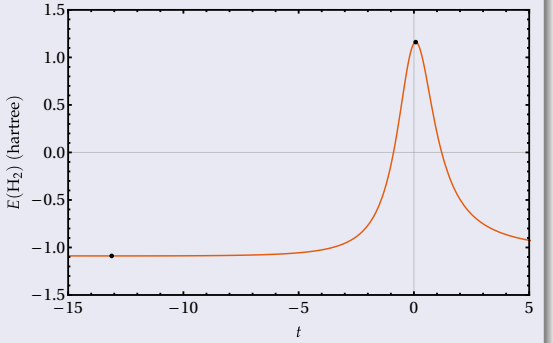


# VpCCD energy landscape for $H_2$/STO-6G for $R = 1$ bohr

## VpCCD energy for ground-state reference




## VpCCD energy for excited-state reference



# Lowest doubly-excited state of $CH^+$

| molecule | method | $\Delta E$ (eV) | $\Delta\Delta E$ (eV) |
|---|---|---|---|
| $CH^{+1}$ | $\Delta$oo-TpCCD | 8.36 | $-0.19$ |
| | FCI[2] | 8.55 | 0 |
| | EOM-CCSDT[3] | 8.62 | $+0.07$ |
| | EOM-CCSDt[3] | 8.64 | $+0.09$ |
| | EOM-oo-pCCD-LCCSD[4] | 8.84 | $+0.29$ |
| | EOM-pCCD-LCCSD[4] | 7.61 | $-0.94$ |
| | CC3[5] | 8.78 | $+0.23$ |

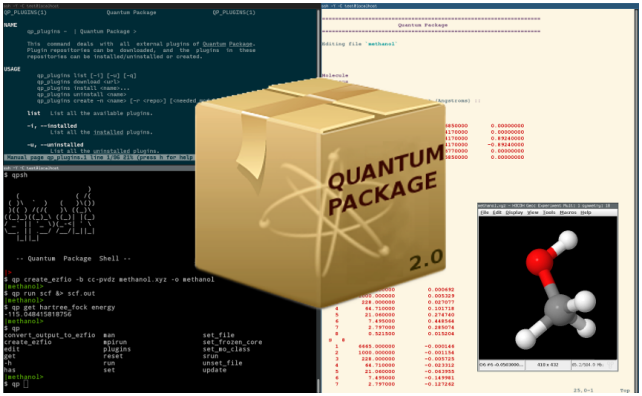
[1] Basis set and geometry taken from Olsen et al. CPL 154 (1989) 380
[2] Results from Olsen et al. CPL 154 (1989) 380
[3] Results from Kowalski & Piecuch, CPL 347(2001) 237
[4] Results from Boguslawski, JCTC 15 (2019) 18
[5] Results from Christiansen et al. JCP 103 (1995) 7429

# More doubly-excited states for molecules (6-31+G*)...

| molecule | method | $\Delta E$ (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 Loos et al. 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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  [Marie et al. JCP (submitted) arXiv:2106.11305]
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- Michel Caffarel (CNRS)
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